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Proceedings of the DOE Thermal and Chemical Storage Annual Contractor's Review Meeting

October 14-16, 1980
Westpark Hotel
McLean, Virginia

March 1981

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Assistant Secretary for Conservation and Renewable Energy
Office of Advanced Conservation Technologies
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U.S. Department of Energy
Assistant Secretary for Conservation and Renewable Energy
Office of Advanced Conservation Technologies
Washington, D.C. 20585

FOREWORD

The DOE/Office of Advanced Conservation Technologies (ACT) conducted an annual contractor's review meeting during October 14-16, 1980 at the Westpark Hotel in McLean, Virginia. The review meeting consisted of contractor presentations, brief question and answer periods, and an executive review session held on Friday, October 17th. This year's meeting combined presentations from both the Thermal Energy Storage Program and the Chemical/Hydrogen Energy Storage Program. Overviews for each of these programs are provided within the proceedings by the respective DOE Program Managers, Michael Gurevich and Fred Gornick. James H. Swisher, Director of the DOE/Division of Thermal and Mechanical Energy Storage provided the welcoming remarks. This report is a compilation of papers and speech presentations distributed at the conference.

The proceedings are divided into three sections starting with Thermal Energy Storage Papers and continuing through to the Chemical/Hydrogen Energy Storage papers (page 141) and ending with composite project summaries for each R&D effort. The presentations outlined the progress and accomplishments of each subcontractor during FY 1980 and provided an expanded opportunity for dialogue between formal reviewers, program management and interested researchers. The review committee, comprised of representatives from industry, academia and government provided an assessment of programmatic activities and recommendations for future direction.

The 1980 annual review was planned and managed by Brookhaven National Laboratory program personnel with the assistance and support of Courtesy Associates. Special thanks is extended to Annmarie Pittman of Courtesy Associates, James Martin of Oak Ridge National Laboratory and the Session Chairmen. A final note of appreciation is offered to our very informative guest speaker, John Paul Contzen, Director of Programs for Commission of European Communities.

The proceedings provide information on thermal and chemical energy storage progress through September 30, 1980.

James H. Swisher, Acting Director
Division of Physical and Chemical Energy Storage Systems
Office of Advanced Conservation Technologies
U.S. Department of Energy

C. P. Fredrickson
Associate Program Manager
Chemical/Hydrogen Energy Storage Systems
Brookhaven National Laboratory

IN MEMORIAM

Dr. Kenneth E. Cox

Kenneth E. Cox, a noted scientist in the field of hydrogen energy, died September 27, 1980 in a one-vehicle accident on Pajarito Road near Los Alamos, New Mexico. He is survived by his wife Patricia, and three sons, Ian, Terrence and Kevin.

Dr. Cox joined the Los Alamos Scientific Laboratory in September 1977 to act as a project leader in the Laboratory's program for the development and evaluation of Thermochemical Processes for Hydrogen Production. Previously, he served 12 years as a chemical engineering professor at the University of New Mexico. During this period he also made significant contributions to the development of hydrogen energy. Earlier, he was a resident engineer at Dow Chemical Company in Walnut Creek, California.

As the author of more than 50 papers, Dr. Cox earned world recognition for his work. He received frequent invitations to present lectures at universities and other organizations interested in the production, utilization, or economic aspects of hydrogen. He maintained an active correspondence with other researchers in the United States, Canada, Belgium, Switzerland, France, Germany, England, Italy, Australia, Japan, and China. He was a representative of the United States at the International Energy Agency Technical workshop on Thermochemical Processes held in Ispra, Italy in 1978 and in Los Alamos in 1979. A week prior to his death, he had returned to Los Alamos from a lecture series on hydrogen energy he presented at the Jiaotong University, Xi'an, China.

Dr. Cox was born in Tiensin, China in 1936. He received a B.Sc. in chemical engineering from the Imperial College, University of London in 1956; an M.A. Sc. in chemical engineering from the University of British Columbia in 1959; and a Ph.D. in chemical engineering from Montana State University in 1962.


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OVERVIEW OF THE THERMAL ENERGY STORAGE (TES) PROGRAM

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Program Manager
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Office of Advanced Conservation Technologies

Abstract

The Thermal Energy Storage (TES) Program of the U. S. Department of Energy (DOE) promotes energy savings and fuel substitution by developing and helping to commercialize technologies for storing heat or cold, with short investment payback periods as a cost goal. The sources of energy include industrial and utility waste heat as well as primary sources such as solar, geothermal, nuclear and fossil fuels. The primary source of "cold" for seasonal storage is winter chilled air. The DOE Thermal Energy Storage Program emphasizes near-term (1980's) approaches to energy conservation and displacement of natural gas and oil. It also provides for development of technologies which will allow use of renewable resources such as solar-thermal energy during the mid-term (1990's) and advanced energy storage and transport techniques for the far-term (beyond 2000). The applications include daily storage for active or passive solar and for conventional heating and cooling, heat storage and heat transport for solar thermal electric power generation, and storage for recovery of industrial or utility waste heat.

Thermal Storage has a budget of $17.1 million (MS) for FY 1980, but $8.9M of this is managed by other programs and an additional $3.5M is passed to this program for management, for a net budget of $11.7 million. Program management for policy, planning, and budget issues is provided by the Office of Advanced Conservation Technologies (ACT), within the Office of the Assistant Secretary for Conservation and Solar Energy. Project management is provided by field organizations, including Pacific Northwest Laboratory (PNL) for seasonal thermal energy storage (reports to Underground Storage Program), Oak Ridge National Laboratory (ORNL) for building heating/cooling and waste heat recovery, Solar Energy Research Institute (SERI) for generic thermal energy storage research and assessments, Sandia Livermore Laboratory (SLL) for solar thermal applications, and Brookhaven National Laboratory (BNL) for chemical heat pumps (reports to Chemical Storage Program). The program includes a diverse range of individual projects, from analytic studies of thermo-chemical pipelines, through bench-scale laboratory investigation of individual phase-change materials, to large-scale field testing of thermal storage for industrial heat recovery.

Approximately 40 percent of the total energy demand in the U. S. is used in industrial applications, and both energy savings and displacement of fossil fuels can result from the recovery of reject process heat from industry. The DOE program has identified 20 applications for industrial heat recovery with TES. Of these, six specific industries were selected for detailed study, namely: pulp and paper, primary steel and iron, primary aluminum, food processing, ceramics, and cement. Demonstration contracts have been let in the primary aluminum and food processing industries. Thermal energy storage is already in use in some pulp and paper plants, principally in Scandinavia, and under DOE funding, the results and experience of the existing units will be documented in a commercialization package and distributed to industry.

The development of technology for storing thermal energy in aquifers is now part of an underground storage program in this office (ACT). However, it is worth mentioning here. The emphasis is on seasonal storage, taking advantage of naturally occurring, porous rock formations which contain large quantities of water and which are commonly tapped as a source of water for household and irrigation purposes. Experimental support work involving the operation of hot and cold wells at Auburn University and at Texas A&M has demonstrated attractive energy recoveries. DOE will be funding projects at three sites to demonstrate the application of aquifer thermal energy storage for district heating and cooling.

Heating and cooling of homes, offices, stores, and other buildings represents a large fraction of the U. S. national energy consumption. Part of the problem in this area concerns the peak electrical power demand to heat or cool these buildings. Over a dozen utilities across the U.S. are currently involved in reducing peak-load electricity demand through storage of thermal energy from off-peak periods to on-peak times. To date, over 300 homes have customer side-of-the-meter storage in one form or another. In another part of this program phase change materials are being developed to store both heat and "coldness"; some of these are now commercially available. Chemical heat pump concepts are being developed for building heating and cooling applications. These concepts are part of the chemical energy storage program, but again need mentioning for the sake of completeness. Primary emphasis is placed on the metal hydride system and the sulfuric acid/water heat pump. These two concepts are directed specifically towards incorporation into waste heat recovery, with eventual application to solar energy.

The development of solar-thermal electrical power involves coupling high-temperature solar collection technology to a thermal power cycle. A stable power supply also requires a thermal energy storage system capable of driving the power cycle during brief periods of cloud cover; it is also desirable to store enough for use during the night and during periods of inclement weather. Several thermal energy storage concepts for use with water/steam, molten and liquid salt, liquid metal, gas, and organic fluid collectors/receivers are in various stages of development for this application.

Finally, a number of DOE/ACT programs involve generic research and development (R&D). These programs include the development of a methodology to identify thermal storage concepts for solar thermal applications, research to quantitatively understand the hydrodynamic and heat transfer processes governing the operation of direct contact latent heat storage units, and research to establish the feasibility of transporting high temperature heat for moderate to long distances.

ORNL THERMAL ENERGY STORAGE PROGRAM OVERVIEW*

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Abstract

Development of thermal energy storage (TES) technologies and subsystems is relevant to national energy objectives in energy conservation and in the deployment of new energy sources. Oak Ridge National Laboratory (ORNL) acts as a Lead Technical Laboratory in managing for DOE-STOR those elements of the program dealing with Building Heating and Cooling and Industrial Applications. The scope of ORNL activity in these two activities is described, and a summary of each of the in-house and subcontracted projects current or anticipated for the next fiscal year are presented. The major thrust of each of the elements of the ORNL program is given.

1. Introduction

The DOE-Division of Thermal and Mechanical Energy Storage Systems (STOR), Office of Advanced Conservation Technologies, has assigned to Oak Ridge National Laboratory (ORNL) responsibility as a Lead Technical Laboratory for those elements of the national program on Thermal Energy Storage (TES) technology development dealing with Building Heating and Cooling Applications and Industrial Applications. Responsibility for Building Heating and Cooling was accorded in April 1979 in consequence of DOE-STOR program restructuring. Responsibility for Industrial Applications was assigned in March 1980.

It is the role of ORNL in managing the TES Program to implement, expedite, review, and control the performance of the various program elements and to support STOR in defining, justifying, and promoting these program elements. The overall objective of the program is to develop, demonstrate, and encourage commercialization of energy storage systems that will:

- Increase the substitution of coal, nuclear, and solar energy for petroleum and natural gas
- Enable solar and other intermittent energy sources to provide continuous service
- Promote conservation by recovery, storage, and utilization of industrial waste heat

The program is composed of four major activities:

- Building heating and cooling applications
- Industrial applications
- Use promotion
- Applications assessment and program integration

2. Building Heating and Cooling

Building Heating and Cooling Applications address both residential and commercial buildings. Elements of this sub-program are Utility Load Management, Solar Applications, and Conservation.

The specific target for Utility Load Management is reduced gas and oil consumption effected through use of customer-side-of-the-meter storage devices to shift electrical load from peaking electrical generation equipment (frequently gas or oil-fired) to base-load equipment (mostly coal or nuclear). This is to be accomplished by developing storage technology including prototype storage devices for both hot and cold storage. The major thrust of the FY 1980 program was in the Utility Load Management element. Seven programs are either on-going or in the contracting process. FY 1981 will see continued strong support of this effort.

Research Triangle Institute has completed the simulation of six alternative phase-change TES/heat pump configurations, each operating in one or more of six representative cities which cover a range of U.S. climatic conditions. Annualized life-cycle cost data are being analyzed to assess the value of combining storage with a heat pump and to establish which areas of development, if any, are indicated by promising economic predictions. Performance curves of baseline heat pump components and a heat transfer model of phase-change storage material were combined with SOLMET-TMY hourly weather data over an average year for each city to establish energy usage of the various TES/heat pump configurations. Existing or projected time-of-day electricity rate structures specific to each of the six cities were used to project life-cycle costs.

Residential storage heaters for off-peak electrical charging and peak time storage discharge are widely used in Europe. One of the two commonly used ceramic materials in the European bricks is olivine. Because North Carolina has extensive deposits of olivine, the North Carolina Energy Institute has sponsored the development of brick technology by North Carolina State University utilizing domestic olivine. A program to assess the thermal and physical performance of bricks fabricated under the Energy Institute Program is sponsored by the TES Program. In addition, a commercially available heat storage furnace will be used for comparative testing of German magnesite bricks and the North Carolina State olivine bricks in the TES test facility at Purdue University.

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*Research sponsored by the Division of Energy Storage Systems, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation-Nuclear Division.

A contract is being negotiated with Energy Systems Division of Carrier Corporation for development of a cool TES system for residential space cooling utilizing off-peak charging. The development will be of an ice storage system. R&D resulting in a competitive prototype design will be conducted in a 2 1/2-year program. The system chosen for funding from among proposals submitted in response to an RFP was selected because of its strong potential for commercialization.

An RFP for the adaptation of ceramic heat storage brick technology as it exists in Europe to U.S. materials, manufacturing capability, and market requirements has been issued. The program requested will examine the factors (e.g., domestic raw materials availability, production techniques) affecting the transfer of existing technology to the U.S. It will determine what cost and performance improvements over existing practices are possible. The program is the first phase of a program which will, if based upon a review of Phase I results it is determined to be necessary, lead to establishment of a domestic source of TES ceramic bricks. Subsequent phases will be solicited independently of Phase I and will require substantial cost sharing.

The second of two heating season demonstrations of TES units in Maine and Vermont was completed this spring. The objective of this program is to demonstrate performance of residential TES units, determine customer acceptance, define TES unit sizing requirements for the U.S. market, and provide load impact data for the participating utilities. Approximately 75 residences both with TES and control are involved. Data are being analyzed, and results will be available in early FY 1981.

A demonstration of cool storage in the Delaware-developed CHUB for supplementing air-conditioning capacity is complete this fall. The program is conducted by NYSERDA and involves one residence in the LILCO utility service area. The configuration of storage/air conditioning is that which minimizes electrical demand. By combining a half-capacity air conditioner with storage and drawing from both in parallel during peak periods, the sudden increased demand for power possible from a full-size air conditioner, which is required for a system designed to draw only from storage during peak times, is precluded.

A calorimeter test chamber for electrically heated TES units was built and is operated by Purdue University for the TES Program. The principal objective of the program is to provide inputs to the development of the ASHRAE test standard. One room-size unit has been tested, and seven are on hand for further tests. Provisions have been made for testing residential central heating-size units outside of the calorimeter chamber, and an initial test has been completed.

Solar Applications is the second element of Building Heating and Cooling Applications. The target for this element is oil and gas conservation through the use of storage to increase the fraction of building heating and cooling loads which can be met with solar energy. Four programs are in progress or planned for this element of the TES Program.

ORNL has initiated testing of PCM storage units in the water loop of its Thermal Energy Storage Test (TEST) Unit. The purpose of TEST is to provide test data from prototype TES units for the developers of such units, to allow in-house development of units, and to define test procedures which allow meaningful definition of TES unit performance. Devices charged and/or discharged by means of a heat transfer fluid are accommodated in TEST. An air loop which will allow parallel development of air charged/discharged units will be constructed in FY 1981.

An RFP will be issued in FY 1981 for the development of practical building components which incorporate thermal storage. An in-house analysis of applications and requirements is being conducted in order that the requested development be directed towards realistic goals.

The University of Dayton has developed the process of stabilization of polyethylene by electron-beam irradiation. A phase-change storage material which retains its shape is thus available for solar applications requiring storage at 130°C. A 15,000-lb batch of material has been prepared and is being considered for a variety of system demonstration projects.

It is planned to issue an RFP for further development of heat storage in phase-change materials for residential space heating applications during FY 1981. The economics of such systems may be unfavorable, and thus any program which is a result of the RFP will address not only the technology but an assessment of the potential for producing an economically viable solution.

Conservation is targeted around reduced fuel usage in operation of building heating and cooling conventional subsystems. In residential applications the thrust is for recovery of low-grade heat from systems for augmentation of space heating. In commercial buildings the emphasis is on recovery and storage of waste heat and storage of cool to reduce peak demands.

TRW has completed an assessment of the effect of increased thermal capacitance within residential structures on energy conservation. Without accounting for solar input, there is little benefit shown. A second study of the effectiveness of storage in recovery of flue gas heat shows potential for large increases in furnace efficiency.

Data on the number and characteristics of commercial-sized water TES projects that have been built and are in operation in the U.S. and Canada are being obtained by Franklin Research Center. Analysis of the data will be undertaken to optimize the performance characteristics being achieved by commercial TES. The results will be utilized in establishing goals for assessing proposed improvements in TES technology.

An in-house program is ongoing to define the heat transfer processes involved and measure the benefit from preconditioning residential heat pump inlet air by ducting it through the crawl space. Three experiments are completed, and analysis of the data is completed. An energy saving has been found. However, a more definitive experiment in two similar structures (with and without air pre-conditioning) is being designed. Computer simulation of the earth/air heat transfer process is being developed to allow further generalization of the projected gains.

Mathematical modeling of phase-change storage material has been an on-going in-house program at ORNL. During FY 1980, the moving boundary problem has been examined in detail in a book authored by the principal investigator, Allen Solomon, which is to be published next year. A two-dimensional model of the crawl space heat transfer to heat pump inlet air supply has been completed. The model includes freezing of the earth. Preliminary test data compare favorably with the results of the simulation. The CHUB cool storage configuration of the NYSERDA cool storage demonstration has been modeled with the effects of inlet air humidity included. Predictions of the performance of that test configuration have been generated for comparison with the test data.

Two programs of data collection and performance analysis in commercial-stratified water storage installations are underway. An installation of storage tanks for both hot water and chilled water in a new public school in Oliver Springs, Tennessee, is being evaluated by The University of Tennessee. Each of the several tanks involved is a two-temperature tank with thermal separation provided by a commercial membrane system. A labyrinth thermal separation system is installed in a new University of New Mexico building. Stratified-hot water derived from solar collectors will be stored, and stratified-cold water derived from chillers operated during off-peak periods will be stored. The collection and analysis of performance data is being provided by the University of New Mexico.

3. Industrial Applications

The Industrial Applications activity includes programs leading to and including demonstrations of on-site utilization of process and waste heat in selected industrial plants. In addition, the transfer of demonstrated technology, industry-wide, is a major element of this program. The demonstration in Bellingham, Washington, of TES applied to the use of industrial waste heat in district heating is included as part of the Industrial Applications activity.

The objectives of Industrial Applications programs are to stimulate and implement TES technologies that:

- Provide for more efficient and more economic use of intermittent energies
- Provide for utilization of waste heat to replace primary fuels
- Provide for economic use of off-peak electrical power

Programs in progress or planned for FY 1981 in pursuit of these objectives follow.

Rocket Research Company (RRC), a division of ROCKCOR, and Trans Energy Systems, Inc., a subsidiary of ROCKCOR, are investigating the use of industrial process reject heat as a source of energy for large-scale district heating. The city of Bellingham, Washington, is the site-specific user; the industrial reject heat is obtained from the Intalco Aluminum Corporation plant located in Ferndale, Washington. The baseline district heating system is a network of closed-loop hot water pipes that recover energy at approximately 220°F from the fume hood ducts at the Intalco plant and transmit the energy to commercial, residential, and institutional users for space and hot-water heating.

The current program effort is directed toward achieving the following program objectives: (1) accurately assess economic viability, (2) verify institutional compatibility, (3) achieve public acceptance, (4) evaluate technological risk areas, and (5) evaluate alternate sources of thermal energy. The specific approach to the program objectives is described below, along with the current status of each of the five program tasks.

Marketing Analysis

A detailed thermal energy demand analysis was conducted for each of the 22 neighborhoods in the city. This data was then used to map preliminary routing for the service area. In addition, a market analysis plan to determine the rate of subscription and achieve public acceptance has been prepared. Conversion costs to retrofit buildings to use hot water from the district heating system have been developed for the types of buildings and heating systems prevelant in the anticipated service area. As part of the public information program, which should lead to public acceptance, a community advisory group (CAG) was formed. The CAG includes a cross-section of the community and meets every month to review and discuss issues concerning the project.

Technology Review

An evaluation of the impact that the district heating system will have on the Intalco facility did not indicate that there would be any major adverse impacts. A second major activity concentrated on the performance and life of the heat exchanger placed in the Intalco exhaust fume. Probe tests reveal that a hard, conductive buildup occurs in the stagnation region for tubes in a cross-flow configuration. In contrast, a soft, fluffy buildup takes place on the back side of the tube. The third activity includes a comparative evaluation of storage options. Included in this assessment are above-ground insulated tanks, aquifers, and use of an abandoned coal mine. The current baseline case uses tanks, although use of a portion of the coal mine appears feasible.

Evaluation of Additional Thermal Sources

Ten alternate sources of thermal energy have been identified and evaluated. A selection has been made, and four of the facilities are undergoing a detailed analysis.

Institutional Consideration

Identification of legal, political, and institutional constraints is being pursued. Ownership/management options are being evaluated, and at present it appears that municipal ownership (Bellingham has the legal charter to own and operate a district heating system) is the favored option. The city is also in the process of selecting a bond counsel team to assist in exploring financing options for full-scale development.

System Cost Analysis

A preliminary system cost analysis has indicated that the consumer would derive substantial benefits by subscribing to the system. The utility would finance the building retrofit costs and offer heat the first year at a price of 80% of the least-cost alternative (presently gas). Throughout the assumed 30-year lifetime, the consumer would continue to pay considerably less for heat than if he were using fossil fuel because energy costs for the district heating system escalate less rapidly than fossil fuel.

Howard Edde, Inc., is conducting a program to collect and disseminate information concerning thermal energy storage systems for the pulp and paper industry. This effort includes (1) a survey of Scandinavian and North American mills to identify thermal energy storage concepts presently in use, (2) selection of four representative systems for detailed cost/benefit analysis, and (3) dissemination of this information throughout the industry.

The preliminary survey has been completed, and representative concepts have been chosen for the cost/benefit analysis.

A team consisting of Heinz USA and Westinghouse conducted the Phase I program to evaluate the technical and economic feasibility of using TES to recover and reuse reject heat. Because the feasibility results were positive, negotiations have begun with Heinz for the demonstration phase.

The objectives of the Phase II work are to design, construct, and operate a TES system that will recover waste heat from canning operations, store the recovered heat, and reuse for water preheating and third-shift cleanup operations.

The National Food Processors Association will also be a member of the study team and be responsible for effectively informing the food industry, particularly the canning segment, concerning the costs and benefits of the TES system.

Burns and Roe, Inc., is investigating the benefits of using a once-through heat supply system for the Bellingham district heating system. This project, begun August 1, 1980, will include a conceptual design of the system, preliminary cost estimate, and review the environmental impacts.

An RFP was issued by NASA-Lewis in FY 1980 calling for TES concepts for industries other than Paper and Pulp and Food Processing. The winning proposals are being chosen, and programs will be implemented in FY 1981.

Use Promotion is presently an integral part of each Industrial Application project. Promotion/commercialization activities for Building Heating and Cooling presently consist of both preparation of implementation plans and customer acceptance studies.

Applications Assessment comprises in-house studies in support of program development and guidance. Initiation of each new project is preceded by technical economic or use assessments. Integration of the TES program with the overall program of DOE is a vital part of the program in that uses and needs for storage development in great part are drawn from other DOE departments.

Simulation and Evaluation of Latent Heat Thermal Energy Storage Heat Pump Systems

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J. M. Doster, Research Triangle Institute
J. F. Martin, Oak Ridge National Laboratory
J. A. Edwards, North Carolina State University

ABSTRACT

A ranking analysis of six latent heat Thermal Energy Storage (TES)/Heat Pump Systems, for residential heating and cooling applications, has been completed for different climatic regions of the U.S. The primary basis for this evaluation was system annualized life cycle cost. Annual system performance was determined at six sites using a computer simulation of the performance of the alternative TES/Heat Pump designs. The systems considered were required to satisfy building heating and cooling loads calculated using TRNSYS (Ref. 1) under existing or proposed electricity rate structures at each simulation site. The load simulation was driven by hourly weather data provided by Sandia National Laboratory (Ref. 2). Predetermined performance characteristics of the TES/Heat Pump systems were interfaced with the thermal loads from which energy use and cost profiles were computed. The alternative systems were compared at the different geographic locations on the basis of performance and life cycle costs and preferred systems identified for each particular climate.

INTRODUCTION

Heat pump systems coupled with thermal energy storage have the advantage of: 1) providing a means of substituting lower cost thermal energy during heating operation for that which is normally supplied by resistance heaters, 2) improving the efficiency of heat pump systems during both heating and cooling operation, and 3) decreasing heat pump operating cost by allowing the heat pump to operate primarily during periods in which low cost electricity is provided under time-of-day (TOD) electricity rate structures. Although the focus of previous work has been aimed at heat pumps coupled with sensible heat storage subsystems, the advantages associated with latent heat storage has precipitated research and development efforts considering latent heat TES/Heat Pump systems as well. Latent heat systems in general store more energy per unit volume than do sensible heat systems and allow for storage at a constant temperature.

Six different TES/Heat Pump system designs were considered in this analysis. These designs include: 1) direct TES/Heat Pump systems in which the storage subsystem is charged within the refrigeration cycle itself and discharged by direct heat exchange between indoor return air and storage material, 2) indirect systems that are both charged and discharged within the refrigeration cycle of the heat pump, 3) hybrid systems that act as direct systems during cooling operation and indirect systems during heating, and 4) hybrid systems that act as indirect systems during both heating and cooling. A conventional heat pump with no storage was considered as a baseline for comparison. The storage subsystem considered is a rectangular design which provides for heat transfer between both storage material and refrigerant, and storage material and air.

TECHNICAL APPROACH

TES/Heat Pump Systems

The six TES/Heat Pump configurations considered are classified depending upon the method used to discharge the TES subsystem. Direct systems are discharged by the transfer of heat between the storage material and the indoor air stream, while indirect systems are discharged by using the TES subsystem as a low temperature sink (cooling) or high temperature source (heating) for the heat pump. All six configurations involve charging the TES subsystem within the refrigeration cycle of the heat pump by using the storage subsystem as either an evaporator or condenser as appropriate. The heat pump components were sized to provide a 3-ton heating and cooling capacity.

Figures 1 and 2 show schematically two of the six configurations analyzed. Figure 1 is a representation of an indirect system that stores thermal energy for use only in the heating mode. The system operates as a conventional heat pump during cooling. During the charging cycle, the TES subsystem acts as a condenser, while at the same time storing energy by means of the change of phase of the storage material from solid to liquid. During discharge, the TES subsystem behaves as an evaporator for the heat pump cycle and rejects heat to the refrigerant by means of the change of phase from liquid to solid. The direct system used for storage heating charges in the same manner but the storage temperature (114°F) is at a level that can be used for direct heating so that discharging involves operation of the indoor fan only.

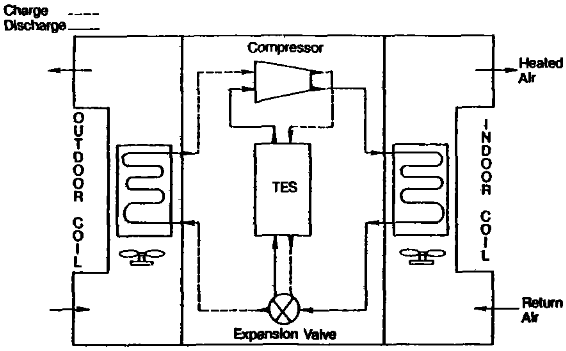

Figure 1. Indirect Heating System

Figure 2 is a schematic of an indirect TES/Heat Pump system used for cooling purposes. The system operates as a conventional heat pump during heating operation. During the cooling season the

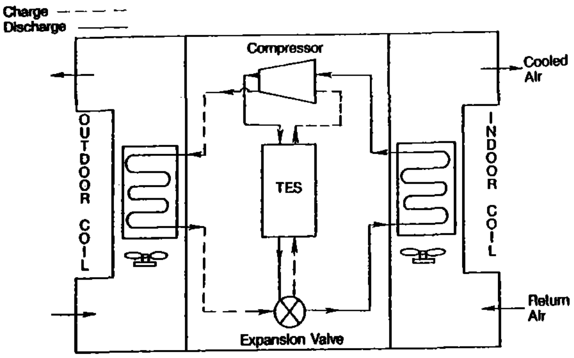

Figure 2. Indirect Cooling System

storage subsystem is charged by converting the storage material from a liquid to a solid by allowing the TES subsystem to act as an evaporator. The subsystem is then discharged by reversing this process. The direct system used for storage cooling is dicharged directly with a storage temperature of 32°F. A complete list of the systems evaluated is given in Table 1.

TES Subsystem

The TES subsystem rectangular design, shown in Figure 3, consists of alternate layers of storage material and refrigerant and air flow passages. The TES material is contained within individual storage modules in contact with the refrigerant circuit. The TES subsystem has been sized to provide a total storage capacity of 300,000 Btu for each system.

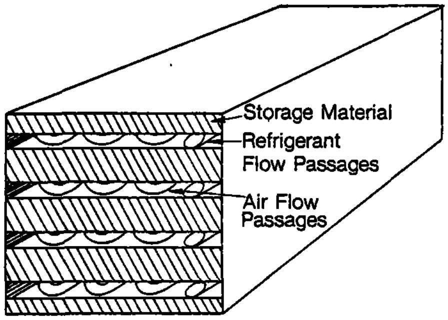

Figure 3a. TES Subsystem Design

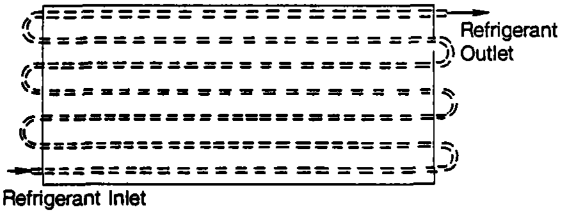

Figure 3b. TES Subsystem Design (Top View)

Table 1. TES/Heat Pump Systems

System	Storage Material	Melt Temperature (°F)	Heating Operation	Cooling Operation	Storage System Use
Base	Heat Pump		Heat Pump	Heat Pump	None
1	STP (sodium thiosulfate pentahydrate)	114	Heat Pump/ Direct Heating	Heat Pump	Direct space heating
2	Thermol 81	81	Heat Pump/ Indirect Heating	Heat Pump	High temperature source for heat pump during heating
3	Ice	32	Heat Pump	Heat Pump/ Direct Cooling	Direct space cooling
4	Delaware Glauber Salt	55	Heat Pump	Heat Pump/ Indirect Cooling	Low temperature sink for heat pump during cooling
5	CalMac	45	Heat Pump/ Indirect Heating	Heat Pump/ Direct Cooling	High temperature source for heat pump during heating -- Direct space cooling in cooling mode
6	Delaware Glauber Salt	55	Heat Pump/ Indirect Heating	Heat Pump/ Indirect Cooling	High temperature source for heat pump during heating -- Low temperature sink for heat pump during cooling

TES/Heat Pump Model

A computer simulation was used to compute performance characteristics of each TES/Heat Pump system. The basis of the simulation is the determination of equilibrium values for heat transfer and refrigerant mass flow within the refrigeration cycle of any TES/Heat Pump system for each mode of operation. The method used to compute this balanced condition is a modification of the procedure offered by Oak Ridge National Laboratory (Ref. 4). These equilibrium values were found using manufacturer's performance data for the conventional heat pump components, and a detailed mathematical model describing the melt/freeze process taking place within the storage subsystem and the refrigerant or air side heat transfer process. Total system capacity and input power to the system as a function of ambient temperature, and time during charging ahd discharging operation, were computed.

Simulation Site Location

The following six cities were chosen as simulation sites: Boston, MA; Fort Worth, TX; Miami, FL; Nashville, TN; Phoenix, AZ; and Seattle, WA. Hourly weather data for the six cities were provided through the Solmet Typical Meteorological Year (TMY) weather tapes. These cities possess a wide range of climates. Therefore, the performance of the TES/Heat Pump systems were evaluated under a wide range of operating contraints.

Building Design

The basic building design consists of a rectangular, single story, 140 m^2 (1500 ft^2) wood panel residence with a full basement. The building design, orientation, and construction is the same for each of the sites; however, insulation levels were varied to characterize existing practices in different regions of the country.

Thermal Load Characterization

The thermal loads at each site were computed using the TRNSYS computer simulation. Total hourly latent and sensible heating and cooling loads were determined for the house using the TMY hourly weather data and the previously described house design.

Rates

Public electric utilities serving the simulation sites provided both standard and time-of-day (TOD) rate structures. These rate structures were used as input to the TES/Heat Pump simulation and to compute energy costs for the systems.

TES/Heat Pump System Performance

TES/Heat Pump system operational performance was determined for each site by interfacing the thermal loads computed using TRNSYS with the performance data for each system. A system control strategy subroutine defined the operating strategy for each system with the objective of minimizing operating costs. The electric utility rate structures were input to the control strategy to identify the time periods suitable for each mode of operation. Those combinations of site and TES/Heat Pump systems simulated are shown in Table 2.

Life Cycle Costs

Annualized system life cycle costs were computed for each combination of geographic location, storage system, and rate structure considered. The annual cost of the system was computed by considering initial investment costs, annual energy costs at present prices, rate of change in the real price of energy, annual real discount rate, lifetime of the system, and maintenance cost. The annual energy cost is that computed by the simulation using the rate structure of each particular site; however, the other variables listed were treated as parameters.

RESULTS AND CONCLUSIONS

The TES/Heat Pump simulation accurately predicts the performance of the six designed systems. These various systems were compared on the basis of total annual energy usage and an annualized life cycle cost analysis. Total annual energy usage in kWh and energy costs and percent change in energy usage compared to the base system are given in Table 3 for Nashville. Table 4 lists the system life costs computed for Nashville.

The indirect heating systems require more electrical energy than the baseline heat pump system for all the simulation sites. Energy usage

Table 2. Combinations of Site and Systems Simulated

Site	Heat Pump	Option 1	Option 2	Option 3	Option 4	Option 5	Option 6
Boston	X	X	X	X			
Phoenix	X			X	X		
Miami	X			X	X		
Fort Worth	X			X	X		
Nashville	X	X	X	X	X	X	X
Seattle	X	X	X				

Table 3. Annual Energy Use and Cost for Nashville

System	Total Annual Energy Usage (kWh)	Change in Total Annual Energy Use (%)	Total Annual Energy Cost (1980 Dollars)	Change in Annual Energy Cost (%)
Heat Pump	20,773	0	765	0
Option 1	19,590	-5.7	538	-30
Option 2	21,010	1.1	653	-15
Option 3	20,195	-2.3	730	- 5
Option 4	20,661	-0.5	711	- 7
Option 5	20,343	-2.1	730	- 5
Option 6	21,476	3.4	740	- 3

for the indirect cooling system is also slightly higher than the conventional heat pump system for each of the sites with the exception of Nashville and Fort Worth where slight decreases are seen.

The direct systems proved to be much more efficient at shifting energy usage from peak to off-peak periods with total on-peak energy use decreased by over 90 percent. Direct systems provided for a decrease in total energy use by as much as 5.7 percent.

Table 4. System Life Cycle Cost
(1980 Dollars, Nashville)

Heat Pump Life Cycle Cost = $1,148

	Capital Cost			
Option	$3,000	$4,000	$5,000	$6,000
Option 1	958	1,081	1,205	1,328
Option 2	1,073	1,196	1,319	1,443
Option 3	1,150	1,273	1,379	1,520
Option 4	1,131	1,254	1,377	1,501
Option 5	1,150	1,273	1,397	1,520
Option 6	1,160	1,283	1,406	1,530

Annual Rate of Change in Real Price of Energy = 0.0
Annual Real Discount Rate = 0.04
Lifetime of System = 10 years
Annual Maintenance Cost = $50

By operating under TOD electrical rate structures total annual energy costs were decreased using the direct systems by as much as 30 percent and for the indirect systems by as much as 23 percent; however, this decrease in cost was accomplished with corresponding increases in energy use for the indirect systems. This increase in energy used is reflected in the life cycle cost analysis which shows the direct systems to have shorter payback periods.

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DESIGN AND DEMONSTRATION OF A STORAGE-ASSISTED AIR CONDITIONING SYSTEM

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Abstract

This paper discusses the design and demonstration of a residential storage-assisted air conditioning system that imposes the minimum electric demand on a utility system. Hence, the system is a peak-shaving system designed to provide a levelized air conditioning load. The system also requires minimum air conditioner and thermal storage capacity.

The storage-assisted air conditioning system uses a Glauber's salt-based phase change material in sausage like containers called CHUBS. The CHUBS are two (2) inches in diameter and 20 inches long. They are stacked in modules of 64 CHUBS which are appropriately spaced and oriented in the storage system so that air may pass perpendicular to the long axis of the CHUBS. The phase change material, which is produced by the Institute of Energy Conversion at the University of Delaware, has a thermal storage capacity in the range of 45 to 50 Btu/lb and a transition temperature of approximately 55°F.

The storage-assisted air conditioning system consists of a conventional central air conditioning system (of reduced capacity), a storage bin of CHUB modules, a fan, appropriate ducting and controls. This system is being tested in a single family house on Long Island. Testing began in August of 1980. For this reason time did not permit the inclusion of test data into this paper.

I. Introduction

Due to the widespread use of air conditioning throughout much of New York State and other parts of the country, many utilities are faced with large summer peak loads and poor annual and daily load factors. In the past, there generally have been no incentives for residential customers to reduce peak electric usage. In the last few years, however, high costs for generation, transmission and distribution facilities and the high cost of operation of peaking units have had a great impact on utility costs and the rates that must be charged to recover these costs. In order that the burden of these costs be placed on those responsible, and that proper economic signals be given to consumers, New York State (and other states) are adopting marginal cost-based rates. On Long Island, where this demonstration is being conducted, the Long Island Lighting Company (LILCO) has implemented mandatory time-of-day rates for large commercial customers and large residential customers. Storage rates for residential customers are available on a voluntary basis. Other rate forms are possible and their implementation will depend upon utility and customer costs and benefits.

Various types of storage air conditioning systems are being developed and evaluated to shift the entire air conditioning load off-peak. Because of the length of the peak and the shortness of time to charge the storage system, such systems have been found to impose a high requirement for storage and air conditioner capacity. The question has arisen as to whether total off-peak cooling is the optimum approach, which can only be answered by the examination of alternate systems. This project will evaluate a storage-assisted air conditioning system which will impose minimum electric demand on the utility system. This approach offers the potential for minimum air conditioning system and storage system capacities and costs, minimum impact on utility distribution systems, and avoids the possibility of moving peaks from one time to another.

The storage air conditioning system to be demonstrated under this project will use CHUBS developed by the University of Delaware under contract to Oak Ridge National Laboratory. The CHUBS are long cylindrical packages, looking like big sausages, containing a Glauber's salt-based phase change material. The CHUBS offer the potential for a low-cost storage system.

OBJECTIVES

The objectives of this project are as follows:

a) To define a storage-assisted air conditioning system using CHUBS which will impose the minimum electric demand on the utility system.

b) To evaluate the characteristics of the storage-assisted air conditioning system with respect to:

   1. Air conditioner system performance
   2. Energy storage sub-system performance
   3. Electrical demand and energy requirements
   4. Temperature and humidity control capability
   5. System cost

   (These characteristics are to be evaluated by comparison to those of a non-storage system).

c) To determine the thermal behavior and assess the integrity and stability of the CHUBS under actual service conditions.

d) To obtain customer load data for assessing potential utility benefits.

e) To assess economic feasibility based on estimated system cost and potential utility and customer benefits.

APPROACH

The storage-assisted air conditioning system is designed to impose the minimum demand on the utility system. This design criterion dictates that the air conditioning system be sized to meet the average cooling requirements for the home on the worst case or design day, rather than the maximum cooling requirements for that day. "Cool storage" is provided to assist the air conditioning system to meet the cooling requirements for the home which are in excess of the average. The cool storage system is charged during times when the cooling requirements for the home are below the average and hence the air conditioning system is not needed full time to provide cooling for the home. The design concept may be more clearly described by reference to an example. This example reflects the characteristics of the demonstration site for this project.

The demonstration is being conducted in a single-family split-level home in Melville, Long Island, New York. The air conditioning system is designed to provide a 78°F indoor temperature under conditions of 98°F outdoor temperature and a 30% latent heat load. The maximum cooling requirements under these conditions for the design house are 25,800 Btu per hour. Typically a 2½ ton air conditioning system with a nominal cooling capacity of 30,000 Btu per hour would be selected.

The required capacities for the air conditioning system and cool storage system for a storage-assisted air conditioning system are determined from the hourly cooling requirements for the design day. These cooling requirements are presented in Figure 1.

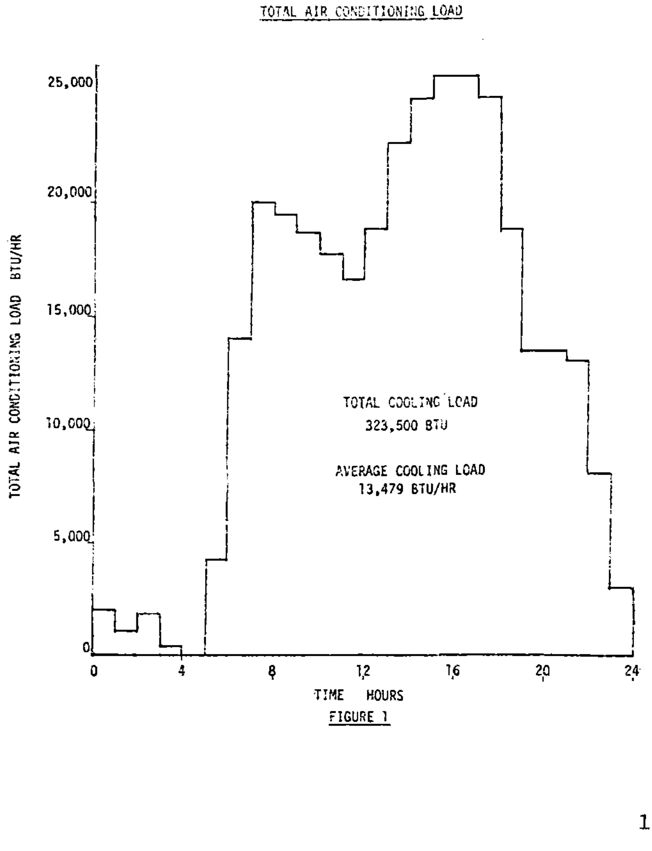


FIGURE 1

The total cooling requirements for the design day are 323,500 Btu. This represents an average cooling load for the design day of 13,479 Btu/hr. It should be noted that this average cooling load is slightly more than half (52.2%) of the design day maximum cooling load. The smallest air conditioner capable of meeting the design day average cooling load is a 1½ ton unit with a nominal cooling capacity of 18,000 Btu/hr. A unit of this size (1½ tons) has been selected for use in this storage-assisted air conditioning system. The selection of the reduced size unit represents a decrease in cooling capacity of one-ton and would decrease the peak power requirements of the air conditioning system by approximately 1.7 kw (40%).

SYSTEM CONFIGURATION

Several storage-assisted air conditioning system configurations and control strategies are possible within the general constraint of providing a system which imposes a minimum demand on the electric utility. A schematic of the storage-assisted air conditioning system which was selected for demonstration is presented in Figure 2. The system configuration was chosen because it offers both simplicity and flexibility. In the house cooling mode, the storage system (CHUBS) is in parallel with the evaporator and supplements the air conditioning system in meeting the maximum cooling requirements of the house. In the storage system charging mode, two dampers close, isolating the storage-assisted air conditioning system from the house, and leaving the evaporator and storage system in a series circuit. In this mode, the airflow is induced by the evaporator fan only and flows through the storage system and fan assembly in the reverse direction.

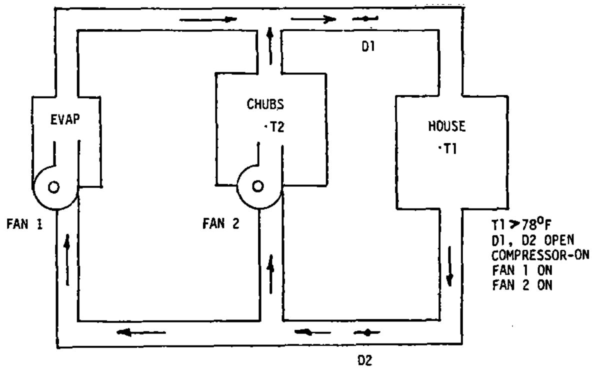
It should be noted that cooling of the storage system with an air conditioner is off-nominal operation. The CHUBS have a transition temperature of approximately 55°F, and hence a significantly lower evaporator temperature than normal is required to provide air which is capable of cooling the CHUBS to below their transition temperature. The air conditioner used was equipped with an accumulator and freeze protection to limit problems which may occur from this off-nominal operation. It is anticipated however that a reduction in air conditioner capacity of up to 30 percent may occur in the charging mode.

CONTROL STRATEGY

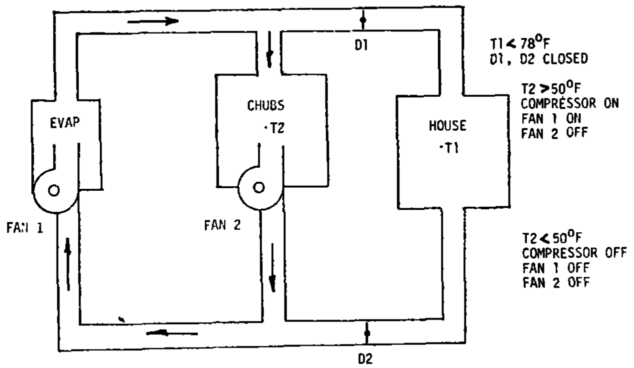
With the above described storage-assisted air conditioning system configuration, several control strategies are possible. One such strategy would be to use the air conditioner as the primary cooling system and to utilize storage only when the air conditioning system is not capable of meeting the cooling load. This might be accomplished by setting the thermostat which controls the cooling from storage a few degrees lower than the thermostat which controls air conditioner operation. Under this scheme the storage system would be utilized as a peak shaving system. The analysis of the system on an hourly basis using this control strategy is shown for the design day in Table 1. This system would require a storage capacity of 53,800 Btu, but on the design day would still have the cooling capacity to provide 95,800 Btu of storage system cooling.

An alternate control strategy, described on Figure 2, would activate the air conditioner and storage system cooling whenever cooling is called for. This control scheme would take more cooling out of storage than is actually required to supplement the air conditioner cooling capacity. In this scheme, the air conditioner may never be providing cooling to the house continuously. The air conditioner would cycle on and off in accordance with house cooling requirements. Under the control logic shown in Figure 2, the charging and discharging of the storage system would occur alternately during the same hourly periods. This control scheme may not be optimum if the loss in air conditioner performance during charging is found to be as high as 30 percent. The analysis of the system under this control strategy is shown for the design day in Table 2. This system would require a storage capacity of 65,412 Btu and on the design day would still have the cooling capacity to provide 88,148 Btu of storage system cooling. Although this control strategy is initially being employed, it is expected that both of these control approaches and possibly others will be evaluated during the test phase of this project.

HOUSE COOLING MODE



STORAGE SYSTEM CHARGING MODE



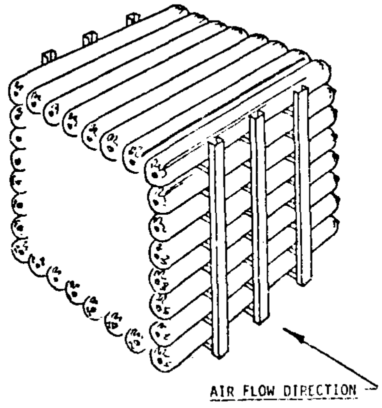
STORAGE ASSISTED AIR CONDITIONING SCHEMATIC

FIGURE 2

For this demonstration, it was decided to provide considerably more storage capacity than is believed to be required. This will allow for the testing of alternate approaches if desired. The storage capacity may easily be reduced in size by removing CHUBS to facilitate testing of actual storage requirements.

STORAGE SYSTEM

The storage system is made up of CHUBS (cylindrical packages 2" dia x 20" long containing sodium sulfate decahydrate and other salts required to adjust the transition point to approximately 55°F, and a gelling agent which prevents segregation of the salts). The CHUBS are assembled into modules of 64 CHUBS as shown in Figure 3. Each module wieghs approximately 208 pounds and has a nominal storage capacity of 10,400 Btu. The storage system contains 18 modules in a configuration which is three modules wide, two modules high and three modules deep. The total storage capacity of the system is 187,200 Btu. The storage bin containing these modules is 5 ft. wide, 3 1/3 ft. high and 5 ft. deep.



CHUB MODULE

64 CHUBS
208 POUNDS (3.25 POUNDS EA.)
10,400 BTU (162.5 BTU EA.)

FIGURE 3

INSTRUMENTATION

A Campbell Scientific CR5 data loger is used to continuously monitor parameters of interest during the test phase. Approximately 18 temperature measurements, 2 humidity measurements and 3 power measurements are monitored. The measurements will be used in the analysis of both total system performance and performance of the storage system.

PROJECT STATUS

The storage-assisted air conditioning system and the instrumentation system were installed in July of 1980. System checkout was completed during the first week of August. The system was operational as of August 8, and data is now being collected. However, time did not permit inclusion of data analysis in this paper.

System optimization and refinement of the data collection process will be on-going throughout the program. Data will be taken throughout the remainder of the 1980 air conditioning season, and during the 1981 air conditioning season, as required.

TABLE I

Hourly and Daily Air Conditioning and Storage Status for the Storage Assisted Air Condioning System

Time	Hourly Cooling Load BTU	Cooling by Air Condtioner BTU		Cooling Out Of Storage BTU
		To House	To Storage	
1 AM	2,000	2,000	10,700	
2 AM	1,100	1,100	11,350	
3 AM	1,800	1,800	10,750	
4 AM	400	400	11,750	
5 AM	0	0	12,100	
6 AM	4,100	4,100	9,250	
7 AM	13,700	13,700	2,500	
8 AM	19,900	16,600		3,300
9 AM	19,500	16,600		2,900
10 AM	18,800	16,600		2,200
11 AM	17,800	16,600		1,200
12 AM	16,600	16,600		--
1 PM	18,900	16,600		2,300
2 PM	22,400	16,600		5,800
3 PM	24,700	16,600		8,100
4 PM	25,800	16,600		9,200
5 PM	25,800	16,600		9,200
6 PM	24,500	16,600		7,900
7 PM	18,300	16,600		1,700
8 PM	12,600	12,600	3,300	
9 PM	12,600	12,600	3,300	
10 PM	12,000	12,000	3,700	
11 PM	7,100	7,100	7,150	
12 PM	3,100	3,100	9,950	
Total Daily Cooling Load =	323,500 BTU	269,700 BTU	95,800 BTU	53,800 BTU

Average Hourly Cooling Load = 13,479 BTY/HR

Net Cooling to Storage = 42,000 BTU

TABLE II

	Hourly Cooling Load BTU	Cooling Provided by A/C	Cooling Provided by Storage BTU	Cooling Provided to Storage BTU	Net Cool Into Storage	Net Cool Out of Storage
1 AM	2,000	1,270	730	11,226	10,496	
2 AM	1,100	700	400	11,626	11,226	
3 AM	1,800	1,140	660	11,311	10,651	
4 AM	400	250	150	11,928	11,778	
5 AM	0	0	0	12,110	12,110	
6 AM	4,100	2,600	1,500	10,294	8,794	
7 AM	13,700	8,680	5,020	6,031	1,011	
8 AM	19,900	12,610	7,290	3,282		4,008
9 AM	19,500	12,170	7,330	3,233		4,097
10 AM	18,800	11,730	7,070	3,548		3,522
11 AM	17,800	11,110	6,690	4,008		2,682
12 AM	16,600	10,360	6,240	4,553		1,687
1 PM	18,900	11,790	7,110	3,500		3,610
2 PM	22,400	13,600	8,800	1,453		7,347
3 PM	24,700	15,410	9,290	860		8,430
4 PM	25,800	16,100	9,700	363		9,337
5 PM	25,800	16,100	9,700	363		9,337
6 PM	24,500	15,290	9,210	957		8,253
7 PM	18,300	11,420	6,880	3,778		3,102
8 PM	12,600	7,980	4,620	6,515	1,895	
9 PM	12,600	7,980	4,620	6,515	1,895	
10 PM	12,000	7,560	4,440	6,782	2,342	
11 PM	7,100	4,500	2,600	8,961	6,361	
12 PM	3,100	1,960	1,140	10,729	9,589	
		202,310	121,190	143,926	88,148	65,412

Net Cooling to Storage = 22,736

EXPERIMENTAL EVALUATION OF THERMAL ENERGY STORAGE: STATUS REPORT

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1 Abstract

Thermal energy storage (TES) for space heating is a load management technique that has successfully been used in Europe. Early results from the ANL assessment of energy storage technologies indicated that customer-owned TES units of the type used in Europe could provide a cost-effective means for utility load management in the U.S. It is only necessary, therefore, that the technical and economic viability of this technology be examined under U.S. climatic, institutional and other conditions. In Vermont, utilities had already begun to investigate thermal energy storage and off-peak rates as one form of load management and had instituted programs to reduce loads by direct utility control of storage hot water heaters. New England, with its strong dependence on oil and scarcity of natural gas, is a regional area with a great potential market for TES and was selected as the site for the experiments reported here.

2 Objectives

We report here some results of two heating seasons, involving a collaborative effort among the following participants: ANL, the Universities of Maine and of Vermont, and several local cooperating electric utility companies (Central Maine Power Co., Central Vermont Public Service Co., Green Mountain Power Co. and Vermont Electric Cooperative). In a separate report, Purdue University (a subcontractor to ANL) summarizes the status of its effort to develop standardized test procedures for TES devices.

The principal objectives of the study are to:

- o Determine the technical performance of commercially available TES units under severe U.S. weather conditions.
- o Assess the benefits and costs of TES.
- o Determine customer and utility acceptibility of customer-owned TES.
- o Identify and define TES issues, R&D needs and barriers to commercialization.
- o Establish optimal sizing procedures.
- o Establish uniform TES testing standards.

3 Findings

3.1 Technical Performance

Field studies in Vermont and Maine were carried out to evaluate the performance of TES systems. The experiment involved 45 TES-heated homes; 30 electric baseboard-heated homes served as controls. Monitoring equipment recorded the electric heating demand and the inside and outside temperatures every 15 minutes in these homes. Data were collected monthly from the test and control sites. All of the participating homes had been energy-audited by the local electric utility company. Most of the TES units in the test homes were room-type ceramic storage heaters, but six hydronic storage heaters and one central ceramic storage furnace were also being tested. All units were sized by the vendor to meet the full design-day heating load and were commercially installed. The standard charge period is eight hours.

Functional performance of the TES systems has generally been good, and it has been concluded that TES units, if properly sized for the home, perform well. This conclusion applies to dispersed and central ceramic units and to hydronic units.

The major criterion for this assessment was the maintenance of essentially identical inside temperatures in thermally matched test and control homes throughout the heating season, e.g., on typical January days, on October days (which have more volatile temperature fluctuations), and on the coldest day of the year. In Vermont the lowest temperature recorded at the sites was -28^{O}F on February 12, 1979; in Maine 70 degree-days were accumulated on February 14 of that year, providing rare opportunities to observe heating-system performance under design conditions and to evaluate shortcomings in sizing. Graphical records of daily electrical demand and inside temperatures of test homes clearly distinguished adequately sized storage heating systems that use only off-peak electricity generated during high-use times.

Table 1 shows the monthly relative energy use in similar adjoining apartments at one of the sites. Considering the variations in energy use expected because of different living habits, there is no significant difference to be discerned between energy utilization in TES-heated and baseboard-heated apartments (5569 vs. 5467 kWh/apt).

Table 1. Total Electrical Demand (kWh) in "Identical" Apartments (Waldoboro, ME. 1980)

	Month				
	January	February	March	April	Season
TES Equipped Houses*					
Original Data	1619	1442	1297	920	5277
Adjusted For Heat Loss (VA), Inside Temperature and Apartment Size	1799	1518	1336	916	5569
Control Houses**					
Original Data	1978	1758	1556	875	6167
Adjusted For Heat Loss (VA), Inside Temperature and Apartment Size	1754	1549	1335	840	5476

* Average of four apartments

** Average of three

System load curves for Central Vermont Public Service Corp. and Central Maine Power Co. are shown in Fig. 1 and 2. Both utilities have two daily peaks and a major valley from about midnight to 6 a.m.; both provide off-peak energy for 8-hours between 10 p.m. and 6 a.m. at special low rates. Also shown in the figures are the hourly

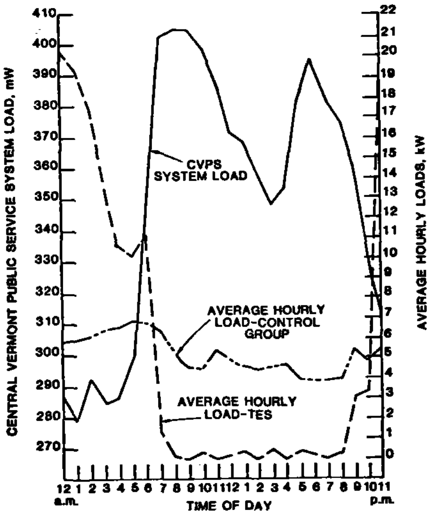

Fig. 1. Daily Load Curve (Central Vermont Public Service Co. Area)

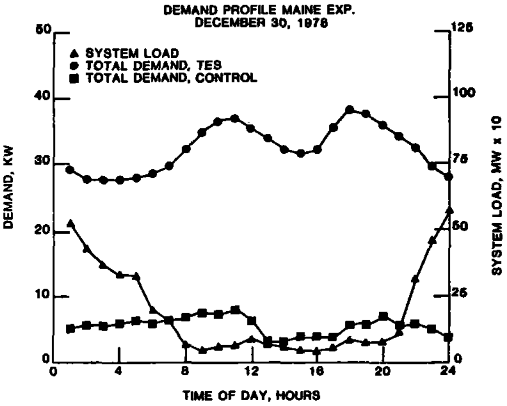

Fig. 2. System Load Curve for Central Maine Power Company and Measured Demand for TES and Electric Resistance Heated Homes

load (or demand) curves for the TES group and the control group. It may be seen that there is virtually no demand for electric heat from the TES homes during the on-peak hours, but a high demand during the off-peak period when the TES homes avail themselves of electricity at a lower price.

The Vermont Electric Cooperative provides a mid-day boost. As shown in Fig. 3, during the peak periods between 7 a.m. and 1 p.m., and between 5 p.m. and 11 p.m., none of the TES homes is demanding on-peak electricity for heating.

Figure 4 is a record of one week's variations in total and electric heat demand in TES homes in Maine; during the 16-hour on-peak period there is no demand for electricity for heating yet there is no change in the inside temperature (uppermost curve) which is maintained at a constant temperature.

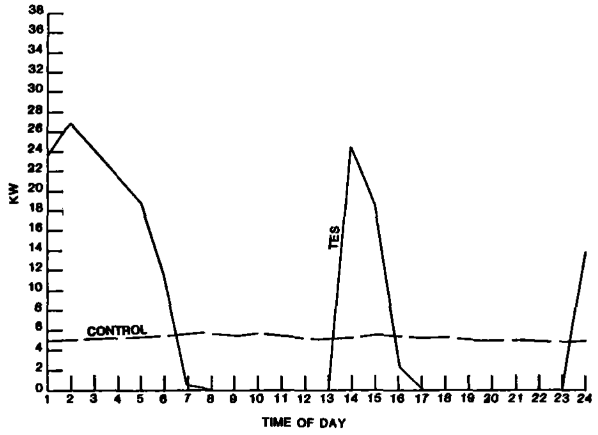

Fig. 3. Daily Load Curve; TES with Mid-Day "Boost" (Vermont Electric Cooperative, January 21, 1980)

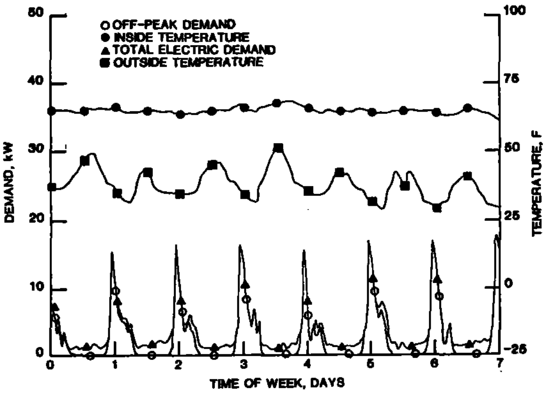

Fig. 4. Weekly Load Curve, Total and TES Heating Demand (Central Maine Power Co., March 1980)

3.2 Fuel Bills

The operating costs of TES heaters using only low-cost off-peak electricity are generally lower than those of electric resistance (baseboard) heaters. In Maine there is presently a 2¢/kWh price differential between the standard rate and the storage off-peak rate. In similar homes the fuel bills for the period January 1 to April 30, 1980, were 30% lower for the TES group ($198/TES home, $284/control home). Similar savings are experienced in Vermont.

3.3 Social Benefits and Costs

Studies of the economics of TES in Maine and Vermont using a social welfare approach indicate that there are net social benefits and that benefits can accrue to both user and utility. This conclusion is based upon a comparison of the estimated costs and consequent savings. Factors taken into account include:

(1) additional customer costs, compared to direct baseboard systems, of installed TES systems (room units and central furnaces) in homes having a wide range of heat loss;

(2) utility costs of special controls, meters and transformers;

(3) utility returns due to estimated future savings in foregone generation, transmission and distribution needs (discounted to present value.)

In Maine, the total savings are estimated to be about $344 per kilowatt of heat loss, and the additional capital cost with respect to electric baseboard heaters is about $225 per kilowatt of heat loss. The cost of electric baseboard heaters is about $150/kW. In Vermont the savings are comparable and lead to benefit-cost ratio estimates in excess of 3 for room units and 5 for central units. The higher ratio for central units is due to their lower capital cost per kilowatt of heat loss.

3.4 Customer Acceptance

A consumer survey firm was commissioned to determine user acceptance of TES. The survey was performed by telephone in June, 1979 and covered a total of 133 homes, 108 with TES (including 23 from our study) and 25 with conventional electric heating systems as controls. Over 95% of the owners of homes with TES units would recommend TES to a friend (the same as for users of baseboard heaters). The improvements most frequently suggested were decreasing the physical size of the room units and improving their appearance. The survey revealed equal satisfaction with storage heaters and with baseboard heaters.

3.5 Rate-Setting

The problem of increasing the number of TES users is that of transferring some of the anticipated utility savings to the customer so that TES will be an attractive investment. The problem is complex but solvable, and is utility- and device-specific. Based on our analysis, a load management agreement between customer and utility seems better than either a time-of-use rate format or a time-of-use plus demand-charge rate. Load management agreements insure more control of utility capacity growth and less customer risk of rate instability. Time-of-use rates open up the possibility of using undersized storage units.

3.6 Sizing

The value of TES is very sensitive to the amount of storage capacity installed. The sizing problem has several interrelated elements:

1. the incentive of the vendor to make a sale by lowering the capital cost (i.e., recommending smaller capacity than may be required),
2. the goal of the customer or real estate developer to minimize initial cost (thereby impacting the utility on its peak demand days),
3. different sizing methods used by different vendors, and
4. the intrinsic uncertainty and arbitrariness, due in part to variable weather extremes, in the storage margin required by different users and types of use. Energy-use studies of TES in Maine indicate that the sizing method for an 8-hour charge period is marginal for extreme weather conditions. Simulation studies have underscored the potential problem of developing a shoulder peak of demand for supplemental heat near the end of the on-peak period.

3.7 Test Facility

As an aid to commercialization a test facility for commercial and experimental storage devices has been established to develop test procedures and a facility which can be duplicated at commercial, governmental and manufacturer's laboratories to rate TES units. The status of this work at Purdue University's School of Mechanical Engineering is reported separately.

4 Conclusions

The field studies support the expectation of earlier studies: TES is technically and economically viable in winter-peaking electric service areas of the U.S. that rely on electricity for space heating, where the underutilized baseload energy is supplied by coal or other cheaper baseload fuels. Proper electric rates and adequately sized heat storage systems are the keys to attaining economic benefits, and consumer understanding of TES and off-peak rates is the key to market penetration.

DEVELOPMENT OF AN OPTIMUM PROCESS FOR ELECTRON BEAM CROSSLINKING OF HIGH DENSITY POLYETHYLENE PELLETS

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Abstract

The University of Dayton is conducting an investigation of the crosslinking of high density polyethylene by electron beam irradiation. The objective of the program is to define the optimum conditions for electron beam irradiation of the polyethylene which will produce a thermally form stable material with the optimum value for the retained enthalpy of fusion. Commercially available high density polyethylene pellets have been irradiated to total doses of 2, 4, 6, and 8 megarads in a single pass through an electron beam. Radiation doses of five to six megarads are sufficient to maintain the thermal form stability of high density polyethylene pellets. The enthalpy of fusion at these radiation doses is approximately 90 percent of the value of the unirradiated pellets. The melting temperature of the pellets does not change with the radiation dosage, and the pellets may be successfully irradiated in air. The irradiated pellets have been thermally cycled through their melting point for more than 100 complete cycles and have maintained an open structure that is porous to the flow of the heat transfer fluid. We expect to have completed the electron beam irradiation processing of 15,000 pounds of material for delivery to DOE for full scale application tests in August.

Introduction

The University of Dayton is conducting a program on the crosslinking of high density polyethylene pellets by electron beam irradiation processing. The objectives of the program are (1) to determine the optimum conditions for crosslinking high density polyethylene (HDPE) pellets for thermal energy storage applications by electron beam irradiation and (2) process 15,000 pounds of HDPE pellets for delivery to DOE for full scale application tests. Crosslinked HDPE pellets have the unusual property that when they undergo the solid-liquid phase transformation, they do not flow but retain the physical form they possessed as a solid pellet. Thus, a pellet bed of crosslinked HDPE pellets remains porous to the flow of the heat transfer fluid even after the pellets have been heated through the liquid-solid phase transformation temperature. In contrast to other phase change materials which utilize the liquid-solid phase transformation for thermal energy storage, crosslinked HDPE pellets do not require any additional containment vessel. The crosslinked pellets serve as their own container even while in their liquid state. High density polyethylene melts congruently and can be repeatedly cycled through its melting point with no decrease in its value for the enthalpy of fusion. The melting temperature occurs in a temperature interval between 125°-145° Celsius. The crystalline phase appears as a white opaque solid, while the viscoelastic liquid is a clear transparent phase. Although its melting temperature is especially suited for applications in solar absorption air conditioning units, crosslinked HDPE pellets merit consideration as a thermal energy storage media for applications in solar heating and/or off-peak utilization of electric generating capacity.

In our previous investigation we characterized the melting temperature and the enthalpy of fusion of several different commercially available HDPE specimens. On the basis of these tests we selected four different specimens for the electron beam irradiation experiments. During the course of that project we established: 1) that the crosslinking of HDPE is primarily dependent on the total radiation dose and is insensitive to either the electron accelerating potential or the electron beam current; 2) that the HDPE pellets can be satisfactorily irradiated in air; 3) that HDPE pellets irradiated to a dose of eight megarads have sufficient thermal form stability and retained enthalpy of fusion to be utilized as a thermal energy storage media; 4) that the retained enthalpy of fusion decreases with increases in the radiation dose, however the melting point appears to be insensitive to the total dose; and 5) that the HDPE pellets irradiated to a dose of eight megarads maintained an open structure porous to the free flow of the heat transfer fluid, ethylene glycol, even after more than 100 thermal cycles through their melting point.

Experimental

The goal of the present work has been to crosslink 15,000 pounds of HDPE pellets by electron beam irradiation processing. The crosslinked HDPE pellets must have sufficient thermal form stability and retained enthalpy of fusion to be suitable as a thermal energy storage material. The DuPont Alathon 7040 HDPE pellets were selected as the polyethylene product for this processing scale-up for the 15,000 pound production run. The selection of the DuPont HDPE pellets was based on the evaluation of the thermal form stability and retained enthalpy of fusion performed during Tasks 1 and 2 of this project. Prior to the irradiation of the 15,000 pound lot of HDPE pellets, we conducted a set of irradiation tests to confirm our earlier results. A series of electron beam irradiation tests were conducted on small samples sizes, approximately 10 pounds each, on the DuPont Alathon 7040 HDPE pellets. These tests were conducted at four different irradiation doses, 2, 4, 6, and 8 megarads. The thermal form stability and the enthalpy of fusion and melting temperatures were measured on the irradiated pellets.

The thermal form stability of the irradiated pellets was evaluated by placing the pellets in ethylene glycol at 150° Celsius for a 24 hour time interval. The thermal form stability of the pellets was evaluated for two different initial conditions. In one set of experiments the irradiated pellets were simply placed in the high temperature ethylene glycol bath. In a second set of experiments, the irradiated pellets were placed in a one inch diameter die at 150° Celsius at a pressure of 4,000 pounds per square inch for 30 minutes. The hot pressed HDPE specimens were cooled to room temperature under pressure. The pressure was relieved after reaching room temperature and the samples were recovered in the form of a solid smooth surfaced right circular cylinder. These cylinders were placed in the ethylene glycol bath and maintained at 150° Celsius for 24 hours. The appearance of the pellets was examined after the thermal treatment in the ethylene glycol. Those samples which had been irradiated to doses of six or eight megarads were observed to be porous and individual pellets could be readily fractured from the bulk specimen. The pellets irradiated to the two megarad level were fused solidly together; those pellets which received a four megarad dose showed a lesser tendency to fuse together and exhibited considerable porosity.

Shown in Figure 1 are the pellets with a six megarad dose after the thermal treatment in ethylene glycol. The specimen on the right is one of the original hot pressed cylinders after the thermal treatment. The specimen on the left is the condition of the loosely packed irradiated pellets after the thermal treatment. In both cases, individual pellets could be readily separated. One of the hot pressed cylinders prepared from the irradiated pellets and prior to the high temperature exposure in ethylene glycol is shown on the left in Figure 2. The pellets recovered from the ethylene glycol after the thermal treatment of one of the hot pressed cylinders are shown on the right of the same figure. In all these tests, the pellets had been maintained above their melting point for a 24 hour time period. As shown in these pictures, the hot pressed cylinders reverted back to the individual pellet shapes. This is an impressive display of the thermal form stability of the irradiated HDPE pellets. As a result of our tests, we have concluded that pellets which have received at least a four megarad dose have sufficient thermal form stability to be used as a thermal energy storage media.

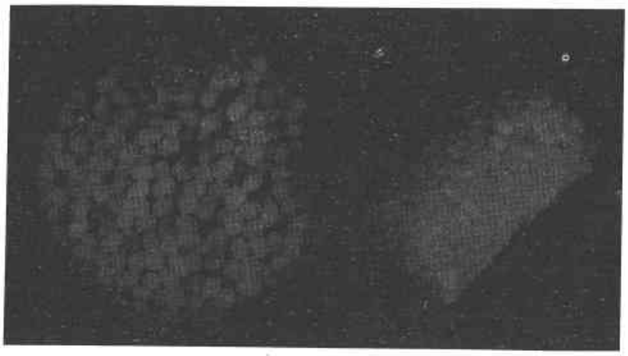

Figure 1. Condition of DuPont Alathon HDPE Pellets With a Radiation Dose of Six Megarads After Exposure in Ethylene Glycol at 150° Celsius for a 24 Hour Time Period. On the <u>left</u>, pellets exposed in a beaker; on the <u>right</u>, a hot pressed right circular cylinder.

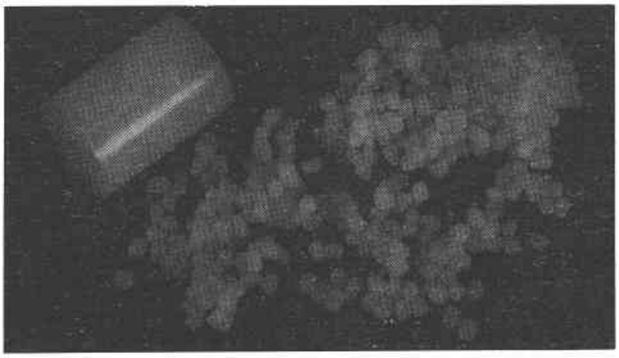

Figure 2. DuPont Alathon HDPE Pellets With a Radiation Dose of Eight Megarads. Shown in this view on the <u>left</u> is one of the hot pressed cylinders before immersion in the ethylene glycol. On the <u>right</u> are the pellets recovered after thermally treating a hot pressed cylinder in ethylene glycol. The pellets show almost complete recovery to their original shape after the thermal treatment.

The values for the enthalpy of fusion and the melting temperatures of irradiated pellets were measured in a Perkin-Elmer Differential Scanning Calorimeter. These values were measured on both heating and cooling cycles at a scanning rate of 10° Celsius per minute. The results of these measurements are presented in Table 1. The HDPE samples were contained in the standard Perkin-Elmer aluminum pans and a nitrogen atmosphere was maintained around the sample during the measurements. The instrument was calibrated by measuring the area under the temperature/time scan during the melting of a measured quantity of high purity indium.

TABLE 1

THE ENTHALPY OF FUSION AND THE MELTING TEMPERATURE OF DUPONT ALATHON 7040 HDPE PELLETS AS A FUNCTION OF ELECTRON BEAM IRRADIATION DOSE

Radiation Dose	Heating Cycle		Cooling Cycle	
	Melting Temp.	Enthalpy of Fusion	Melting Temp.	Enthalpy of Fusion
(megarad)	(Deg. K)	(cal./g.)	(Deg. K)	(cal./g.)
0	405	42.3	385	42.4
2	406	39.5	384	41.6
2	407	40.0	385	40.9
4	407	39.1	384	39.2
4	405	36.4	385	39.2
6	404	38.8	386	37.0
6	403	35.4	384	37.0
8	406	35.6	384	35.4
8	405	34.3	384	36.6

We have observed that the enthalpy of fusion of the commercially available HDPE pellets varies over a range of 38.2 to 50.5 calories per gram. Since the present commercial applications of polyethylene have not been concerned with its application as a thermal storage material, the manufacturing processes optimize its physical properties for other applications (e.g. injection molding). A developmental program directed to optimizing the value for the enthalpy of fusion may consistently produce values as high as 60 calories per gram for fully crystalline linear polyethylene.

Since the irradiation dose of six megarads imports adequate thermal form stability to the HDPE pellets and retains a greater value for the enthalpy of fusion than the pellets irradiated to eight megarads, a 270 pound lot of the pellets was irradiated with a dose of six megarads. The irradiation processing was conducted by placing 10 pound quantities on aluminum trays and exposing them to the electron beam. The pellets were given a six megarad dose in a single pass through the electron beam. Test samples of the pellets were collected from each of the aluminum trays after the irradiation processing. The thermal form stability of each of the 27 samples collected was evaluated as described above. All of the 27 samples showed excellent thermal form stability after the high temperature exposures in ethylene glycol. A representative specimen, sample number 14, is shown in Figure 3 after this high temperature exposure.

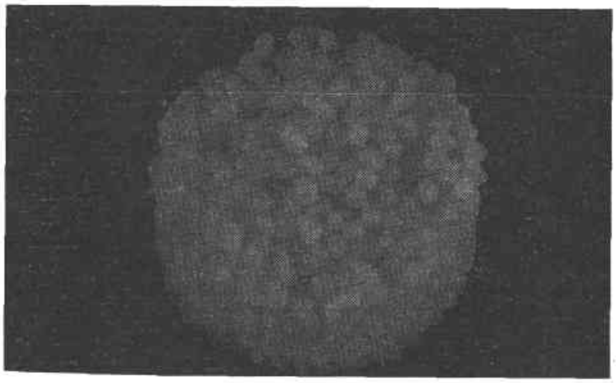

Figure 3. Condition of Irradiated Pellets After a Thermal Treatment in Ethylene Glycol at 150° Celsius for a 24 Hour Time Period. Radiation dose = 6 megarads. (Sample 14 of 27.)

A 225 pound quantity of the irradiated pellets was loaded into our 60 gallon thermal energy storage test unit for thermal cycling tests. The pellets were cycled between 115° and 138° Celsius. The time interval required to complete a combined heating and cooling cycle is approximately 90 minutes. The pellets were cycled through their melting point for 122 complete cycles. The cycling tests were conducted without any incidents; at the completion of the cycling tests the pellets were inspected and were observed to have retained their original form.

As a result of the satisfactory completion of these tests, we have completed arrangements with Radiation Dynamics Incorporated located in Plainview, New York, to process the 15,000 pound lot of HDPE pellets by electron beam irradiation to a dose of six megarads. We will evaluate the thermal form stability, the enthalpy of fusion, and the melting temperature of random samples selected from the irradiated pellets. The 15,000 pounds of irradiated pellets will be delivered to DOE for full scale application tests.

During the course of this project we have established:

1. That the crosslinking of HDPE pellets is dependent primarily on the total radiation dose of the pellets and is insensitive to the electron accelerating potential or electron beam current.
2. That the HDPE pellets can be irradiated satisfactorily in air, in a single pass under the beam, in a pellet bed depth of ∿ 1/4".
3. That HDPE pellets irradiated to a dose of five to six megarads have sufficient thermal form stability and retained enthalpy of fusion to be utilized as a thermal energy storage media.
4. That the melting temperature is independent of the irradiation dosages over the range of 0 to 12 megarads.
5. That the enthalpy of fusion shows a trend to lower values with increasing value of the irradiation dose.
6. That the thermal form stability and retained heat of fusion of the HDPE pellets are excellent after more than 100 complete cycles through the melting point.
7. That a program directed to optimizing the property of the enthalpy of fusion of HDPE may result in a commercial product with a value as high as 60 calories per gram.

Acknowledgement

This work was performed at the University of Dayton under ORNL Subcontract Number 7641. The electron beam irradiation of the polyethylene pellets was performed in the facilities of the Radiation Dynamics Incorporated at Plainview, New York.

THERMAL ENERGY STORAGE TEST FACILITY*

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ABSTRACT

Two loops making up the Thermal Energy Storage Test (TEST) Facility, using either air or liquid as the thermal transport fluid, are being designed and developed. These loops will be capable of cycling residential-size thermal energy storage units through conditions simulating solar or off-peak electricity applications to evaluate the unit's performance. Construction of the liquid cycling loop has been completed, and testing of thermal stratification techniques for hot and cold water is currently underway. Four PCM TES units are on hand, with their performance testing and evaluation to begin upon the completion of the stratification studies. The detailed design of the air cycling loop will be initiated during the 1981 fiscal year.

1. DISCUSSION

The Thermal Energy Storage Test (TEST) Facility will be a set of two loops, using either air or a liquid as the thermal transport fluid, capable of cycling both hot and "cool" residential-size thermal energy storage devices through a series of charge and discharge modes which simulate either solar or off-peak electricity TES applications. The TEST facility will be used to (1) independently evaluate the performance of storage systems using testing procedures which simulate working environments under which the system will operate, as well as using procedures proposed by ASHRAE and NBS and (2) to provide support in further R&D work related to TES. Total storage capacity, storage efficiency, charge and discharge rates, temperature profiles, and pressure drop across the storage device are, among others, the performance characteristics of interest.

Both cycling loops will be capable of fully charging or discharging a residential-size storage unit [52,800 to 528,000 KJ (50,000 to 500,000 BTU) capacity] within four hours [required heat rate of 36.6 KW (125,000 BTU/h)]. The liquid loop will have a temperature range of 0°C to 140°C (32°F to 284°F) and will be able to use either water, ethylene glycol, or salt brine as the working fluid at flow rates between 7.6 ℓ/min and 76 ℓ/min (2 and 20 GPM). The temperature range of the air loop will be from 0°C (32°F) to some maximum temperature as yet undetermined. The loops will possess a high degree of versatility and controlability to produce a variety of input conditions called for by the testing procedures; specifically, they will be capable of providing varying temperature, flow rate, and, for the air loop, humidity input schedules in step function, sinusoidal, and stochastic patterns to fully simulate actual conditions and usage of solar and off-peak electricity storage units.

Three feedback loops, one each for temperature control, flow rate, control, and humidity control, all capable of sensing loop parameters and making adjustments accordingly, will therefore be required. An integral part of these feedback systems will be an LSI-11 computer which will interface between the sensing and control devices; the computer will also serve as the main data acquisition system. Twenty-eight K of core and two floppy disks provide program and data storage; and furthermore, the mini-computer will be interfaced with a remote computer to provide additional storage and computational capabilities.

The basic piping and instrumentation layout for the liquid loop is shown in Fig. 1. Mixing value A, functioning with a feedback system initiating from temperature probe D, indirectly diverts the necessary amount of return liquid through either of the thermostated liquid holding tanks, as determined by valve B, and thereby reconditions the working fluid to its required inlet temperature. The loop flow rate will be monitored by a turbine flow meter C, which also feeds back information to the loop flow control valve E. Platinum resistance temperature probes, capable of measuring temperature to within a few tenths of a degree F, will be placed throughout the loop as well as in the storage device itself in sufficient quantity to effectively evaluate the storage system performance and to monitor the loop dynamics. Pressure differential cells complete the major instrumentation requirements of the loop. The air loop will be similar to the liquid loop in its basic layout, control systems, and instrumentation, with the additional requirement of measuring and controlling humidity.

2. STATUS

Construction of the liquid cycling loop has been completed. Tests are currently being performed to study the effect of various thermal stratification techniques for hot and cold water on the storage efficiency and stratification behavior of an 800-gal square cylindrical tank. The stratification tests will continue into November 1980 and will be immediately followed by the testing and evaluation of four PCM TES units which are currently on hand. The first PCM unit which will be tested was developed privately by OEM Products, Inc., Dover, Florida, and is an immiscible fluid direct contact system using Glauber's salt as the PCM and an oil as the heat transfer fluid. The Tennessee Valley Authority has recently installed 25 such units as a "heat battery" coupled to a water-to-air heat pump in private residences throughout the valley. These installations are part of their Thermal

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*Research sponsored by the Division of Energy Storage Systems, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation-Nuclear Division.

Storage Field Test Program studying off-peak electrical use. The three remaining PCM storage units were developed by Calmac Manufacturing Corporation, Englewood, New Jersey, under subcontract to the Storage for Active Solar Heating and Cooling Program managed by Argonne National Laboratory. The units have been forwarded to ORNL for testing and evaluation. Each of the units contains a different PCM, and thus each has its own specific transition temperature. One unit has been designed for "cool" storage [7°C (45°F)], one for warm storage [45°C (113°F)], and one for high-temperature storage [115.5°C (240°F)].

The detailed design of the air cycling loop will be initiated during FY 1981.

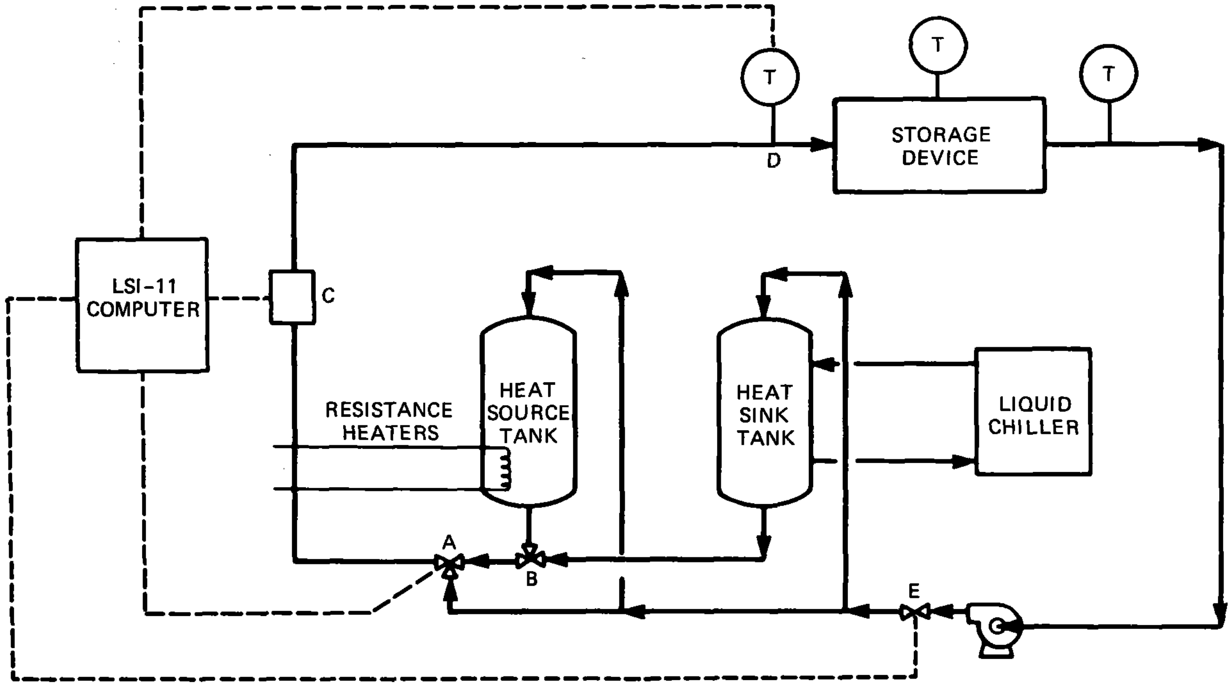

Fig. 1. Liquid cycling loop.

CRAWL SPACE-ASSISTED HEAT PUMP*

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ABSTRACT

A variety of experiments and simulations have been performed or are being prepared to determine the feasibility of conditioning the source air of an air-to-air heat pump using stored ground heat or "cool" to produce higher seasonal COP's and net energy savings. Winter data has shown that significant preheating occurs consistently for both the single-pass and total-recycle modes, with the latter showing the better results between the two. Preliminary summer data shows that precooling does occur, but that the heat pump system should be operated in the single-pass mode only. Comparison between experiments has led to the conclusion that the preconditioning is due mostly to the stored earth heat or "cool" and is not due in any great part to heat exchange with the house. A computer model of the crawl space has been developed, and the development of heat pump models for performance and economic studies is currently underway. Complete data analysis will begin as actual data in digitized form becomes available. Planning for a definitive test addressing the concept's performance and economics has begun.

1. DESCRIPTION

The crawl space-assisted heat pump concept utilizes heat or "cool" stored in the undisturbed earth under a house to precondition the source air of an air-to-air heat pump and thus increase the heat pump's seasonal performance. A schematic representation of this concept is shown in Fig. 1. During the winter, the source air is preheated by the warmer ground and, as a result, the instantaneous capacity and COP of the heat pump are increased (as can be observed from a capacity and COP curve for a typical heat pump). Consequently, the heat pump's overall winter performance is improved (the heat pump's winter season COP is increased), the need for supplemental resistance heating (at a COP of one) is diminished because of the higher output capacity for a given outdoor temperature, and the energy consumed for defrosting is reduced because the number of defrost cycles and their duration is diminished. Combined, a significant reduction in energy consumption could thus occur. During the summer the source air is precooled by the earth which would, in the end, slightly increase the heat pump's summer performance and again be accompanied by a decrease in energy consumption. For the homeowner, this reduction in energy use translates directly into monetary savings; for the utility, the peak electrical loads occurring during both the summer and the winter would be reduced as more such crawl space systems are installed. Additional savings may be realized by the homeowner through a reduction in maintenance costs since the strains on the compressor and other components caused by defrost cycles and temperature extremes are nearly eliminated.

There are two different operating configurations in which the heat pump could be installed, the first being the single-pass mode and the second being the total-recycle mode. In the single-pass mode, shown in Fig. 1, outside air is drawn through the crawl space where it is preconditioned, delivered to the outside unit of the heat pump, and then discharged to the outside. In the total-recycle mode, shown in Fig. 2, the heat pump discharge air is recirculated through the crawl space where it is preconditioned, delivered to the outside unit of the heat pump, and then discharged back to the crawl space.

Four field experiments have been conducted over the past year to study the concept, three being actual field installations in private residences and one being a controlled experiment. In the first field installation, the Holman House, the heat pump was configured in the single-pass mode. A plastic moisture barrier covered the crawl space's surface to prevent moisture evaporation. This is felt to be important so that a moisture problem in the crawl space does not develop and, more importantly, because the conductivity of wet soil is ten times that of dry soil. The same type of plastic was also hung from the underside of the house to the earth surface, forming a "plastic curtain," so that the outside air would be forced to travel over as much crawl space ground as possible and to prevent short-circuiting of outside air directly to the heat pump from occurring. Outside temperature, crawl space air temperatures, ground surface temperatures, and earth temperatures 0.15 m (6 in.) below the surface were continuously recorded throughout the year using Type K thermocouples and a 12-point Honeywell recorder in the winter and a recently installed data logger over the summer. Figure 3 shows a schematic of the crawl space and the thermocouple locations, with representative winter data shown in Fig. 4. The important finding from this experiment was that outside air between -15°C (5°F) and 4.5°C (40°F) could be preheated by the stored earth heat consistently throughout the winter to -4°C (26°F) and 6.5°C (45°F), respectively. Preliminary summer data indicates that precooling also occurs, though to what extent is not known as of this writing.

In the second field installation, the Betz House, the heat pump was configured in the total-

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*Research sponsored by the Division of Energy Storage Systems, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation-Nuclear Division.

recycle mode, with data being taken for the winter months only. Again, a plastic moisture barrier covering the ground was employed as well as the "plastic curtain" to direct the flow of air through the crawl space. The same temperatures were recorded using Type T thermocouples and a 16-point Honeywell recorder. Figure 5 shows a schematic of the crawl space and the thermocouple locations, with representative data shown in Fig. 4. As expected, it was found that the heat pump discharge air was preheated as it was circulated through the crawl space and that the heat pump intake air was at a significantly higher temperature than that outside. Furthermore, it was found that for a given outdoor temperature, the intake air temperature of the heat pump was, on a quantitative basis, significantly higher for the total-recycle mode than for the single-pass mode (absolute comparisons should not be made as crawl space dimensions, flow path, air flow rates, etc., are not necessarily the same).

In the third field installation, the Nestor House, the heat pump was configured in a combined single-pass/total-recycle mode, the mode of operation being determined by humidity and differential temperature controllers, with data being taken for the summer months only. Again, a plastic moisture barrier and the "plastic curtains" were used, and the same temperatures were recorded using Type T thermocouples and a 12-point Honeywell recorder. Figure 6 shows a schematic of the crawl space and the thermocouple locations. Preliminary indications from this installation suggest that summer operation in the total-recycle mode is not advantageous, and provisions should thus be made to allow a total-recycle system to be converted to a single-pass system for summer operation.

The final field experiment, the ACES Duct, involved measuring the temperature rise of ambient air drawn by a portable fan through a specially built insulated duct located in the crawl space of an experimental control house being used in conjunction with energy conservation projects at ORNL. Three sides of the duct were formed of closed-cell polystyrene sheeting 0.3-m (12-in.) thick, with the remaining side being open to the ground. All joints between the sheeting were sealed with a continuous bead of silicone rubber, as well as duct tape. The fan was cycled through different "on/off" sequences with the use of a 24-hr timer and was operated at various flow rates with the use of a variac so that the effect of different operating parameters could be studied. A moisture barrier was again employed, and temperatures were recorded using Type T thermocouples and a 12-point Honeywell recorder. A plan view of the duct, along with the thermocouple locations is shown in Fig. 7, with representative data from the winter tabulated in Fig. 4. The temperature increases obtained through the duct compare reasonably well with those obtained from the Holman House (again, absolute comparisons should not be made). Since heat conduction and air infiltration into or out of the duct were, in practicality, eliminated, then the temperature change of the air as it passed through the duct was due solely to heat exchange with the ground. Likewise, it can then be concluded that any preconditioning of the air experienced in the Holman House was due mostly to the stored earth heat or "cool" and was not due to heat exchange with the house.

Three other efforts have taken place concurrently with the running of the above field experiments. A digitizing program was developed under subcontract by Lockheed Missiles and Space Company, Inc., allowing the data recorded on the above strip charts to be digitized with the use of a Tektronix 4051 terminal and other supportive hardware. The computer modeling effort of the crawl space has continued throughout the year. The model will be used to increase our understanding of the crawl space's behavior: the storage and recovery capabilities of the earth when exposed to cyclic temperatures, the effectiveness and importance of the daily temperature swings in charging the earth system, and the applicability of the crawl space concept to other regions of the nation. This modeling work is being performed by Alan Solomon of ORNL and is further described in a paper in these proceedings. Finally, a heat pump modeling effort has been initiated to examine the effect the conditioned source air has on different aspects of a heat pump's performance (COP, capacity, required supplemental heat, defrost) and to estimate the electrical savings which may be expected to occur.

2. STATUS

Data for summer operation continues to be gathered at the Holman House, the Nestor House, and the ACES Duct experiments. Data digitization has started and will continue until all data has been processed. Data reduction and analysis will begin when an appropriate amount of digitized data becomes available. The digitized data will also be used to confirm the accuracy of the crawl space model, after which simulations of crawl space behavior for other climatic conditions will be made and analyzed to determine if the concept is viable elsewhere. The development of heat pump models using actual or modeled data has been initiated, and work will continue into FY 1981. Economic savings due to a reduction in heat pump maintenance will also be examined. Lastly, planning is currently underway to conduct a definitive test of the crawl space concept to determine its actual performance and economic benefits.

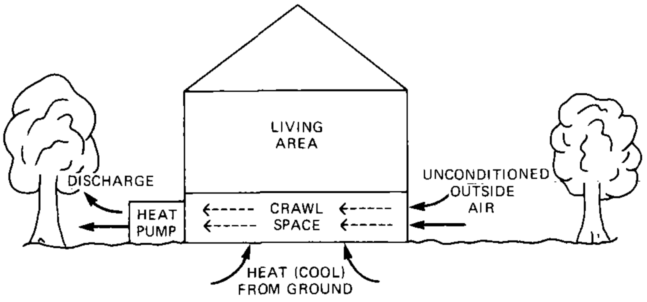

Fig. 1. Single-pass mode.

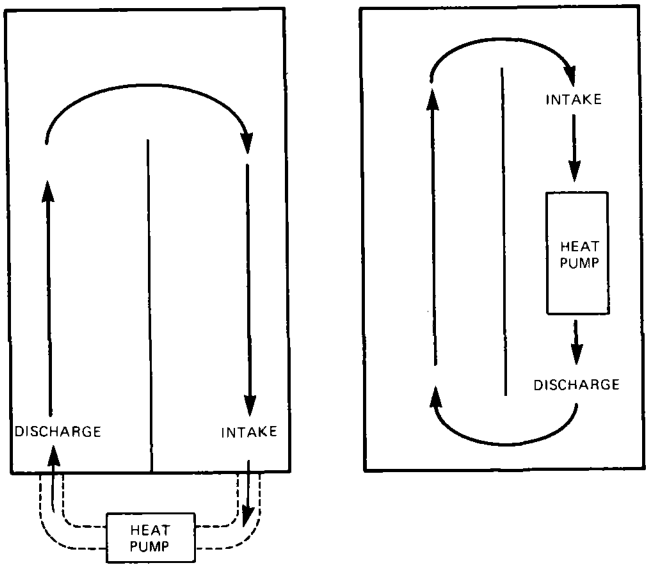

Fig. 2. Total-recycle mode.

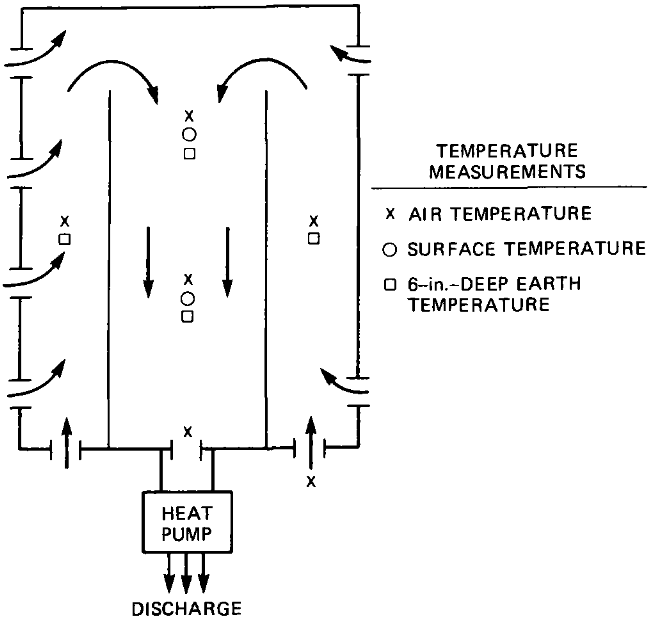

Fig. 3. Holman house.

HOLMAN HOUSE:

OUTSIDE TEMP (°C)	HEAT PUMP INTAKE (°C)
-15.0	-3.0
- 7.0	0.0
- 1.0	4.5
4.5	7.0

BETZ HOUSE:

OUTSIDE TEMP (°C)	H.P. DISCHARGE (°C)	H.P. INTAKE (°C)
-15.0	-3.0	2
- 7.0	0.0	5
- 1.0	2.0	8

ACES DUCTS:

OUTSIDE TEMP (°C)	TEMP LEAVING DUCT TEST 1 (°C)	TEST 2 (°C)	TEST 3 (°C)
-15.0	-7.0		-4.0
- 7.0	-3.0	-1.0	-1.0
- 1.0	-2.0	-2.0	-2.0

Fig. 4. Winter experimental data.

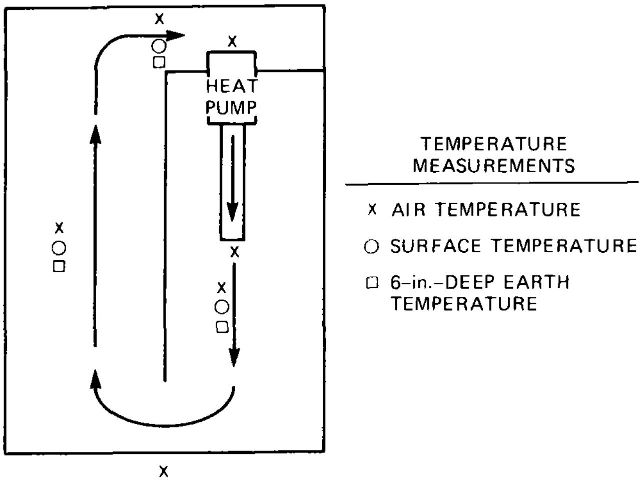

Fig. 5. Betz house.

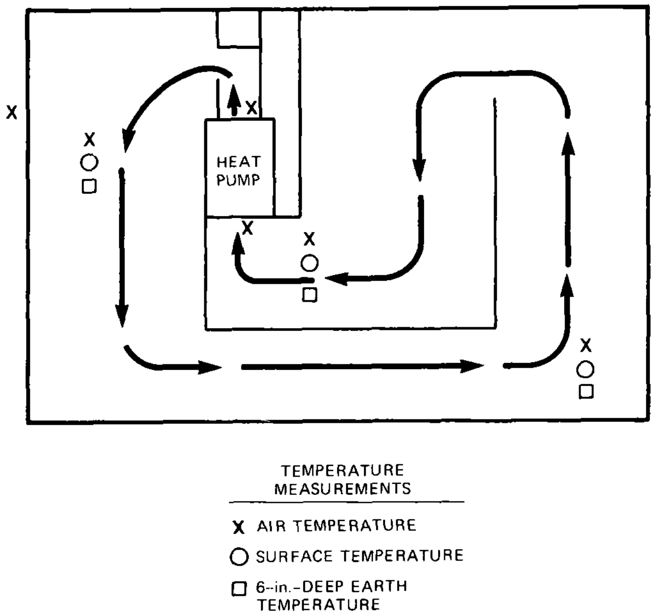

Fig. 6. Nestor house.

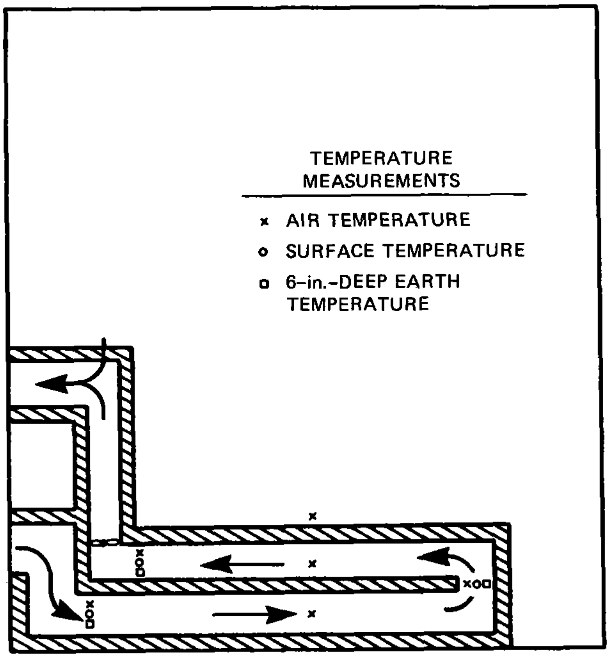

Fig. 7. ACES duct.

MATHEMATICAL MODELING OF MOVING BOUNDARY PROBLEMS IN THERMAL ENERGY STORAGE

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Abstract

In this paper we describe some recent results obtained in the mathematical modeling of moving boundary problems in thermal energy storage. These results can be placed into three categories: a) results of an analytical nature, including the development of approximations allowing us to predict the behavior of systems; b) simulation development and (where possible) validation via comparisons with experiments, exact solutions to model problems and other methods; and c) numerical analysis problems that arise from the simulation development.

I. Introduction

Moving boundary problems arise in thermal energy storage as time dependent fronts that separate the various distinct phases of the material under study. The mathematical models that arise from them are complex and difficult to study under all but the most simple conditions. Thus the only class of moving boundary problems for which closed form expressions can be given for the temperature distribution and phase change front are those in which the PCM is in a slab geometry, occupying either an infinite or semi-infinite line, with a constant initial and imposed temperature within the body and at its surface [1]. If we wish to predict the behavior of a TES system governed by the conditions of a moving boundary problem we must turn to either extensive approximation techniques- in which significant assumptions must be made in order to simplify the resulting problems, or to computer simulations, from which information is costly and difficult to acquire. In our efforts we have attempted to meld the approximation and computer techniques in a way designed to derive maximum information from both. On the one hand we have used simulations to obtain closed form approximations for such important parameters as melting time and heat fluxes in problems for which solutions are unknown, but in which only a small number of free (dimensionless) parameters are present. These expressions yield both quantitative and qualitative information about the system behavior. On the other hand we have attempted to develop computer simulations paying particular attention to questions of validity, reduction of computing effort and derivation of qualitative information. In the following lines we discuss results obtained within the last year in the areas of analytical approximation, simulation, and questions arising from the validation and the need for proper interpretation of computational results.

II. Analytical Approximation Results

A slab, cylinder or sphere of PCM, initially at its melting temperature and in solid state, is subjected to convective heat transfer at its surface, from a warm transfer fluid of temperature T_{in}. If its radius is L, and its thermal diffusivity is α, then its melting time is given by

$$\frac{L^2}{\alpha St(1+\beta)} \{.5+\frac{1}{Bi} + .5[.25+.17\beta^{.7}]St\}$$

where $\beta = 0,1,2$ according as the body is a slab, cylinder or sphere, Bi and St are the Biot and Stefan numbers respectively. The Stefan number representing the ratio of sensible heat drop (from T_{in} to the melting temperature) to the latent heat, is the key parameter in phase change models. This relation is accurate to within a ten percent relative error over the range $0 \leq St \leq 4$ and $.1 \leq Bi$. [2]

A PCM rectangle of side lengths a and b is initially in its solid state at the melting temperature, and is subjected to a constant, uniform boundary temperature above its melting point. The melting time of the rectangle is then given by

$$\frac{a^2}{8\alpha\ St} [1 + .25\ St],\ \text{for}\ \frac{a}{b} \leq \frac{2(1+.42St)}{\pi(1+.25St)}$$

and

$$\frac{ab}{4\pi\alpha St}[1+.42\ St],\ \text{for}\ \frac{a}{b} > \frac{2(1+.42St)}{\pi(1+.25St)}\ .$$

Here a is assumed to be the shorter side, $a \leq b$. This relation has been found to be accurate to within a ten percent relative error for $St \leq 4$. [3]

Other similar results have[4] been derived and will appear in the future.

We have found the approximations derived thusfar to be useful in a number of ways. The first is in scoping of experiments- be they in the laboratory or via the computer. The second is in obtaining information about the relative importance and sensitivity of, e.g., the melting time, to other variables. The third is as a source of easily obtained answers- not requiring a computer, to relevant questions. With the availability of hand held calculators we believe that these expressions are of greater value than graphical ones, or ones derived from non-numerical procedures such as the methods of Goodman and Megerlin.[5]

III. Simulation Results

We will now report on three simulations done within the past year. The first, partially reported in the previous information meeting, concerns experiments performed on the melting and solidification of N-Octadecane Paraffin Wax. The principal purpose of the experiments was to verify the numerical models (TES and others). At this point we have completed the comparisons between the computer models and experimental results in which natural convection in the melt plays a minor role. We have found good agreement with data and in the process we have been able to identify certain features of the experiments and the PCM which have not been known previously. These include an adjustment to the value of the solid-phase thermal conductivity of the PCM, and will be reported elsewhere in the near future.

In support of the study of the crawl-space heat-pump augmentation concept[6] a simulation program was prepared for a 10-foot deep, 40-foot long rectangular region in the ground below a tunnel which is thermally insulated from the house above. The simulation includes air which is being pumped through the tunnel from the (cold) ambient air, and predicts the temperature of the air at points including its outlet, and in the earth at various depths. The program includes the effects of possible surface freezing of the ground moisture. Using the program comparisons were made between observed temperature values and computer predictions during a period of February, 1980, for a tunnel beneath a test house. The computer model was found to accurately predict temperature trends and to differ by only a few degrees at most from the recorded data. A typical result is that obtained for 12 PM on February 12:

Thermocouple	Observed (^{o}F)	Predicted (^{o}F)
1	31	32
2	39	35
3	39	37
4	37	34
5	41	37
6	44	39
7	37	36
8	40	38
9	42	39
10	23	20
11	29	27
12	33	31

Here thermocouples 1-9 are located at various positions and depths in the earth, while 10-12 are the air duct temperatures. In particular thermocouple 12 is the air duct outlet temperature, reflecting the warming effect of the ground.

There is a great deal of current interest in examining the potential use of the University of Delaware PCM Chubs for various TES purposes. One such purpose is in storage assisted air conditioning, involving the use of Chub arrays in parallel with a lower-power air conditioning system in a home. The study of this system requires a simulation tool which will a)accurately model the temperature distribution and phase change process within the chub, while at the same time b) take into account the fact that an <u>array</u> of chubs at lower temperature may dehumidify the warmer, humid air flowing over them. Towards this purpose we have extended the TES program[7] to model arrays of PCM cylinders with an air transfer fluid undergoing possible dehumidification. We assume convective heat transfer at each cylinder surface, and make use of a package simulating the psychrometric table for humid air. The program is undergoing an analysis of its sensitivity, and will be compared with data obtained from tests currently being carried out.[8]

IV. Numerical Analysis Results

While results of computer simulations may be gratifying and indeed "seem" correct, their understanding and proper validation is a step which may well be ignored. The validation of a computer program simulation must involve a number of steps. The first is that the basic physical and mathematical laws be obeyed by it. One such law is that mass and heat be conserved. Thus the "output" of a simulation must include the appropriate heat and mass balances. Another is that the qualitative behavior of the simulation be correct. Thus for example, the improper choice of a mesh size may cause certain schemes for the solution to heat conduction problems to "act" as if they were solving wave propagation problems instead. The "ultimate" validation of a model might be considered comparisons with experimental results. However even if good agreement is observed, we may not be sure that this implies "goodness" of the model in predicting other, more subtle effects. Our analytical and simulation studies have led us to a number of problems which are now under study. The first, arising from simulations such as that of the earth simulation, concerns the role of the mesh size. If the spatial mesh size is large (as in finite difference or finite element simulations over long time intervals), we must gain a proper understanding of "what" the numbers derived from the simulation actually mean. Thus the "temperature T_{ij} at the mesh point x_i,y_j" may well mean the <u>average</u> temperature over the grid interval and not the pointwise temperature that is gotten from a thermocouple located at the point.

At the present time many numerical schemes are available for dealing with phase change processes in heat transfer. How do they compare for low Stefan numbers (e.g., the cases relevant to TES applications)? In the spirit of this question we have obtained some improvements to phase change simulation methods which have been implemented in TES, resulting in greater reliability of the program.

V. Other Work

One of the inhibiting features of complex computer simulations is the high cost of using them- often possibly reaching the scale of a physical experiment. This is especially so in heat transfer simulations where requirements of accuracy and stability impose severe limitations on the time-step size. Thus as a rule of thumb, simulations of hundreds of hours may cost large amounts of money, or be unreliable. As an area of peripheral interest to our work, we have undertaken an effort to significantly reduce the time requirements of a long-term simulation by the incorporation of learning and artificial intelligence techniques. Simply stated, we are incorporating procedures into the codes which will permit the program to ask whether the thermal state currently observed was seen at an earlier time, and if so, how it evolved. If this is known, then the computer can avoid the need to redo a previously done calculation. A discussion of the incorporation of artificial intelligence into heat transfer codes has been given recently[11].

VI. Future Work

Future work to be done includes a) the completion of simulation programs for phase change with natural convection in the melt; b) the derivation of a closed form expression for the melting time and heat flux of a simple body which is subject to a radiation (fourth power) boundary condition; c) further development and testing of simulation models for TES processes of increasing complexity.

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DISTRIBUTED THERMAL ENERGY STORAGE IN THE RESIDENTIAL SECTOR: COMMERCIALIZATION READINESS ASSESSMENT AND IMPLEMENTATION STRATEGY

Task Force on Commercialization Readiness Assessment for Distributed Thermal Energy Storage*
presented by
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Argonne National Laboratory

Significant national benefits can result from the use of customer-sides-of-the-meter thermal energy storage (TES). It appears that TES for residential space heating and hot water heating can capture a market large enough to yield annual oil savings of approximately 80 million barrels (0.3 quads) by the year 2000. These savings would result from the substitution of coal and nuclear energy for oil and gas in electric power generation. It would also make electric space heating systems competitive with oil heating.

The readiness of each of three candidate TES systems for near-term commercialization has been examined. It was concluded that of these, TES for residential space and hot water heating are technically and economically ready for commercialization. TES systems are unlikely to be more attractive than standard heat pump systems in all areas of the country; however, in many regions, particularly in the northeast and north central states, TES appears to be more attractive. In the not too distant future, use of TES with heat pumps may prove to be the best system nationwide. For the third system, TES for residential space cooling, it was found that those units which are presently technically viable would be too costly except in a few parts of the country; more development will be required before these systems could be commercialized on a national scale. TES systems which might be used in commercial buildings (e.g., stores and office buildings) were not examined.

The primary barriers to the immediate commercialization TES heating systems are all economic or institutional in nature. In roughly decreasing order of importance, they are

- Provision of electric power rates which encourage TES,
- Size of required rate differences,
- The present form of proposed Building Energy Performance Standards (BEPS),
- Availability of market estimates,
- Manufacturing capability,
- Equipment certification,
- Financing.

The economic benefits of TES units stem from the replacement of high cost energy from oil and gas by lower cost energy from coal and nuclear. A mechanism by which these cost differences can be reflected in the price of electricity is required if the residential customer is to have any economic incentive to purchase a TES unit. Several techniques of providing this incentive were examined. Even though some utilities have been investigating these techniques, positive action to assure their widespread implementation is recommended.

The size of the rate differences required to provide a significant commercialization incentive proved to be a problem for the residential TES space cooling systems. For this reason, the commercialization of these systems was deemed to be premature at this time; additional R&D is recommended.

The BEPS standards, as presently proposed, establish weighting factors for each form of energy expected to be used annually in each new building and an annual budget. The proposed weighting factor for electricity is three times that proposed for oil and gas and, more importantly, is time-of-day and seasonally invariant. If adopted, this standard would effectively eliminate the market for TES heating systems and eliminate the associated benefits. Three alternative modifications of these standards are proposed for consideration by DOE.

An examination indicated that the manufacturing capability needed to meet the projected demand for TES units either exists or can be made available within the heating, ventilation, and air conditioning (HVAC) supply industry. However, the availability of detailed market assessments will be needed to ensure the timely participation of individual manufacturers. Continued performance of these studies and wide publication of the results is recommended.

Certification and the development of nameplate rating standards are needed to gain consumer confidence in this new product. A program to encourage the certification of sufficient different units to provide for a competitive market is recommended. A program to expedite the promulgation of standards by the traditional professional societies is also recommended. Finally, a program to educate the public (e.g., exhibits at home shows) to expedite the spread of consumer confidence is recommended.

The availability of capital for home improvements will allow the TES unit purchaser to spread the cost over time and thus facilitate TES commercialization. The availability of these funds will, to a large extent, depend on the prevailing economic conditions.

Only two areas of environmental concern were identified as part of this study; the impact of shifting electric power generation from peaking units to baseload units and the impact of mining activities to provide a domestic source of refractory brick. Neither of these issues are expected to be significant, although both will require additional effort.

In order to assure the success of commercialization of TES heating systems, it is recommended that DOE establish a commercialization program containing the following seven elements:

- Standards development,
- Product assessment,
- Production and distribution capability and incentives assessments,
- Market analysis data,
- Environmental assessment,
- Institutional barrier assessment and amelioration,
- Production incentives program.

These program elements correspond to the most serious of the commercialization barriers that have been identified. If a decision is made to pursue a formal commercialization effort, a detailed program or implementation plan will be prepared.

Commercialization schedules for TES will ultimately be determined by the timing of introduction of TES incentives for customer purchase of TES systems. A five-year schedule of implementation of the seven elements of the commercialization program is proposed. *

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THERMAL ENERGY STORAGE TESTING FACILITY*

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Abstract

Development of a prototype testing facility for performance evaluation of electrically heated thermal energy storage units is being pursued. Laboratory apparatus and test procedures are being evaluated by means of measurements and analysis. Testing procedures have been improved, and test results have been acquired for commercially available units. A 30kW central unit and several smaller individual room-size units have been tested. This work is associated with a parallel effort by ASHRAE to establish a standard for performance evaluation of units of this type.

I. Introduction

In this project experiments and analysis are being pursued using residential electrically heated thermal energy storage (TES) units. In these devices high heat capacity ceramic bricks are employed as the energy storage medium. Large central units are currently available for replacing conventional residential furnaces. Also on the market are small self-contained room-size units which avoid the necessity for ductwork and a central air handling system. Energy charging of these devices occurs at night using less expensive off-peak electrical energy. During this period the electrical heaters inside a TES unit are activated, heating the ceramic bricks to a high temperature. Air then is caused to flow over the bricks intermittently throughout the day and evening as required to maintain the residence air temperature. The air flowing over the bricks is heated during this process, and the bricks are correspondingly cooled. Their temperature level is eventually lowered substantially, thus permitting another energy charge during the next night-time period.

Although electrically heated TES units are now on the market in the U.S., standard performance testing procedures have not yet been fully established in this country. Available information useful in the development of such procedures includes a German Standard, DIN 44572[1], which has been established specifically for electrically heated TES units. Within the U.S. a standard has been established for testing of other types of TES units by the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE), ASHRAE Standard 94-77[2]. Both of these documents have been quite helpful in guiding the present work.

This project is associated with a parallel effort by ASHRAE to establish a standard for performance evaluation of electrically heated TES units. A preliminary draft of ASHRAE Proposed Standard 94.2P[3] was released December 14, 1979, and comments were requested from all interested parties in March 1980[4]. In response to this request an extensive list of comments was submitted to ASHRAE based on experience acquired in the current project.

Certain advantages are obtained by testing the smaller room-size units inside a calibrated calorimeter chamber. Central TES units, on the other hand, are tested in a typical laboratory environment. Figure 1 contains a photograph showing a 30kW central TES unit which has been tested in the laboratory (foreground), and also a partial view of the calorimeter chamber used for testing of the smaller room-size units. Figure 2 shows the opposite side of the calorimeter chamber as well as some of the instrumentation.

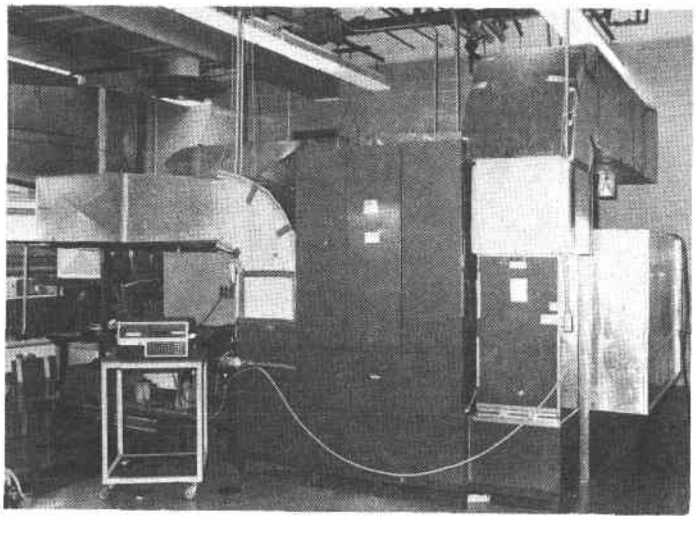

Figure 1. Central TES Unit (Foreground) and Calorimeter Chamber for Testing of Room-Size TES Units

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*This project has been supported by Argonne National Laboratory, Energy and Environmental Systems Division, Special Projects Group, under Contract No. 31-109-38-4666.

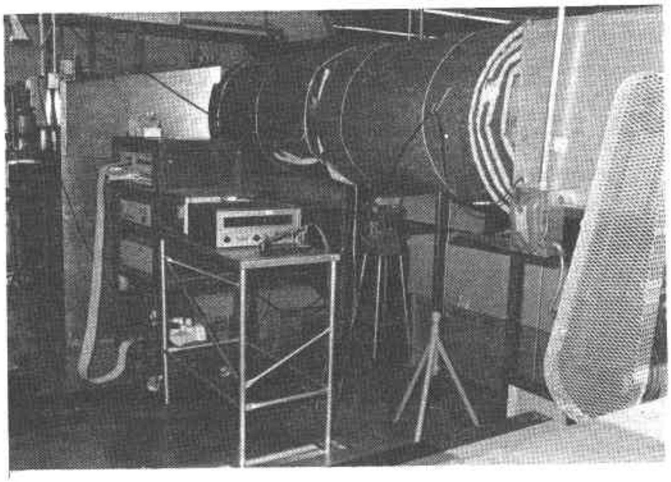

Figure 2. View of Calorimeter Chamber from Opposite Side

II. Results and Discussion

Some of the technical problems and early test results associated with the calorimeter chamber have been reported previously^5. Additional test results and further details are contained in Ref. 6. Figure 3(a) contains a diagram illustrating the essential features of the test configuration and the energy flow rates which are pertinent to the method of testing. During both calibration and testing, air is drawn slowly through the chamber by a blower located at the right end of the outlet duct [not shown in Fig. 3(a)]. Figure 3(b) shows a calibration chart generated experimentally under steady state conditions prior to testing. Figures 3(c) and 3(d) contain test results obtained with a 2kW TES unit in a dynamic discharge test (internal fan within the TES unit turned on after the unit is fully charged). Employing the measured inlet to outlet air temperature difference and the calibration chart shown in Fig. 3(b), a plot of the thermal output rate of the unit was generated [Fig. 3(c)]. Notice that the thermal output rate rose abruptly when the internal fan was turned on. By integrating the thermal output rate curve of Fig. 3(c) the thermal energy delivered by the TES unit was obtained, as

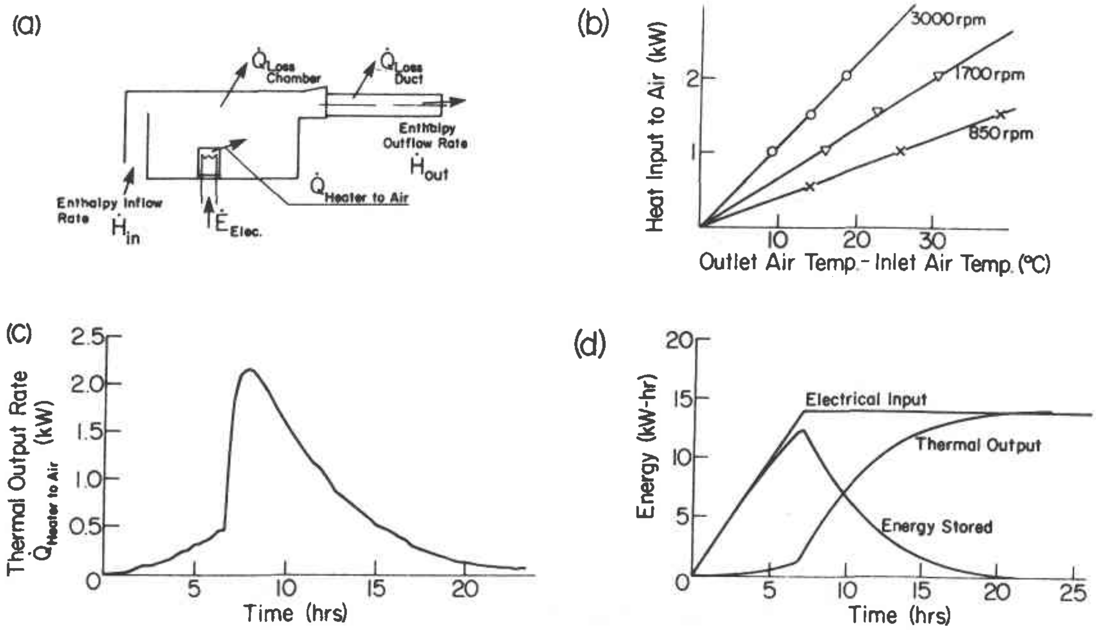

Figure 3. Testing of Room-Size TES Units: (a) Schematic Diagram of the Essential Features of the Calorimeter Chamber Illustrating the Various Energy Flow Rates, (b) Calibration Chart Obtained Under Steady State Conditions with Calorimeter Blower Speed as Parameter, (c) Thermal Output Rate During a Dynamic Discharge Test of a 2kW TES Unit (Calorimeter Blower Speed = 850 rpm), (d) Energy Graph Associated with the Test Corresponding to (c).

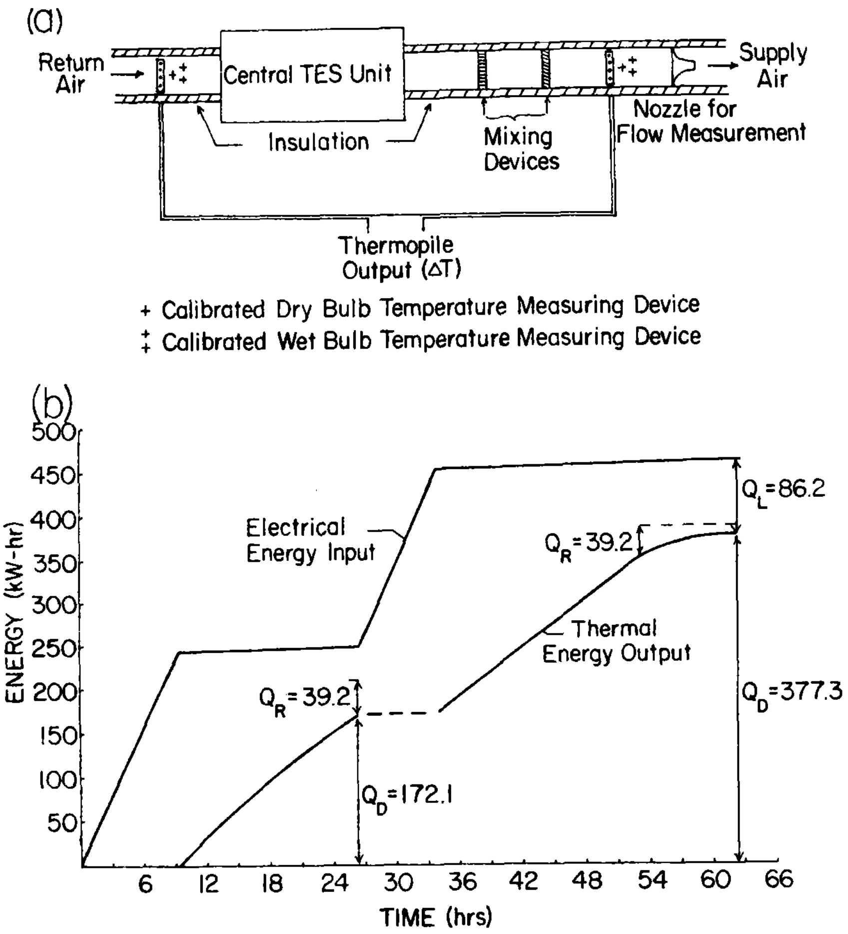

Figure 4. Testing of Central TES Units:

(a) Schematic Diagram Indicating the Test Configuration

(b) Energy Graph Associated with a Discharge Test of a 30kW Central TES Unit [Q_D is the thermal energy delivered, Q_R is the residual capacity (energy stored at the end of each nominal discharge period), and Q_L is the heat loss from the cabinet over the entire duration of the test.]

shown in Fig. 3(d). The upper curve in Fig. 3(d) represents the electrical input energy, which was delivered to the TES unit at constant rate for approximately 7 hours and then terminated. At any time the difference between the electrical input energy and the thermal output energy represents the thermal energy stored within the unit. This is also shown in Fig. 3(d). Notice that the total energy output of the TES unit over the extended duration of the test was essentially equal to the total electrical energy input, as expected.

Figure 4(a) contains a diagram illustrating one of the configurations used for testing of the central TES unit shown in Fig. 1. Utilizing measurements of air flow rate and inlet to outlet air temperature difference, the thermal output, residual capacity (energy stored at the end of each nominal discharge period), and heat loss from the cabinet can be displayed along with the measured electrical energy input on an energy graph as shown in Fig. 4(b). In this test the unit was charged, discharged, recharged, and then completely discharged.

During the past fiscal year one central unit and several room-size TES units have been tested. Some tests have been performed according to ASHRAE Proposed Standard 94.2P, while others have been performed employing various other test configurations and procedures. Results obtained using these different methods have been compared, and the advantages and disadvantages of each have been assessed. This information has been provided to ASHRAE to assist in incorporating desirable modifications into ASHRAE Proposed Standard 94.2P.

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SURVEY OF THERMAL STORAGE INSTALLATIONS IN THE UNITED STATES AND CANADA

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Abstract

A survey is to be made of commercial and industrial thermal storage installations (either hot, cold, or both) in the United States and Canada. Thermal storage installations that serve primarily to store solar heat are not to be included in the survey. This survey is to be published by ASHRAE in a special publication. A Committee has been set up by ASHRAE to review the work to ensure it is in conformance to ASHRAE publication standards.

No site visits are to be undertaken. The survey is to be performed by mail and telephone. Major sources for the survey are: "Survey of Utility Load Management and Energy Conservation Projects" by EUS, Inc., performed for ORNL and EPRI, 2nd edition, 1979, and "Assessment of Thermal Storage for Off-Peak Cooling of Buildings" by Ayres Associates, performed for Southern California Edison Company, 1980. Other sources are utilities that promote off-peak rates and, therefore, encourage off-peak storage,and design engineers that specialize in the design of thermal storage installations.

A project specification form has been prepared, more than 100 letters have been mailed out, and many more telephone calls have been made. It appears that many more thermal storage installations exist than had been thought before the initiation of the project.

I. Introduction

Thermal energy storage is a powerful tool for energy conservation. Energy available at a time it is not needed can be stored for later use, or energy peak demands can be decreased by producing and storing heat (or cold) during times when there is a low demand on an electric utility system and using it during a time of high demand. This is called peak shaving or load levelling when performed by the utility. If it is done at the consumer's location, it is frequently called load limiting.

At various meetings of engineers concerned with thermal storage it was pointed out that a major impediment to the wider use of thermal storage is the unfamiliarity of engineers with such systems. Many engineers hesitate to design thermal storage systems because they believe them to be difficult, applicable to European conditions only, and experimental in nature. It is thought that publishing a document that lists all of the operational thermal storage systems in North America would demonstrate that thermal storage has a long and diversified history of successful application. This, in turn, would overcome some of the hesitation of engineers to design such systems. Listing the name of a person that could be contacted for each project for additional information would further assist in overcoming this barrier.

II. Project Definition

A contract was awarded to the Franklin Research Center by the Union Carbide Corporation at Oak Ridge, TN on behalf of the U.S. Department of Energy for the performance of a survey of thermal storage installations. The survey is limited to non-experimental commercial and industrial installations. Storage devices that primarily store solar energy are not to be included since they are covered in other DOE publications. No site visits are to be undertaken except in special circumstances; the survey is to be performed by mail and by telephone.

It is believed that the best method of disseminating the results of the survey is an ASHRAE (American Society of Heating, Refrigerating and Air Conditioning Engineers) publication. Accordingly. an informal inquiry was made by the Franklin Research Center to determine whether ASHRAE would undertake the publication of the survey results in a special document. A favorable reply was received. An ASHRAE Technical Evaluating Committee (TEC) was appointed under the chairmanship of Mr. Byron Engen, the Vice Chairman of ASHRAE Technical Committee (T/C) 9.6, Thermal Storage. The TEC will review the progress of the project and will ensure that the final document product meets ASHRAE publication guidelines.

III. Status

A project specification form was prepared and approved by the ASHRAE TEC. It lists the information desired for each project as follows:

THERMAL STORAGE SURVEY
PROJECT SPECIFICATION FORM

BUILDING LOCATION (complete address)
BUILDING SIZE, HEATING/COOLING LOAD, DESIGN TEMPERATURES
MECHANICAL DESIGNER (address and phone number)
COOPERATING UTILITY (including name and phone number of project engineer, if applicable)
DESCRIPTION OF THERMAL STORAGE (storage medium, size, weight, volume, container, heat exchanger, etc.)
PURPOSE (peak shaving, demand reduction, load levelling, other)
LENGTH OF DUTY CYCLE (3-hour, daily, weekly, annual)
CONTROL METHOD AND LIMTS (temperature, pressure, cut-off points)
EQUIPMENT DESCRIPTION
PERFORMANCE AND MONITORING HISTORY (if available)
INSTALLED COST, PROJECTED OR ACTUAL SAVING
NAME AND PHONE NUMBER OF PERSON PROVIDING THIS INFORMATION
DESIGN DATA AND OTHER ADDITIONAL INFORMATION (please attach)

More than one hundred letters were mailed out with more than 200 copies of the specification form to engineers, utility executives, building operators, U.S. state and Canadian federal and provincial agencies asking the recipients to fill out the specification forms for each thermal storage project that they had knowledge of. They were also asked to list other knowledgeable individuals you might have information about other thermal storage installations. As is customary for "cold" mail surveys, the response to this survey has been slow. We have begun follow-up telephone calls in order to improve the return rate to these letter requests. The return rate from people who were personally known to the Principal Investigator was better, say 10%, and the follow-up effort will concentrate on them.

An excellent source for projects sponsored or cosponsored by the Department of Energy, the Electric Power Research Institute, and electric utilities is a report entitled, "Survey of Utility Load Management and Energy Conservation Projects," prepared by EUS, Inc. for ORNL and EPRI.[1] In most cases, that publication contains the information required, and all that is needed is to call the contact person and bring the project information up-to-date.

The second most productive source is the work performed in 1980 for Southern California Edison Company by Ayres Associates and summarized in a report, "Assessment of Thermal Storage for Off-Peak Cooling of Buildings".[2] The project manager of that utility, Mr. Donald Geistert, kindly made all results available although the report has not yet been officially published.

A third source is Mr. Robert Tamblyn of Engineering Interface Ltd in Willowdale, Ontario, Canada who is probably the most vocal advocate of thermal storage. He graciously promised to provide the names and telephone numbers of approximately 15 large Canadian thermal storage project engineers.

The Principal Investigator attended an EPRI meeting[3] dealing with solar energy and load management. During the course of the meeting he obtained data on a number of storage installations other than those reported upon during the formal part of the meeting program.

Utility executives throughout the United States and Canada have been fruitful sources of information, so have consulting engineers that specialize in off-peak storage applications. A number of manufacturers have also been very helpful, either in supplying that information directly or in steering us to people who are able to supply the information.

IV. CONCLUSIONS

While it is too early to draw definite conclusions from the project, it appears that there are many more thermal storage installations in operation than was assumed at the beginning of the project. That fact alone can be regarded as a major success, and it provides ample justification for the project.

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OLIVINE-BASED HEAT STORAGE REFRACTORIES

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Abstract

High-heat capacity refractory ceramics have been employed in European electric heat storage furnaces for over two decades. In these systems, ceramic refractories are heated to approximately 1500°F, using low-cost electric energy during the off-peak demand hours. During the peak demand hours, heat is extracted as needed by controlled circulation of air through the core to meet residential or commercial space conditioning requirements. Heat storage furnaces represent (a) valuable load-leveling capabilities for central electric utilities and (b) safe, convenient, reliable heat sources for consumers. Because of its relatively high-heat capacity and relatively low cost, olivine is one of the more attractive candidate materials for such ceramics, and North Carolina has extensive but rather under-utilized deposits of refractory grade olivine. This paper summarizes results which have been achieved to date with University and North Carolina Energy Institute funding in an evaluation of the usefulness of North Carolina olivine in ceramic refractories for thermal energy storage applications. Also included are the goals for the current DOE-funded study, along with a discussion of equipment currently being installed to facilitate more precise performance evaluations.

I. Introduction

For almost three years, we at North Carolina State University have investigated the processing properties and performance of special refractory shapes produced from North Carolina olivine (an abundant mineral in the western part of our state) for prototype evaluations in heat storage furnaces. Heat storage furnaces and related consumer-owned thermal storage units are energy conversion/storage devices of the sensible heat type. They are not yet well known in the U. S., but similar systems have been used in Europe for more than two decades. For example, approximately 1 of 8 homes in England are heated with off-peak electric energy by means of heat storage furnaces,[1] and in West Germany the ratio is approximately 1 in 5.[2] Their primary purpose is to permit electrical load-leveling of large generating/distributing systems. Load-leveling enables power generating plants to operate more efficiently thus contributing to better overall energy utilization. In particular, operation of main generating plants under near-100% base load conditions permits conservation of high quality fuels (which would otherwise be required for peak loads) and greater reliance on more readily available coal or nuclear energy sources.[3]

The principal application now envisioned for these ceramic thermal energy reservoirs is in home or business heating (furnaces, space heaters). There are evidences of growing industrial interest in other potential larger scale applications of such an effective, economical, technologically-proven heat storage capability.

The primary objective of our initial work, undertaken with support from the University and from the North Carolina Energy Institute, was to demonstrate in a feasibility study that an important North Carolina mineral resource, olivine, can be used to make heat storage bricks (refractory ceramic shapes) of quality equal to or better than those which have been used for such applications in Europe. The results of that successful earlier study have been presented elsewhere,[4] and are summarized in this paper as well. Additional research tasks are now being undertaken under U. S. Department of Energy sponsorship through Oak Ridge National Laboratory. They are directed toward more complete evaluations of the performance of University-produced olivine refractories for the central system furnaces (typically, 30kw) being developed in the US from English-based designs, and toward similar evaluations of the German-style ceramics, also produced from North Carolina olivine, intended primarily for small, room-sized heat storage furnaces. Under this new program, further laboratory-scale studies of optimization of properties and performance of olivine-based refractories will also continue.

To some degree, there has been serendipitous involvement of the University in this ongoing effort: there is both a long and strong history of academic, research and extension involvement in ceramic engineering, a similar long and strong commitment toward development of North Carolina mineral resources, and in recent years, growing involvement in energy issues of all sorts.

The state of development of sensible heat storage systems in the US and of their utilization both by consumers and by power generating systems, is still quite fluid. As we understand it, decisions leading toward substantial commitments to off-peak storage systems depend not only on favorable demonstrations of capability, performance and customer acceptance of such systems, but also upon favorable economics of the whole system, at all levels. In a nutshell, the price and performance of the ceramic storage media influence the cost of the furnace to the consumer, which in turn influence the power system's off-peak rate structure required to assure an appropriate payback period for the consumer's investment.

Though all parties involved would like to have access to hard economic data at all levels in this multi-tiered system, to date, the unfortunate truth is that no bonafide domestic manufacturing capability for suitable heat storage ceramics exists in the US. For this reason, and because our earlier feasibility study was carried out on a very limited and inefficient scale, there is not yet any adequate basis for making realistic projections of the economics of production of olivine-based heat storage refractories for such applications. Presumably, this leaves all the other economic questions in something of a state of limbo.

While the processes employed in producing olivine heat storage refractories are not unlike those used elsewhere in the refractories industry, the performance criteria required for this application are significantly different from those that are required for more conventional refractories, which are usually either for high-temperature ceramic kilns and furnaces or for metallurgical applications. Furthermore, olivine materials are compositionally incompatible with many of the other refractory mixes routinely produced by major refractories manufacturers, so there has been understandable reluctance to risk serious in-plant cross-contamination by undertaking small-scale industrial production to meet the needs of the emergent U.S. heat storage furnace industry.

Though neither our prior feasibility study nor the program now being undertaken under DOE funding have been scaled at a level which could address these economic issues directly, we clearly recognize their considerable importance.[7] Hopefully, our continuing efforts to characterize the technical performance of existing grades of olivine-based refractories for heat storage applications, and our parallel, continuing development studies to improve processing and product quality, can provide a sound technical basis and some additional performance-related incentives for undertaking further scale-up studies which will be able to address the economic issues as well.

In this paper, we examine from this viewpoint some of the knowns-and unknowns-which must be dealt with in reaching sound technological and economic decisions relating to ceramic heat storage systems.

II. Sensible Heat Storage

Conservation of electrical energy has become particularly important to the maintenance of personal, civic and national economies and lifestyles throughout the world in the last several years. Management problems for the utility and pricing problems for the consumer have been created by excessive peak power loads coupled with low usage during off-peak periods which require installation of ineffectively utilized generating equipment. In Europe, the use of heat storage units for more than two decades has resulted in this complex supply-demand problem being offset and in some instances virtually eliminated.

In a sensible heat storage system, the thermal energy is stored at moderately high temperatures within a well-insulated, large mass of refractory ceramic shapes (bricks) (Fig. 1). Electrical resistance elements are embedded in the grooved bricks and are used during the off-peak demand period (6-8 hrs) to heat the ceramic refractory mass. During the remainder of the 24 hr period, heat is extracted from the refractories by circulating air through the channels within the storage core. This air is then blended with cool air to produce a temperature-controlled warm air flow to heat the dwelling or business. Typical maximum core temperatures are on the order of 760-815°C (1400-1500°F). By using sensible heat storage (large ΔT's) large quantities of energy can be stored in relatively small volumes compared to other, low ΔT storage systems (i.e., passive; phase change). This allows sensible heat storage systems to be used for retrofit applications as well as new installations without encountering many of the problems associated with other storage systems. Wide consumer acceptance and increasing use of sensible heat storage systems represent an excellent means by which the utility can hope to achieve a high degree of load-leveling.

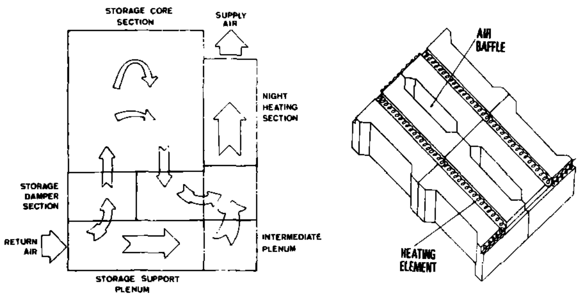

Fig. 1. Schematic of central heat storage furnace showing direction of air flow (at left) with a portion of heat storage core, showing heating element and air channels (at right) (after Palmour et al[1]).

III. Ceramics As Storage Medium

The typical central home-heating system will require a storage core weighing approximately 2400 lbs. This storage core will be cycled repeatedly between approximately 1400°F and 200°F (or lower). In the climatic areas where this type system is most likely to be used (i.e., in winter-peaking areas) there typically will be 175-200 heating days per year. If the useful furnace life is estimated to be 30 years, this system would experience between 5250 and 6000 charge/discharge cycles during its service lifetime. One can easily see the need for high-quality thermal shock resistant refractories to be able to successfully store and give up heat under deep discharge conditions through so many cycles. Some of the qualities that the bricks must possess include high volumetric heat capacity, favorable heat transfer characteristics (high thermal conductivity) and good thermal shock resistance. Also, it cannot be over emphasized that these thermal properties must occur in proper combination. Certain ceramics exhibit the proper combinations of the thermal properties together with excellent physical properties and high electrical resistivity. When compared to materials for other types of storage applications, this favorable combination of thermal and physical properties, inertness and relatively low cost make ceramics an almost ideal media for sensible heat storage applications. (See Table I).

IV. Olivine Raw Materials

In evaluating various minerals for use as ceramic raw materials for these applications, one must consider availability, composition, ceramic behavior and both the short-run and long-term costs of the material. One of the most promising candidates is the mineral olivine.

Olivine is a magnesium-iron-orthosilicate mineral derived from the ultra-basic rock, dunite.[4]

Table I. Preliminary comparisons of densities and thermal properties for English and (experimental) (1978) North Carolina olivine bricks (After Palmour et. al.[4])

		Typical English Olivine Brick	Kaolin-Bonded NC Olivine Brick
Bulk density, g/cm^3		2.57	2.69
Pycnometric density, g/cm^3		3.20	3.29
Fractional density		0.802	0.818
Volumetric heat capacity, $cal/cm^3/°K$	@100°C	0.568	0.609
	250°C	0.626	0.674
	400°C	0.651	0.688
	550°C	0.660	0.682
Thermal conductivity $\frac{\text{cal.cm}}{\text{sec.cm}^2\,°\text{K}} \times 10^3$	@100°C	4.31	5.03
	250°C	4.30	4.29
	400°C	4.15	3.52
	550°C	3.96	3.06

Large olivine deposits exist in Scandinavia (particularly in Norway), in smaller deposits in Austria, and elsewhere in Europe.[4] Japan has known deposits of olivine and various other points around the world have smaller deposits. In the United States there are two major areas containing extensive olivine deposits: one in western North Carolina, the other on the west coast, in the state of Washington.[4] Its largest application in the United States has been in the foundry industry as a foundry sand, an application which requires a material having high thermal shock resistance and low thermal expansivity. Olivine is also known to have high thermal conductivity and because of its relatively high density and specific heat, it also has high volumetric heat capacity. Additionally, olivine is relatively inexpensive, particularly when compared to other candidate materials such as magnesite (principally MgO). [For comparison purposes, the raw materials cost of magnesia is approximately 7 times greater than that of olivine.]

The cost of the ceramic core components will make up a substantial and essential part of the total cost of a heat storage furnace. They will probably influence the market-place acceptability of the whole off-peak storage scheme since, directly or indirectly, they affect installation costs, payback periods to the consumer and, ultimately, utility off-peak rate structures. Therefore, to make the energy storage scheme effective in meeting national energy needs, suitable ceramic products must be available in large quantities and at economical prices. Until now, much U. S. attention has been focused on large central system heat storage furnaces and the ceramic refractories required for them. While the magnesite-based refractories have slightly higher specific heats and, hence, slightly higher volumetric heat capacities than do olivine-based refractories, the increase in the cost of the magnesite vs olivine-based refractories is not justified for the large central systems.

V. Properties and Performance

In our prior studies, there have been several interrelated research objectives: (a) to identify suitable grades of olivine raw materials, (b) to develop suitable ceramic bond types and batch compositions, (c) to develop near-optimal processing and firing methods, and (d) to evaluate the properties and performance of preliminary tests specimens and of full-size heat storage bricks under actual heat storage furnace conditions. These investigations have been extensively reported elsewhere,[4,6,7] and are briefly summarized below.

Materials-Related Behavior

The olivine ore selected for use in this demonstration study [Ellijay No. 9 (Stewart)] displayed good performance in this ceramic application. Not all olivine deposits are alike; rather, they tend to vary in the degree of initial serpentinization, in the makeup of accessory minerals and in the degree of subsequent weathering. Though the primary olivine phase continues to make up the bulk of the ceramic when fired, it is the accessory minerals, including those deliberately introduced as mill additions, which tend to dominate the firing behavior and to exert a very strong influence upon the character of the interfacial bonding between the relatively coarse, rather inert grains of the refractory olivine.

On the basis of experience to date, it is possible to predict good to excellent ceramic performance for these olivine ores like Ellijay No. 9 which display (1) relatively low concentrations of R_2O flux oxides, (2) low ignition losses, and (3) relatively high $MgO:SiO_2$ ratios. Of five such unbeneficiated materials, two appeared to have ceramic potential equal to or better than Ellijay No. 9, while two others appeared to be somewhat inferior. It remains to be demonstrated whether or not appropriate combinations of mineral benefication before ceramic processing and/or adjustments of the accesory mineral makeup by means for appropriate mill additions and firing conditions during ceramic processing can ultimately be employed to make the ceramic performance of olivine refractory products less sensitive to these natural variations from deposit to deposit.

In the most recent laboratory-scale studies, (See Table II) significant improvements in green and fired densities were observed at higher forming pressures, particularly for beneficiated olivine ore from which most of the serpentine, enstatite and other lower density, lower melting materials had been removed. Though prior mining and marketing practices have produced essentially unbeneficiated NC olivines for foundry sands, etc. the present trend, even for non-ceramic product lines, appears to be moving toward large volume benefication at the plant. This trend appears to bode well for ceramic applications, potentially making much cleaner, more predictable grades available, in quantity, and presumably at only modest increases in price over unbeneficiated grades.

Table II. Dependence of Fired Density of North Carolina Olivine on Materials Selections, Bond Phase and Process Parameters (After Palmour et al[4,6])

Process Conditions	Green Density g/cm^3 (D_0)*	Fired Density g/cm^3 (D_f)*
Unbeneficiated Ellijay No. 9(Stewart)Olivine, 2.5% Kaolin Bond		
Preliminary Lab Scale Experiments (1978): ~51.7 MPa (~7,504psi), ~1390°C	2.49-2.53(0.755-0.768)	2.69(0.818)
Full Sized Heat Storage Bricks(1978-79): 30.0 MPa (4,350psi), ~1371°C	2.46-2.50(0.75-0.77)	2.58(0.78)
Lab Scale Experiments (1979-80): 103.4 MPa (15,000psi), ~1371°C	2.588(0.805)	2.583(0.804)
Beneficiated Field Olivine, Self Bonded		
Lab Scale Experiments (1979-80):		
103.4 MPa (15,000psi), ~1454°C	2.596(0.796)	2.632(0.807)
206.8 MPa (30,000psi), ~1454°C	2.700(0.828)	2.788(0.855)
Beneficiated Field Olivine, 2.5% Kaolin Bond		
Lab Scale Experiments (1979-80):		
103.4 MPa (15,000psi), ~1427°C	2.581(0.796)	2.680(0.827)
206.8 MPa (30,000psi), ~1427°C	2.691(0.831)	2.805(0.866)

*Represents fractional density: [measured (or bulk) density divided by true (pycnometric) density].

Ceramic Bond Phase Effects

There are essentially five types of bonds which can be considered for such a refractory ceramic application: (a) chemically bonded (cured but unfired), (b) refractory, hydraulic-setting cement-bonded (cured but unfired), (c) second phase (clay, shale) ceramic-bonded (low fired), (d) liquid-assisted, sinter-bonded (higher fired with refractory kaolin additive), and (e) self-bonded (still higher fired,with or without MgO additives). In our earlier studies, bond types (a) and (b) were not included, on the grounds that such cured but unfired materials inevitably suffer weight losses from the low temperature bond phase, resulting in loss of bulk density (i.e., lower heat capacity) and degradation of interparticle bonding (i.e., lower thermal conductivity) during inplace firing after the heat storage furnace is put into service. The thermal properties after cycling cannot, therefore, maintain the levels attained and sustained with well designed ceramic-bonded materials.

The prototype English-made olivine brick used as a reference comparison material in this study had the type (c) bond. A rather similar shale-bonded heat storage brick was also produced from N.C. olivine (5% triassic shale additive) in the earlier studies.[4,6,7]

From preliminary studies (Table I), the most promising of the N.C. olivine mixes was of bond type (d); this composition contained approximately 2.5% refractory, plastic Georgia kaolin.

German-made olivine bricks (high density, intended for compact room-sized heaters) have the type (e) bond. Laboratory scale specimens of self-bonded beneficiated N.C. olivine also were produced which displayed high densities and good thermal properties, though they did not achieve the density levels and very favorable thermal properties displayed by similarly processed but lower fired kaolin-bonded material (See Table II).

It is evident that the character of the bond type, coupled with the degree of densification obtained as a consequence of (a) raw material selections and (b) optimal sizing, grading, bonding, compaction and firing will have a very strong influence upon thermal performance and, ultimately, upon durability and furnace lifetime. It should also be evident that the bond type chosen will influence other process steps, production costs, and, hence, overall system economics. Clearly, engineering trade-offs between costs and thermal properties for such applications will be quite sensitive to material selections, and to several other materials processing parameters as well.

Thermal Property Considerations

For heat storage applications, one is concerned with at least three pertinent thermal properties. Volumetric heat capacity determines how much heat can be stored in a fixed-volume ceramic heat reservoir at given temperatures. The coefficient of thermal conductivity determines in large part how rapidly heat can be safely stored at given temperatures during the charge cycle and how effectively it can again be extracted during the discharge cycle, and particularly so near the low-temperature end of the cycle. Finally, thermal shock resistance provides a measure (at least qualitatively, if not quantitatively) of the durability of the brick under thermal shock conditions. Thermal shock resistance under cyclic heating/cooling conditions is strongly influenced by the character of the bond type, the fractional density, the sizing of the grains which make up the refractory mix, and the presence (or absence) of microcracks.

For a given starting material, better ceramic processing (as embodied in higher forming pressures, better material preparation, etc) clearly does offer an important route (by means of higher densities) for accomplishing improvements in heat storage capacity and thermal conductivity (see Table II). However, these improvements may not be entirely penalty-free: higher fractional densities also carry with them a concomitant risk of increased vulnerability to thermal shock failure. For well designed compositions, the optimal fractional density for heat storage applications is thought to be in the 0.85-0.90 range.

Performance Evaluations

During the course of earlier investigations, substantial numbers of full-sized bricks of kaolin-bonded and shale-bonded types were produced from N.C. olivine. They subsequently were evaluated with respect to each other, and with respect to English-made reference bricks, while being cycled in a 30kw rated Off-Peak™ heat storage furnace (a product of TPI, Inc. Johnson City, Tenn.). This commercial heat storage unit has an identical storage core configuration with the residential model of the same rating, and was made available for evaluation tests at NCSU by the manufacturer (TPI, Inc.).

The methodology and results of this evaluation have been reported elsewhere[4-7] and these references should be consulted for the detailed experimental plan and results. Post cyclic evaluation of the bricks supported the theory of microcracking and indicated the NCSU shale-bonded brick to be slightly inferior to the English reference product. On the other hand, the NCSU kaolin-bonded brick was definitely superior to the English reference product.

It should be noted that these in-service performance data were obtained under rather adverse circumstances and with equipment that was inadequate. In fact, all of the data used for computer reduction and printout was manually recorded.

Under the new Department of Energy funding, a much more precise and versatile system is being installed to provide digital temperature readout (to the nearest tenth of a degree), for up to 128 thermocouple (or other sensor) channels, operating through a digital scanner, coupled with micro-computer-based data-logging, -reduction, -printout, and/or -plotting capability. Key components of this new system are on order and planning of experiments and software development is already underway. A complete setting of new kaolin-bonded olivine bricks (1979-80) are available for use in further, much more detailed studies of this type. Similar experiments are planned for smaller room-type units (4 kw Stiebel-Eltron) which use German-style heat storage refractories. A set of these special shapes produced in Germany from North Carolina olivine (Ellijay #9) will be evaluated and compared with normally installed European made magnesite brick.

Out of the previous work, a performance (merit) index has been postulated.[6] This index involves a weighted bulk density divided by unit cost. It is best expressed in terms of the true density of a specific material and a dimensionless weighting factor which is approximated as a quadratic function of the fractional density obtained during processing of that material. Space does not allow further elaboration, but more details are available in Ref.7.

VI. Summary

Results of the work to date have demonstrated that high quality heat storage refractories can be produced from abundant domestic olivine mineral resources. Densities equal to or higher than those of European olivine products have been obtained in the kaolin-bonded composition developed at NCSU. This composition displays good thermal stability, thermochemical inertness and freedom from environmental concerns. The thermal performance and durability of olivine-based ceramic refractories in heat storage furnace applications has been shown to depend sensitively upon compositional and process parameters which influence the fractional density, the character of intergranular bonding, and the propensity for formation of stable microcracks. A performance index has been proposed to reflect the importance of economic considerations as well as technical performance in materials selections for this important new, potentially large, energy storage market.

In conclusion, from the economic standpoint, the key factors are initial cost, the off-peak rate structure (relative both to on-peak rates and to costs of other forms of energy) and the payback period. Obviously, these factors are rather intimately crosslinked and none can be treated as totally independent. So look to the ceramics!

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PERFORMANCE OF STRATIFIED THERMAL STORAGE SYSTEM FOR OLIVER SPRINGS ELEMENTARY SCHOOL: PROGRESS REPORT

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Abstract

This paper is a progress report on the performance of a stratified thermal storage system coupled with a heat recovery refrigeration machine designed to provide space heating, cooling and service water heating. Water storage tanks utilizing a flexible membrane to resist temperature blending will be used as the thermal storage element. The school is presently under construction with an expected completion date of January 1981. The two design goals of the heat recovery and thermal energy storage system are 1) to minimize the need to purchase energy for space heating and cooling and water heating and 2) to minimize electrical demand. An automatic data acquisition system will be used for system performance data gathering. Manual temperature profile measurements will be made on one of the three thermal storage tanks. Data collection is expected to begin in January 1981.

I. Introduction

In many buildings, over a diurnal cycle, there is need for space heating and cooling. Moreover there is often a need for simultaneous heating and cooling. During periods when a cooling load is being satisfied with mechanical refrigeration the potential exists for high side heat recovery from the refrigeration machine precluding the need to purchase additional energy for space heating. Such heat recovery systems have been successfully employed for many years when the heating and cooling loads are simultaneous. However, when space heating and space cooling loads occur during any given day (or other period) but not simultaneously a refrigeration heat recovery system is ineffectual without a thermal energy storage system (TES). Through use of refrigeration heat recovery and TES the need to purchase heating energy can be greatly reduced potentially saving energy and money.

Another means of conserving resources and minimizing operating costs is to reduce electrical demand. The resources conserved through minimization of electrical demand consist, in most cases, of natural gas and various petroleum distillates. The dollar savings as a result of conserving these high cost, non-renewable resources can be passed on to customers assisting utilities to minimize peak demand on the electrical system. The use of TES systems offer the potential to reduce peak demand consumption of electricity at the point of end use.

This paper is a progress report on the performance of a stratified thermal storage system coupled with a heat recovery refrigeration machine designed to provide space heating, cooling and service water heating. The school is presently under construction with an expected completion date of January 1981.

II. Description of System

The Oliver Springs Elementary School is presently under construction in Roane County, Tennessee. The school is approximately 68,117 square feet in conditioned floor area. The design cooling load is 1.32 x 10^6 BTUH and the design heating load is 1.14 x 10^6 BTUH. The HVAC system being installed in the school consists of a double bundle heat recovery water chiller to enable simultaneous heating and cooling as required. There is also a natural gas fired hot water boiler for space heating when chiller heat rejection is insufficient to carry the load. Thermal storage in the form of 3 cast-in-place, concrete water storage tanks is to be utilized in conjunction with the chiller and boiler (see Figure 1). The tanks are equal in size. Each tank is approximately 2860 ft^3, thus the total storage capacity is approximately 64,500 gallons of water. The tank array is insulated on the top and sides with 3 inches of urethane foam and on the bottom with 3½ inches of foamglass. Each storage tank will use a flexible membrane[1] device to resist temperature blending. The flexible membrane is constructed of coated fabric and fastened to the tank walls at mid-height. The membrane can float up and down to suit variable conditions. Water level sensing wells are located in two corners of each tank with appropriate controls to sense when the membrane is at the top or bottom of the tank (see Figure 2). A screen is positioned over the sensing well outlet hole to avoid trapping the membrane against the holes.

The two design goals of the heat recovery and TES system for the Oliver Springs School are 1) to minimize the need to purchase energy for space heating, cooling and water heating and 2) to minimize electrical demand. During periods of the year when there is a need for space heating and cooling the HVAC system can provide such services simultaneously. Through the use of TES the HVAC system can store unwanted refrigeration system heat for later use when the demand for space heating occurs. Additionally, the HVAC system is designed such that the heat recovery chiller can operate only during un-occupied periods at times of otherwise low electrical use thus potentially saving demand charges. Through such a strategy the chiller is selected slightly smaller than the design cooling load and will operate at favorable (night) condensing temperatures for the following day thus saving operating costs, energy and installation costs.

III. Data Acquisition System

An automatic data acquisition system will be used for system performance data gathering. Four types of data sensors will be used. Heat flow meters are being installed in the HVAC system piping to measure heat flow from all heat sources and/

or heat sinks (see Figure 1). The heat flow meters consist of positive displacement turbine meters for the measurement of fluid flow rate and solid state temperature transducers for the temperature difference measurement across the appropriate heat source or heat sink. Heat flow integration circuitry is provided with the heat flow meter and a 5 VDC square wave output proportional to heat flow is fed into the on-site data logger for accumulation. Electric power to each of the motors comprising the HVAC system (exclusive of terminal units) is to be measured using a solid state watt-hr transducer. The output of the watt-hr transducer is again a 5 VDC square wave signal. High and low tank fluid temperature measurements are to be made using solid state temperature transducers with a milli-volt output. Weather data consisting of dew point temperature and dry bulb temperature will also be measured. An aspirated dew cell will be used for the dew point temperature measurement and solid state temperature transducer will be used for dry bulb temperature measurement.

The on-site data logger is capable of receiving the digital output from the heat flow meters and watt-hr transducers, totalizing these data, storing on magnetic tape and hard copy and resetting the counters to zero at a rate of once every half hour. Instantaneous temperature measurements will be made at the same scan interval and stored on magnetic tape and hard copy.

The effectiveness of the flexible membrane at resisting temperature blending (both for hot and chilled water addition and discharge) will be done manually. Five penetrations are arranged symmetrical in the lid of one tank. Weighted thermocouples will be lowered into the tank and read using a potentiometer. Thus a temperature profile can be determined for the tank under various conditions.

IV. Analysis

Using system performance data, a heating, cooling and water heating load profile for the school can be developed for 30 minute time steps. This data will be used as direct input into one of the available energy programs in lieu of the program making the load calculation. Thus comparisons of energy consumption by fuel type can be made for any of the various alternative means of providing the HVAC service for the particular building. In addition electrical demand savings can be determined for this system as compared to alternative systems.

By close monitoring of the temperature profile in the one tank the effectiveness of the flexible membrane at resisting temperature blending can be determined. These temperature profiles are to be developed for the following conditions: 1) charging the tank with chilled water, 2) supplying chilled water to the load, 3) charging the tank with hot water, and 4) supplying hot water to the load.

Data collection is expected to begin in January 1981.

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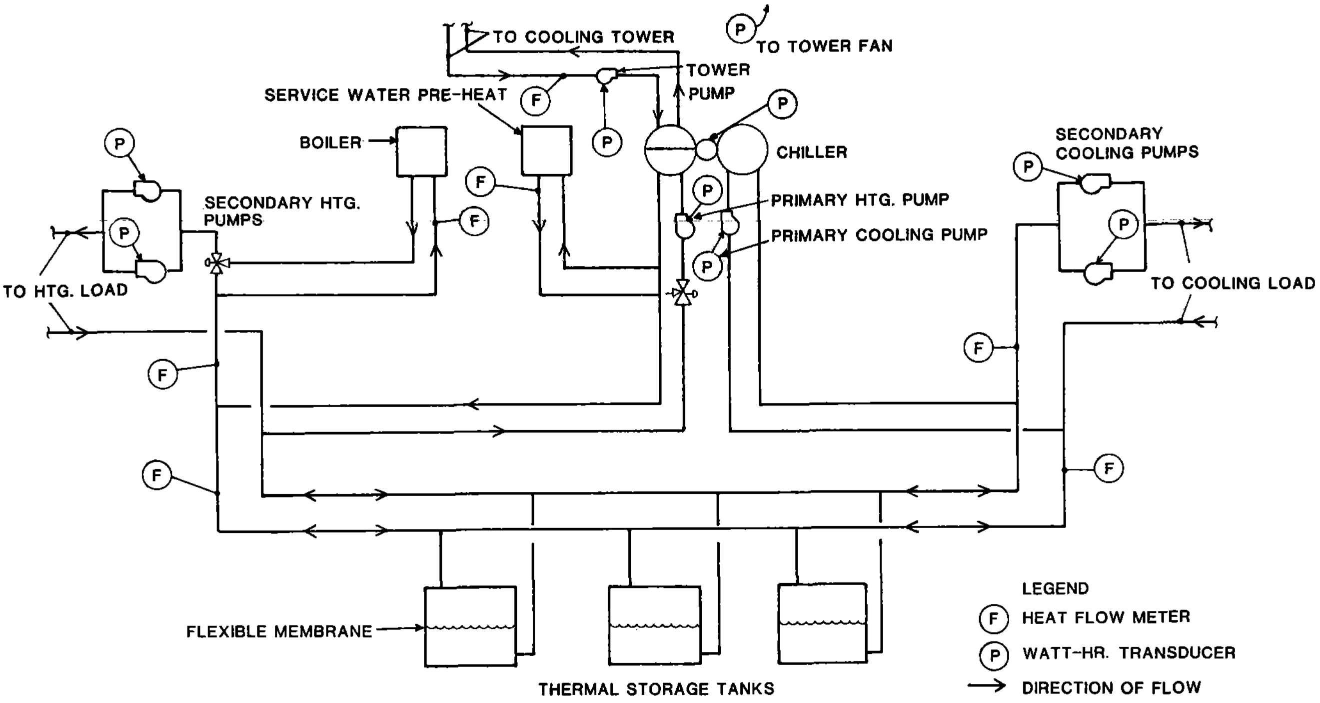

FIG. 1 HVAC SYSTEM SCHEMATIC SHOWING DATA ACQUISITION SYSTEM SENSOR LOCATION

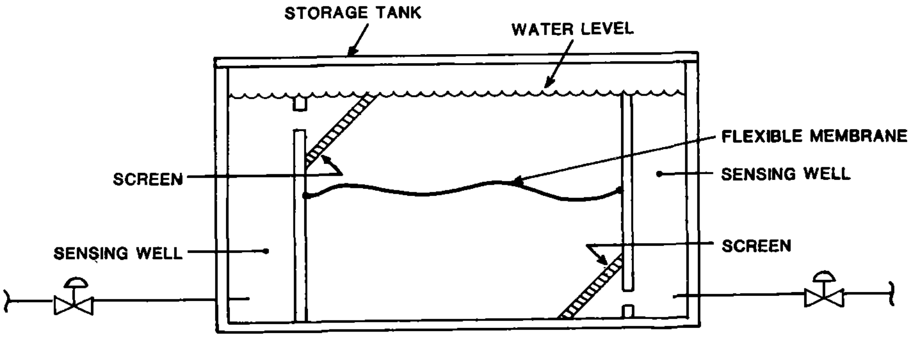

FIG. 2 SECTION OF THERMAL STORAGE TANK

AN OVERVIEW OF THE SERI SOLAR ENERGY STORAGE PROGRAM

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Abstract

The SERI Solar Energy Storage Program is summarized. The program provides research, systems analyses, and assessments of thermal energy storage and transport in support of the Thermal and Chemical Energy Storage Program of the DOE Division of Thermal and Mechanical Energy Storage Systems. Currently, research is in progress on direct contact thermal energy storage and thermochemical energy storage and transport. In addition, activities are being initiated in the definition of new thermal energy storage concepts and thermal energy transport by sensible and latent heat media. Systems analyses are performed of thermal energy storage for solar thermal applications, and surveys and assessments are used to coordinate thermal energy storage activities for solar applications, particularly in building heating and cooling.

Introduction

As part of the Thermal and Chemical Energy Storage Program of the DOE Division of Thermal and Mechanical Energy Storage Systems, thermal energy storage technologies are developed for identified application areas by the laboratories designated with the appropriate lead responsibility. The SERI Solar Energy Storage Program supports the Thermal Energy Storage Program by researching thermal storage and transport technologies and performing analyses and assessments on thermal storage and transport systems (Figure 1).

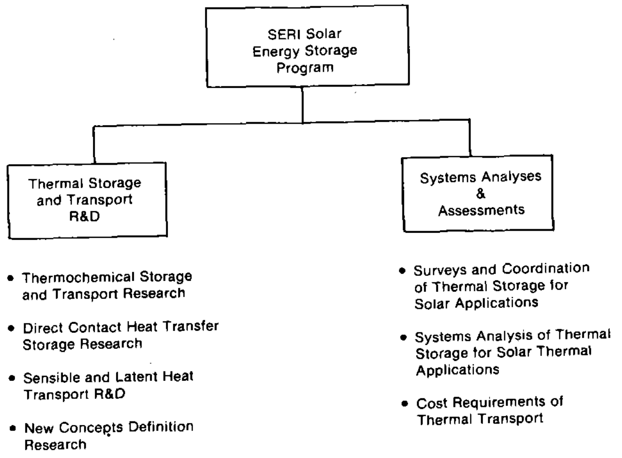

Figure 1. The FY80 SERI Solar Energy Storage Program

The objectives of the SERI Solar Energy Storage Program are to develop a better understanding of thermal energy storage and transport technologies and to obtain information that allows designers to select promising thermal storage and transport technologies for specific applications. To accomplish this, research and development are performed on thermal energy storage options in an attempt to resolve technical and economic uncertainties that hinder their development. Thermal energy transport by sensible and latent heat media is developed. New thermal storage and transport concepts are also explored. Systems analyses are conducted for defined applications to determine thermal storage and transport requirements and to aid in selecting concepts for development. Surveys and assessments are performed to coordinate thermal energy storage R&D for application areas. Figure 1 lists the activities now included in the SERI Solar Energy Storage Program.

For FY80, the emphasis of these activities is to support the joint plan of the DOE Division of Thermal and Mechanical Energy Storage Systems and the Division of Solar Thermal Energy Systems for developing thermal energy storage for solar thermal applications.[1] The SERI FY80 solar energy storage activities are briefly discussed in the following narrative; two of the areas are discussed in more detail in other papers presented at this meeting.

Thermal Storage and Transport R&D

A new area in the SERI Solar Energy Storage Program for FY80 was thermochemical storage and transport research. Previous studies raised questions as to the efficiency and cost capabilities of reversible thermochemical reactions for energy storage and transport.[2] However, reversible reactions show significant technical promise because of their ability to store large quantities of heat at ambient conditions, an attribute that makes them appear particularly promising for long-duration storage and long-distance thermal transport. Therefore, an effort is in progress to reexamine the efficiency and cost constraints for thermochemical storage and transport and to assess quantitatively the performance of such systems. A review has been completed of the large number of previous studies, and the results have been analyzed to address the widely differing projections of cost and performance. Calculations have been made to determine the efficiency of storage, and basic raw material costs have been compared to other options. The system designs will first be further refined and then more accurate cost projections will be made. This information will be used to determine whether research could make thermochemical energy storage and transport cost effective. If the initial cost and efficiency estimates are promising, laboratory research will be performed to understand the actual behavior of reaction systems.

Research on direct contact heat transfer for thermal energy storage continued in the SERI Solar Energy Storage Program from FY79. Heat exchanger costs are generally significant in thermal energy storage systems, and thermal energy storage has distinct requirements that often make the heat exchange unique. A potential way to lower the cost of heat exchange is to eliminate the need for a surface between the heat transport fluid and the thermal energy storage media. For such a direct contact system, the transport fluid and storage material must be immiscible. Of course, such concepts are employed for solid sensible heat storage media such as rocks in direct contact with the air heat transfer fluid for home heating. However, for liquid storage media, the knowledge of the heat transfer mechanism is too limited to understand either the capabilities or limitations of direct contact heat transfer for thermal energy storage.

The objective of the SERI effort in direct contact heat exchange for thermal energy storage is to provide an understanding of the concept based on fundamental principles. This information will allow developers to determine if direct contact systems are viable and to select and design direct contact storage systems if they are promising. Initially, experimentation and analyses have been carried out for low-temperature latent heat storage systems in which an immiscible heat transfer fluid is bubbled through a salt hydrate storage media, since some previous data exists for comparison to the analysis and the heat exchange experiments can be observed. However, once confidence is established in the understanding of system performance, the studies will be extended to high-temperature sensible and latent heat storage, where direct contact systems seem to have the greatest potential.

In FY80, a preliminary model was completed of direct contact heat exchange based on information gathered from the literature, and the model predictions were found to agree quite well with the limited data available. However, insufficient experimental information is available to accurately assess the model's predictive ability. A single-drop direct contact heat transfer column was constructed in FY80, and heat transfer rates were measured. Additional data were found to be necessary to determine what factors affect performance, and appropriate experiments are now in progress. A multi-drop column was also constructed and checked out with a heat transfer fluid and water. This device is being used to establish the capabilities and limitations of direct contact systems. It will also be used to obtain operational data for comparison to the model. More details on the effort in direct contact heat exchange are presented in another paper in this review.

Another area initiated in FY80 is the definition of new concepts for high-temperature thermal energy storage for solar thermal applications. Research will be supported to provide information on advanced thermal energy storage options that promise cost and performance improvements over known thermal energy storage technologies. In addition, new approaches to high-temperature thermal storage-solar thermal systems will be funded if they provide potentially lower delivered energy costs compared to existing systems.

Systems Analyses and Assessments

The thermal storage technologies under development must fit the intended solar applications. Therefore, continual communication is critical among researchers developing solar and storage technologies. In this area, SERI has surveyed the thermal storage technologies under development within the Division of Thermal and Mechanical Energy Storage Systems and elsewhere. Communications have been developed with the various solar application areas, and their needs are being identified through discussions and analyses. The goal of these activities is to arrive at a coordinated plan that will provide timely development of thermal storage technologies for defined solar applications. Toward this end, coordination meetings have been held between the laboratories managing thermal energy storage RD&D for solar heating and cooling of buildings (SHACOB) in the DOE Office of Advanced Conservation Technologies and the Office of Solar Applications for Buildings. Initial agreements and goals have been developed for thermal energy storage technologies in SHACOB. A workshop has also been held between the program managers of the DOE Divisions of Thermal and Mechanical Storage and Solar Thermal Energy Systems to coordinate their joint program.

SERI is responsible for system analyses of thermal storage to support decision points in the Thermal Energy Storage for Solar Thermal Applications Program.[1] In this program, second- and third-generation thermal storage technologies will be developed to provide lower cost and/or improved performance over the first-generation technologies currently being deployed in Solar Thermal Large-Scale Experiments (LSE). The objectives of the SERI systems analysis effort are to provide value data on thermal storage and rankings of thermal storage concepts. The value data are the basis for thermal storage cost goals, which are then used to screen thermal storage concepts. Those concepts that pass this first screening are ranked on a delivered energy unit cost basis (busbar energy cost for electric power) within a specified program element. The process is then repeated as needed for other elements. In this manner, promising thermal storage concepts will be identified for development.

During FY80, the value of thermal storage in electric power applications was reported.[3] In addition, a ranking methodology was completed for comparing the cost and performance of thermal energy storage.[4] A subcontract was awarded to Stearns-Roger to estimate the cost and performance of thermal energy storage systems for solar thermal applications, and initial data have been prepared for thermal energy storage concepts for water/steam-, organic fluid-, and gas-cooled receiver systems. These activities are reported in more detail elsewhere in this meeting.

Thermal energy transport by sensible and latent heat media is being incorporated in the program in FY80. Initially, studies are being funded to determine allowable prices for thermal transport and to compare them with projected transport costs. Research and development will also be sponsored to improve the cost and performance of the most promising thermal energy transport concepts.

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DIRECT CONTACT HEAT TRANSFER FOR THERMAL ENERGY STORAGE

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Abstract

Direct contact heat exchange offers the potential for increased efficiency and lower heat transfer costs in a variety of thermal energy storage systems. SERI models of direct contact heat transfer based on literature information have identified dispersed phase drop size, the mechanism of heat transfer within the drop, and dispersed phase holdup as the parameters controlling direct contact system performance. However, current information is insufficient to predict these factors a priori. Therefore, tests have been defined and equipment constructed to provide independent determination of drop size, heat transfer mechanism, and hold up. In experiments with heptane dispersed in water, the equation of Kagen et. al. was found to most closely predict the drop size. The velocity at which drop formation changes from dropwise to jetting was overpredicted by all literature correlations. Further experiments are needed to conclusively determine whether the salt in a salt hydrate melt acts to block internal circulation. In addition, the potential of low temperature oil/salt hydrate latent heat storage systems is being evaluated in the laboratory.

Introduction

For both sensible and latent heat storage systems, heat exchange based on conventional equipment accounts for a substantial fraction of the total storage system cost. Direct contact heat transfer, the process of transferring heat across the interface of two immiscible phases without an intermediate heat transfer surface, offers both increased efficiency and decreased cost. However, direct contact heat transfer is not sufficiently understood to accurately assess its performance potential, therefore SERI's research is being directed toward predicting performance accurately enough to judge the potential of the technology.

Research at SERI is directed at understanding the basic mechanisms which govern direct contact heat transfer, assessing operational characteristics, and applying the knowledge to the development of more cost efficient thermal storage systems. During the past year, research at SERI has focused on testing mathematical models of direct contact heat transfer. Experimental work has focused on low temperature oil/water and oil/salt hydrate systems due to the relative ease of working at low temperatures, previous experience available in this temperature range, and the need to provide a definitive analysis of oil/salt hydrate systems.

Controlling Factors

Modeling efforts at SERI identified three parameters which control the rate of heat transfer in direct contact systems:

- droplet size,
- droplet internal heat transfer mechanism, and
- droplet residence time.

Each of these factors depends on the physical properties of the two phases and on designer specified characteristics such as distributor design and the superficial velocities of the two phases.

In FY80, experiments were initiated to independently determine these three parameters. A single drop column (Fig. 1) provides data on drop size as a function of fluid properties, injector nozzle diameter, and dispersed phase flow rate. The heat transfer mechanism between individual drops and the continuous phase is also determined with this apparatus. The multi-drop heat transfer column (Fig. 2) is used to study residence time, and to evaluate possible operating problems such as freeze up and carry over. In this paper, the results obtained to date on drop size and heat transfer mechanism are summarized.

Drop Size

Two regimes of drop formation are of interest in the design of direct contact heat exchangers: dropwise formation and jetting. At low flow rates, droplets grow while attached to the nozzle. When the upward force of buoyancy and the kinetic energy of the fluid leaving the nozzle exceed the retarding forces of interfacial tension and drag, the drop detaches and rises. This force balance is the basis of all the equations for predicting drop size in the dropwise regime (Scheele & Meister, deChazel & Ryan, Kagen et al.).[1]

When a drop begins to detach, a neck of fluid is formed between the nozzle and the drop. The neck elongates and thins, then breaks as the drop detaches. The forces of kinetic energy and excess internal pressure tend to hold the neck open, while interfacial tension attempts to thin the neck. As the velocity through the nozzle is increased, a point is reached where the stabilizing forces are greater than the interfacial tension. Above this velocity, drops are formed by the breakup of the jet. Equations predicting the transition point (Scheele & Meister, deChazel & Ryan, Ruff, and Lehrer) exhibit reasonable agreement among themselves, except at large nozzle diameters where only Lehrer's equation predicts finite jetting velocities.[1,2,3]

Below the jetting velocity, all drops produced are of equal size, during jetting a bi-modal distribution is produced. Two groups have advanced correlations for predicting the mean diameter of drops produced by jets, however, they are merely curve fits.[1]

Drop size is important for several reasons. As the drop becomes larger, its surface to volume ratio decreases; increasing the time required for a rigid drop to transfer a given fraction of its heat. A large-drop rises through the exchanger faster than a small drop, because buoyancy force increases as the third power and drag force as the second power of the diameter. However, the heat transfer rate may also increase with increasing radius due to enhanced internal droplet circulation and oscillation.

The single drop column is used to gather data on drop size and the onset of jetting. The basic apparatus is a four-sided jacketed plexiglass column. Drops of the dispersed (oil) phase are injected through a glass nozzle at the bottom. Other interchangeable nozzles can be used so that the effect of nozzle diameter may be investigated. A heater controls the dispersed phase inlet temperature. Water can be circulated through the jacket to control the temperature of the continuous phase. The oil flow rate is measured with precision rotometers.

At low flow rates, the frequency of drop formation is measured with a stroboscope. Drop size is calculated from the frequency and measured flow rate. During jetting formation, the formation frequency is not constant and drop size is determined from photographs. The jetting velocity is defined as the velocity at which the droplet formation frequency ceases to be regular.

Comparisons of theoretical and measured drop size have been made with the water/heptane system. At low flow rates, the equation of Kagen et al. best describes the experimental data (Fig. 3). However, the velocity at which the transition to jetting occurs is overpredicted by all four available equations. In the jetting region itself, the existence of a bi-modal distribution is confirmed, but more data is necessary to determine the accuracy of the literature correlations. Additional experiments will be performed on oil/salt hydrate systems to determine whether the equations describe drop size for a surface active continuous phase where the continuous phase may be melting or freezing.

Drop Heat Transfer

For low conductivity materials such as oil, internal drop hydrodynamics determine the rate of heat transfer to and from individual drops. Small drops behave as rigid spheres, and internal conduction limits heat transfer. Larger drops may exhibit internal circulation, which will increase the heat transfer rate. Large drops may undergo oscillations which greatly enhance heat transfer. On the other hand, surface active agents may immobilize the interior of drops which would normally circulate.[4]

Heat transfer rates are correlated by an R factor, the ratio of the effective thermal diffusivity inside a drop to the molecular thermal diffusivity which would be exhibited for a non-circulating drop of equal size. The R value of a rigid sphere is 1, that of a circulating drop ranges from 1 to 5, while that for oscillating drops may range up to 100.

Experiments have been conducted with the single drop column to determine the effect of drop size and continuous phase composition on the internal heat transfer mechanism. Hot oil is injected into the column, and the flow rate is raised to a point just below jetting to achieve the highest flow rate possible while still producing equal size drops. Drop size is again determined from stroboscopic and flow measurements. The inlet and outlet temperatures of the dispersed phase and the continuous phase temperature are simultaneously recorded. The terminal velocity of the drops is measured and used to calculate the time required for a drop to move between the nozzle and outlet. The distance from column inlet to outlet is varied from 10 to 100 cm.

E_T is the amount of heat transferred by a drop divided by the maximum amount of heat which could have been transferred. If $\log(1-E_T)$ is plotted against residence time, the slope of the line yields R, and the intercept shows the magnitude of the end effects.

For the heptane/water system, the R value of 0.39 cm diameter drops was 1.4, while for 0.3 cm drops of Dowtherm J rising through molten sodium thiosulfate hexahydrate, the R value was not significantly greater than 1.0. In both cases, internal conduction limits the heat transfer rate. Further experiments will be necessary to determine whether the lack of circulation of the drop rising through the salt hydrate was due to surface active effects by the salt. Since the drop sizes were in the transition regime from rigid to circulating drops, the lower R value for the salt hydrate system may be due to the smaller drop diameter. Experiments will also be run to determine whether drops injected at temperatures below the freezing point of the continuous phase behave differently from hot drops due to the direction of heat transfer.

Conclusions

A column for determining drop size and heat transfer mechanism as a function of the relevant physical and operational parameters has been designed, constructed, and operated. During runs with the water/heptane system, the equation of Kagen et al. best predicted drop size. The nozzle velocity at which the drop formation mechanism changes from dropwise to jetting was overpredicted by all available correlations. The mode of drop formation in the jetting region has been observed, but sufficient data has not been analyzed to make a determination of the accuracy of the available literature correlations. The heat transfer rates observed were similar to those expected for a non-circulating drop, but the drop size was small enough that surface tension may have retarded circulation. Further information is needed to determine whether drop circulation is inhibited by the surface active action of salt in a salt hydrate melt.

Future Plans

Experiments will be continue with the single drop column to determine whether the equations for predicting the transition to jetting and dropsize during low flow and jetting are applicable to salt hydrate phase change systems. Additional experiments will determine droplet internal circulation effects on the salt system heat transfer.

The multi-drop column has been constructed, and is operational. This apparatus will be used to test models of holdup and to provide an experimental assessment of direct contact heat exchange applied to low temperature salt hydrate storage systems. The problems of freeze up and carry over of the continuous phase into the oil loop will be investigated.

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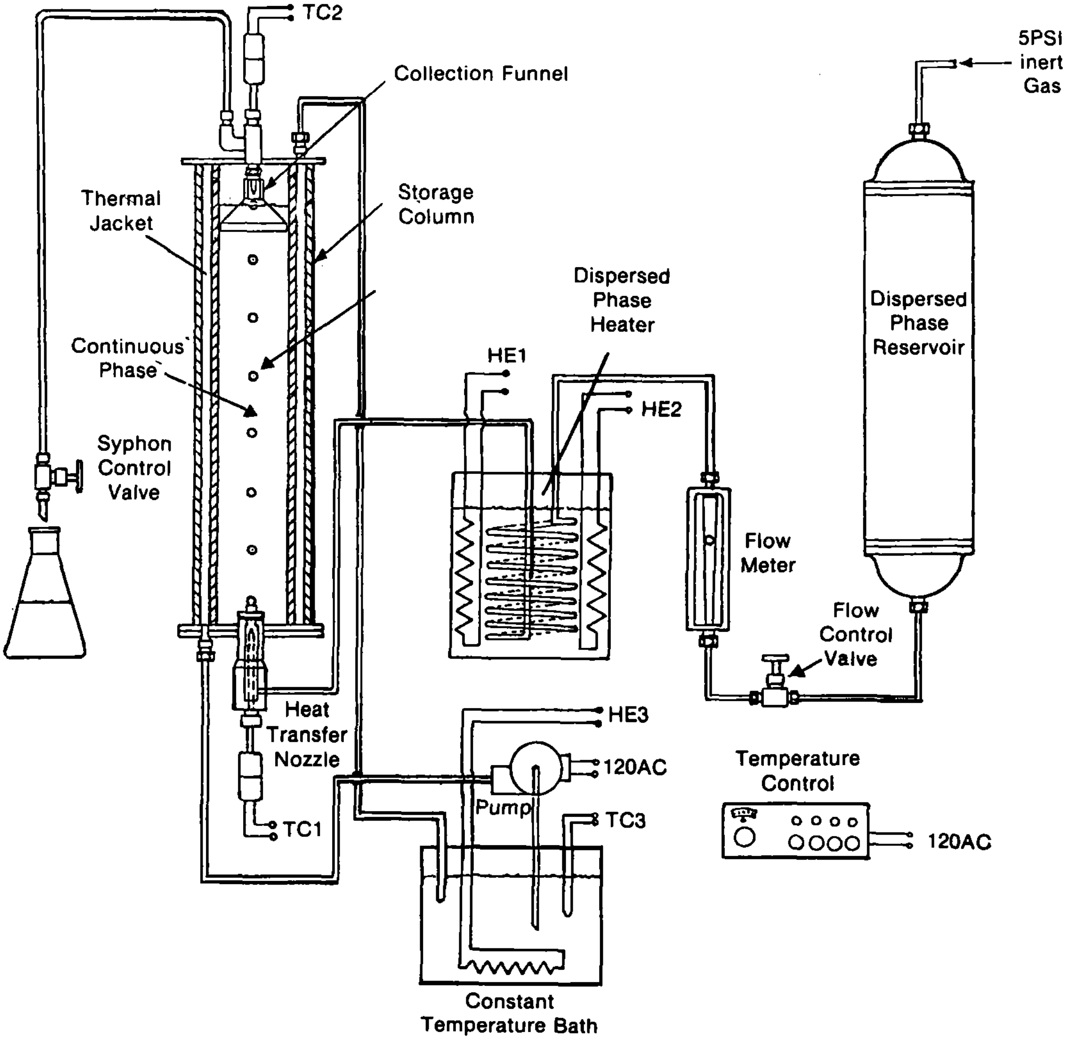

Fig. 1 Single Drop Apparatus

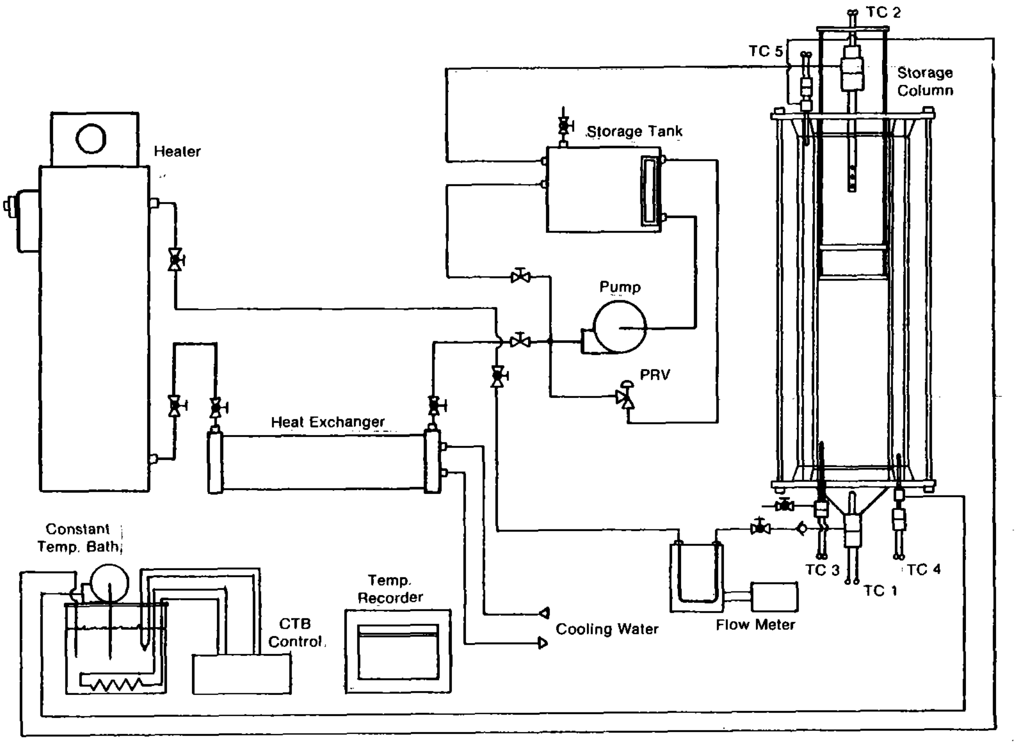

Fig. 2 Multi-Drop Apparatus

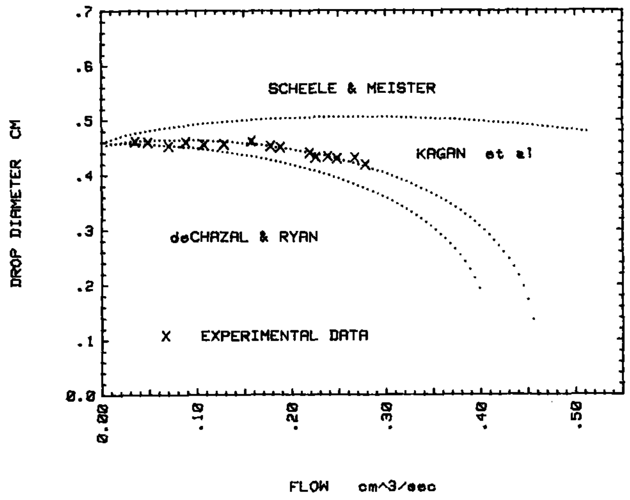

Fig. 3 Drop Diameter vs. Flow Rate for the system Heptane/Water, Nozzle Diameter=0.13cm

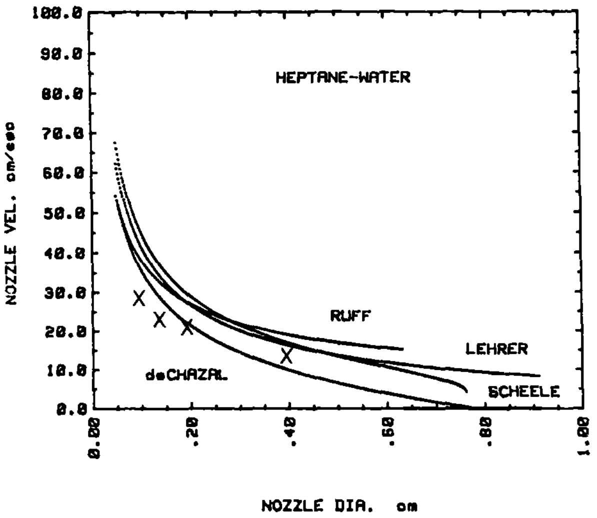

Fig. 4 Jetting Velocity vs. Nozzle Diameter for the system Heptane/Water

SYSTEMS ANALYSIS OF THERMAL STORAGE

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Abstract

During FY80 analyses were conducted on thermal storage concepts for solar thermal applications. These studies include both estimates of the obtainable costs of thermal storage concepts and their worth to a user (i.e., value). Based on obtainable costs and performance, promising thermal storage concepts are being identified. A preliminary screening was completed in FY80 and a more in-depth study was initiated. Value studies are being conducted to establish cost goals. A ranking of storage concepts based on value in solar thermal electric plants was conducted for both diurnal and long duration applications. Ground mounted thermal storage concepts for a parabolic dish/Stirling system are also being evaluated.

Introduction

The systems analysis of thermal storage effort is being conducted to identify promising thermal storage concepts for development. The criteria to be met in this process are:

1. The obtainable cost must be less than or equal to program cost goals.
2. The concept must be more cost effective than alternative thermal storage technologies.

The program cost goals are being established to assure a market place for the developed technologies. This requires an understanding of the potential market places, the potential size of each market, the locations, user economic criteria, and alternative energy systems. From this knowledge the cost of the alternative energy systems are employed as a measure of what the user is willing to pay for a new energy system; i.e., the value. The value of thermal storage is that part of the system value which is due to storage or which can be allocated to storage. The program cost goals for thermal storage are established based on that later value.

The second criterion requires a direct comparison of the various thermal storage concepts. This analysis must be conducted with a consistent cost data base and for a specified application. Furthermore, to assure a fair comparison each technology must perform the same mission. Each storage is not required to have the same efficiency, but there must be a way of accounting for differences. A ranking methodology for conducting the comparisons has been developed by SERI,[1] and SERI is employing that methodology in the analysis of the thermal storage concepts.

In FY80 this effort has focused on thermal storage for solar thermal applications. Cost trade-off analyses are being conducted for water/steam receivers, organic fluid receivers, and gas/Brayton systems. The potential for ground-mounted thermal storage with a parabolic dish/Stirling system is being assessed. The value of thermal storage in solar thermal process heat applications is being analyzed, and a ranking of thermal storage concepts based on value in solar thermal electric power plants was completed. Each of these activities is discussed in the following paragraphs.

Obtainable Cost Analyses

Thermal storage concepts are being developed for solar thermal applications; a plan has been prepared as a cooperative effort of the Solar Thermal Program and the Thermal and Chemical Energy Storage Program.[2] SERI is supporting decision points in that program by conducting comparative rankings of thermal storage concepts for identified applications. The first of these decision points will occur in the spring of 1981 when thermal storage concepts will be selected to develop for the following solar thermal systems:

Water/Steam Central Receiver System

1. Electric power plant; diurnal storage with a second generation receiver.
2. Process heat; diurnal storage with dry saturated steam delivered to the load.

Organic Fluid Receiver System

3. Co-generation system; week-end storage
   3-A) Syltherm transfer fluid
   3-B) Caloria transfer fluid.
4. Process heat; week-end storage with dry saturated steam delivered to the load.

Air Cooled Receiver System

5. Large Brayton cycle; diurnal storage.

The analyses are being done in a two-step manner as described below:

I. Preliminary Screening

This analysis was conducted by SERI to understand the importance of various performance parameters and to provide some early guidance to the program managers. Because of the limited scope, the analysis was done in a generic manner.

II. Decision Data
Stearns-Roger under contract to SERI is generating consistently calculated cost and performance data. SERI will analyze the impact of thermal storage on system-delivered energy cost (using the Stearns-Roger data) and recommend specific concepts for development. The Stearns-Roger work is described in another paper being given at this meeting.

Table 1 summarizes the results of SERI's in-house study. The study has been documented[3] and each of the concepts is described. Each of the concepts was compared on a consistent basis with a first-generation thermal storage technology (i.e., reference system). The conclusions were based upon the delivered energy costs of the storage-coupled solar thermal system with the alternative thermal storage as compared to the reference thermal storage for that same condition. The program goals require a 24% or more lowering of the thermal storage cost relative to the first-generation concept. The concepts with that potential are noted in Table 1.

Table 1. RESULTS OF THE PRELIMINARY SCREENING

Concepts with the Potential of Meeting Program Goals

- Water/Steam Collector/Receiver [1]
  - K-Salt/Glass (Buffer Storage Applications)
  - Two Stage: Draw Salt/Glass and Oil/Rock (Diurnal Storage Applications)
- Organic Fluid Collector/Receiver [2]
  - Trickle Charge Syltherm/Glass

Concepts That Would Increase the Energy System Costs

- Water/Steam Collector/Receiver
  - Draw Salt
  - Two-Stage Draw Salt/Glass and Oil/Rock
  - $NaNO_3$ Phase Change
- Organic Fluid Collector/Receiver
  - NaOH, Phase Change
  - K-Salt [3]

Concepts with Little or No Advantage or Penalty

- Water/Steam Collector/Receiver
  - Improved Phase Change, $NaNO_3$
  - Two-Stage Draw Salt/Glass and K-Salt/Glass
- Organic Fluid Collector/Receiver
  - K-Salt/Glass

[1] For water/stream receivers system, (Barstow Technology), electric power only, oil/rock reference storage concept.

[2] For organic fluid receiver, (Shennandoah Technology), cogeneration only; trickle-charge syltherm/taconite reference storage.

[3] K-salt is similar to Hitec and consists of 50% $NaNO_3$, 35% KNO_3, and 15% $NaNO_2$.

The analysis was conducted in a generic manner. Not all concepts currently being developed were studied; instead, the analysis was configured to study each of the major types of technologies: sensible heat (both organic and inorganic storage media in both single- and two-stage systems) and latent heat. Only one phase change concept was studied, which was described by Honeywell[4] but modified for use in the specific applications. The list of sensible heat concepts was also limited and the ones listed were considered as generically representative of other sensible heat systems. The data in Table 1 are obviously preliminary. While the data are indicative of the type of results anticipated in the Stearns-Roger study, the later effort will study more concepts for more applications and in greater depth.

Value Studies

The value of thermal storage is being analyzed for solar thermal applications. Value data for electric power applications were presented at the last year's annual meeting.[5] Values of thermal storage in process heat applications are currently being generated, but the results are not available as of this writing. The electric power value data were employed to rank thermal storage for diurnal and long-duration storage.

Diurnal Storage

Table 2 presents the results of the ranking of thermal storage concepts based upon value. First-generation thermal storage concepts are those currently being built in large-scale experiments. The first-generation storage for each solar thermal collector/receiver system is noted in Table 2. For areas of high insolation (i.e., Barstow, Albuquerque, Phoenix) all of these first-generation storage meet the value-delivered goal. However, the large markets of storage-coupled solar thermal systems are anticipated to be in medium insolation sites. These areas include most of Texas, Colorado, Utah, Nevada, California, and some of Oklahoma. In that area only molten salt storage with molten salt collector/receivers could meet the value. Table 2 presents the required improvement in the first-generation storage to meet value in the medium insolation sites. Fortunately, development of second generation is in progress.[2] The cost reductions considered obtainable in the current plan are also noted in Table 2. The overall situation is very healthy; a second-generation development effort is needed and concepts have been identified which can meet the need.

Table 2. RECOMMENDED GOALS FOR SECOND-GENERATION DIURNAL THERMAL STORAGE [1]

Collector/Receiver	% Improvement in First-Generation Subsystem Cost for Storage Capacity of:			
	3 Hours	6 Hours	9 Hours	Current Plan [3]
Water/Steam (Oil/rock)	30	30	30	24
Molten Salt [2] (Dual tank, salt external insulation)	√	√	√	50
Liquid Metal (Dual tank, sodium, external insulation)	55	65	70	57
Gas Cooled (Ceramic brick)	50	55	60	31

[1] To meet value at medium insolation sites (most of Texas, Colorado, Utah, Nevada, California, and some of Oklahoma and Kansas). The data are the needed improvements including O&M costs.

[2] Second-generation storage (i.e., internally insulated tanks) are anticipated to meet the value even at low insolation sites. √ = First-generation costs are less than value.

[3] From DOE, 1979. Thermal Energy Storage for Solar Thermal Applications, Multiyear Program Plan," Draft. Oct. 25, 1979.

Long Duration Storage

Third-generation thermal storage developments are to provide a technology base for future solar thermal applications. One of those frequently discussed applications is long-duration storage for base-load electric power plants (i.e., 24 hr/day operation, day after day, regardless of weather). Value for the long-duration storage use has been calculated. The value was found to be a strong function of the thermal storage efficiency (i.e., the ratio of the actual work produced with thermal storage to the amount of work which could have been produced if the thermal energy has not been stored). The effect of location (high, medium, or low insolation) was small. Table 3 presents the results of the study. The cost data were taken directly from the literature. No modifications to the reported data were made except those necessary to place all data in the same format (i.e., same-year money and the power- and energy-related terms). Contingency and spares, interest during construction, or indirects have not been added by this author since the referenced paper may or may not have included those factors. Unfortunately, the references fail to mention which factors are included.

The long-duration value data were derived for a truly baseload application. To meet such load, a very large quantity of storage is needed—on the order of 1000 hours[6]. For an overall capacity factor equal to a coal-fired plant (i.e., equipment outages only), the availability factor need be only 94%, requiring from 250 hours to 830 hours of storage (say a nominal 360 hours). If the availability factor were reduced to 90%, the overall value would be slightly reduced; but the quantity of storage is reduced to only 40 to 100 hours (say a nominal 72 hours). The quantity of storage necessary to achieve the value has not been determined. The quantity of storage will be variable due to differences in insolation and loads at various sites and in different time frames. Thus, the obtainable cost data are compared to the same value for two nominal storage capacities.

The data in Table 3 indicate that only the air/rock and $Ca(OH)_2$ concepts have the potential of meeting their value. The air/rock system has a very high efficiency and thus value. For the $Ca(OH)_2$ concept, the efficiency can be high and also the value. However, the power-related cost for that concept might be very high. Research currently in progress at SERI is examining the issues of both efficiency- and power-related cost. Improvements in efficiency of $Ca(OH)_2$ over previous work have been found. As currently defined, the other concepts examined have both efficiency and cost problems. As the current work at SERI is demonstrating for calcium hydroxide, improvements might be made. Revision of the SO_2/SO_3,NH_4H SO_4, and oil/rock concepts may alter both the cost and value (i.e., efficiency) data of the currently defined concepts. In the future, other concepts might be found which are also low cost and have high efficiency.

Ground Mounted Thermal Storage

Thermal storage placed on the ground with a Stirling engine is being studied. The objective is to assess the potential as an advanced system. Preliminary data indicate that cost and efficiency of transporting the thermal energy to the ground are major factors. Innovative concepts are being identified to solve the problems; the final results are not available now.

Closure

The systems analysis of thermal storage is analyzing the cost and value of thermal storage in solar thermal applications. The ranking of thermal storage based on value has

Table 3. COMPARISON OF OBTAINABLE COSTS AND VALUE FOR LONG-DURATION THERMAL STORAGE (1978 Dollars)

			Cost Data [1]		Total Cost [2] $/kW_e$				
					72 Hours		360 Hours		
	Concept Reference	Efficiency [3]	C_P $/kW_e$	C_S $/kWh_e$	$C_S \cdot H$	C_T	$C_S \cdot H$	C_T	Value $/kW_e$ [4]
THERMOCHEMICAL	SO_2/SO_3								
	Minimum	0.41	300	17.0	1224	1524	6120	6420	-35/+2
	Maximum	0.52	NE	NE	NE	NE	NE	NE	110/120
	$Ca(OH)_2$								
	Minimum	0.42	450	0.5	36	486	180	630	-35/+2
	Maximum	0.76	NE	0.3 [7]	22	NE	108	NE	360/480
	NH_4HSO_4 [6]								
	Minimum	0.44	600	6.0	432	1032	2592	3192	0/40
	Maximum	0.55	NE	1.5 [7]	108	NE	540	NE	130/165
SENSIBLE & LATENT	Air/Rock								
	Nominal	0.9	81	1.7	122	203	612	693	500/700
	Underground Oil/ Rock								
	Nominal	0.7	300	5.0	360	660	1800	2100	300/400
	Latent Heat Mixed Chlorides								
	Nominal	0.62	Modular	50.0	3600	3600	18,000	18,000	210/280
	Media Only	0.62	[5]	6.0	432	NE	2160	NE	210/280

[1] NE: Data not estimated

[2] $C_T = C_P + C_S \cdot H$; sum of power-related and energy-related costs

[3] Work out/work equivalent into storage

[4] Minimum value/maximum value

[5] Storage tanks are modular, each including its own heat transfer system

[6] This author generated all efficiency and "media only" cost data.

[7] Media only, materials cost from Chemical Marketing Reporter, June 1980

shown that the development of second-generation technologies is needed and that the current program can meet that need. Long-duration thermal storage must be both low cost and have higher efficiency. Identified sensible and thermochemical storage concepts have the potential of meeting the long-duration value. In the future other low-cost concepts may also be identified.

A preliminary screening of thermal storage concepts was completed for water/steam and organic fluid receivers. Because of the preliminary and generic nature of that data, the results should not be applied to other concepts unless they are similar. A more in-depth study was initiated; the later effort is being supported by Stearns-Roger and will be employed to recommend specific thermal storage concepts for development.

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COST AND PERFORMANCE OF THERMAL STORAGE CONCEPTS IN SOLAR THERMAL SYSTEMS

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ABSTRACT

The objectives of this study are as follows: To provide consistently calculated cost data, to develop realistic performance data, and to project that data for a mature technology for several thermal storage concepts integrated into several solar thermal systems. Available thermal storage concepts were reviewed through a literature search, and contacts with the Solar Energy Research Institute, National Laboratories, and other contractors. A screening criteria was developed which, when applied, resulted in forty systems being judged suitable for further study. Schematics were made for these systems, quantities were established, and from these rough-order-of-magnitude costs determined. Based upon the foregoing, candidate systems were further reduced. The remaining twenty systems were more fully developed. A technical review will be held in September, 1980. The results of the review will be incorporated in the study, and the storage range will be expanded with further costing refinements being applied. The results of the thermal storage analysis will be documented in a final report late in 1980.

INTRODUCTION

The Department of Energy has recognized the need for thermal storage systems adequate for commercial applications of solar thermal power systems and has prepared a plan to develop appropriate thermal storage technology. The Solar Energy Research Institute is supporting the implementation of that plan with a systems analysis of storage coupled solar thermal systems. Stearns-Roger is a subcontractor to SERI with the mission of providing cost and performance data for solar storage concepts in solar thermal systems. The study carried out to meet that objective consists essentially of the following: establishment of reference systems, review of storage system concept sources, development of criteria for assessing the systems, screening the systems, conceptual design, and costing of the systems.

REFERENCE SYSTEMS

The scope of this subcontract is limited to the evaluation of thermal storage concepts in the following solar thermal systems applications:

°Water/steam central receiver for a 100 MWe electric power plant.

°Organic fluid dish receiver for a total energy application, 400 kW_e.

°Gas receiver for a closed air Brayton, 150 MWe electric power plant.

°Process heat
a) Water/Steam Receiver
b) Organic Fluid Receiver

STORAGE SYSTEM CONCEPT SOURCES

Data was reviewed which had been accumulated from the existing published literature and from contacts with SERI, national laboratories, and contractors developing thermal storage. Over one hundred concepts were identified.

INITIAL SCREENING

Each concept was reviewed within the appropriate system with a common site, environment, and cost base. Several criteria were established to determine whether or not it would be worthwhile to retain a concept for study:

°Safety-engineering judgment as to whether or not the system could be operated in a safe manner according to current industrial practices and standards.

°Technological Feasibility - engineering judgment as to whether or not the system could be developed sufficiently to be practically applicable by the early to middle 1990's.

°Availability of Information - judgment as to whether or not there is currently sufficient information available to make a reasonable determination of the concept's merits.

°Similarity of concepts or materials - judgment as to which concept should be carried forward when there are several which are very similar and use very similar materials.

°Economics - judgment in comparison between similar systems components as to whether or not the cost of a component in one system will far exceed the cost of a similar component in a second system without providing any substantial benefits.

Application of the foregoing criteria reduced the number of concepts suitable for further study to forty.

Schematics were prepared for these concepts with particular regard to the feasibility of each concept. The screening concepts were then reapplied. Additionally, rough order of magnitude costs were developed for concept comparison. The concepts judged most acceptable by these criteria were reduced to twenty and are shown in the accompanying tables.

STORAGE CONCEPTS RECOMMENDED FOR FURTHER STUDY

WATER/STEAM RECEIVER W/REHEAT (POWER)

RECEIVER STEAM 12.5 MPa (1815 PSIA)
510°C (1000°F)/510°C (1000°F)

1st Stage
Sensible Heat
°Caloria/Rock - reference
°Pressurized water - underground cavern

Latent Heat
°Containerized salt (Na OH, Na_2 CO_3)
°Tube Intensive (Na OH, Na NO_3, MnO_2)
°Direct Contact (Na OH, NA NO_3, Mn O_2)

2nd Stage
Sensible Heat
°Draw salt - two tank
°Air/rock
°Sand moving bed
°Latent Salt - one tank

Latent Heat
°None

ORGANIC FLUID RECEIVER (POWER)

Receiver Fluid 399°C (750°F) Ref.

Sensible
°Syltherm/taconite trickle charge - reference
°Draw Salt/taconite

Latent Heat
°Direct Contact - 2 stage (Na NO_3, Na OH)

Alternate Fluid 310°C (590°F)
°Sensible Heat
°Caloria/rock - reference

Latent Heat
°Na_2 SO_4 (Solid/Solid)

WATER/STEAM RECEIVER (PROCESS)

12.5 MPa (1815 PSIA) Receiver Steam (Saturated)
288°C (550°F) Process Steam (Saturated)

Sensible Heat
°Caloria/rock - reference
°Pressurized Water - Underground Cavern

Latent Heat
°Containerized Salt (Na NO_3, Na OH)
°Tube Intensive (Na NO_3, Na OH)

ORGANIC FLUID RECEIVER (PROCESS)

Receiver Fluid 310°C (590°F)
Process Steam 168°C (335°F)

Sensible Heat
°Caloria/rock - reference

Latent Heat
°None

AIR BRAYTON CLOSED CYCLE RECEIVER

Receiver Fluid 816°C (1500°F)

Sensible Heat
°Air/Al_2O_3 Brick (reference)
°Air/Cast Iron

CONCEPTUAL DESIGN

The concepts selected through the initial screening process will have their schematics refined and more detailed costing will be applied through the present worth of required revenue equation.

The results of the study will be reviewed in September, 1980 for technical merit and correctness by personnel of National Laboratories, contractors and the Department of Energy. The comments from this review will be incorporated in further study, the overall period of storage will be expanded, and further costing developed. A final report on the study results is expected to be completed late in 1980.

HIGH-TEMPERATURE MOLTEN SALT THERMAL ENERGY STORAGE SYSTEMS FOR SOLAR APPLICATIONS

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Abstract

The overall objective of this program is to select and test latent-heat alkali and alkaline earth carbonate storage salts, containment materials, and thermal conductivity enhancement (TCE) materials for use in high-temperature (704° to 871°C, 1300° to 1600°F) thermal energy storage systems utilizing advanced solar-thermal power generation concepts. This will be accomplished by screening candidate salt/containment/TCE materials combinations in 1000 (tests completed) and 3000 hour capsule compatibility tests employing both reagent- and technical-grade (low cost) salts. The results of these compatibility tests will lead to the selection of the materials combinations that best meet the anticipated solar power system requirements. Needs for more reliable thermophysical and transport property data will be identified and measurements will then be performed on these salts to support the scale-up of solar-thermal TES subsystems.

Technical Progress Summary

Materials Compatibility Testing

Salt Selection

Alkali and alkaline earth carbonate salts for 1300° to 1600°F TES applications, were chosen on the basis of the desirable physical properties, thermal performance, and endurance/stability exhibited by the materials in previous programs at IGT.[1,2] Since the economic feasibility of latent-heat TES concepts requires the use of low cost salt materials, the potential problems and limitations associated with using technical grade carbonates was also investigated.

The final candidate salts of Table 1 were then selected primarily on the basis of —

- Energy density (Btu/lb, Btu/ft^3)
- Cost
- Melting/solidification temperatures
- Thermal cycling performance in laboratory-scale TES modules
- Vapor pressure and high temperature stability
- Salt impurity levels
- Toxicity, safety, hygroscopicity, and handling considerations
- Volumetric expansion on melting
- Heat capacity

Containment Materials Selection

The materials selected for solar thermal TES applications in the elevated temperature regime of 704° to 871°C (1300° to 1600°F) generally require superior long-term resistance to salt corrosion, air oxidation and bulk thermal aging effects (largely independent of salt environment).

Initial review of the literature data and past IGT experience indicated that alloys forming Al_2O_3-rich protective films may be the preferred type of containment material for molten carbonates (protective films of $LiAlO_2$ or $NaAlO_2$ are relatively insoluble when in contact with the alkali/alkaline carbonates[3]). On the other hand, in actual TES applications, these alloys (as heat exchanger tubes) may encounter hot air/steam on the opposite face, and Cr_2O_3 scale forming alloys are extremely protective against corrosion under these conditions.

Consequently, availability/cost/performance trade-offs between chromium-oxide and aluminum oxide forming alloys need to be considered in corrosion-resistant, long-term containments in specific molten carbonate TES applications.

Based on the above considerations, the following "core" group of containment materials was selected for 1000 hour testing with each of the reagent- and technical grade salt mixtures listed in Table 1:

- AISI 316 stainless steel; Fe-based (Cr_2O_3 former)
- AISI 304 stainless steel; Fe-based (Cr_2O_3 former)
- AISI 310 stainless steel; Fe-based (Cr_2O_3 former)
- Inconel 800; wrought Fe-Ni-Cr based alloy (Cr_2O_3 former)
- Inconel 600: wrought Ni-Cr based alloy (Cr_2O_3 former)

Testing of the following aluminum oxide (Al_2O_3) forming alloys was performed with selected salt mixtures depending on timely availability and capsule fabrication:

- Armco 18SR/Armco 12SR: Fe-Cr-Al based sheet alloy (Al_2O_3 former)
- Kanthal A-1; Fe-Cr-Al based cast alloy (Al_2O_3 former)
- Alonized AISA 316 or 304 stainles steel or Incoloy 800 (Al_2O_3 former)
(Postponed until the 3000 hour test due to shut down and process scheduling delays at Alon Processing Inc.)

- Alloy HK40; a cast, intermediate Fe and Ni plus carbon alloy (Cr_2O_3 former)

Thermal Conductivity Enhancement Selection

The need for TCE materials/configurations development arises from the fact that the thermal discharge performance of a TES subsystem is controlled by the rate at which the latent hea-of-fusion released at the solid/liquid interface is transported to the heat exchanger surface through the growing layer of solid salt. TCE selection criteria thus included material thermal conductivity, expected chemical compatibility with the carbonate environment, cost, availability, and ease of fabrication into a desirable TCE configuration.

A list of candidate TCE materials is provided in Table 2. Although aluminum is very attractive as a TCE material because of its high thermal conductivity of 127 Btu/hr-ft-°F (∿100 X that of solid carbonates and 10X that of austenitic stainless steels), it cannot be used for the 1300° to 1600°F solar-thermal TES applications because of its 1220°F melting point. While iron and nickel-based materials have higher melting points, they are more costly and have much lower thermal conductivities than aluminum and copper, greatly reducing their attractiveness as TCE materials. As a result, copper (both as a reticulated matrix and a solid) and high conductivity graphite (pyrolytic and ATJ) were 1000 hour tested in technical-grade molten carbonate capsules with an inert (nonoxidizing, to prevent the chemical reaction with high temperature air) environment maintained above the melt.

1000 Hour Screening Tests

The 1000 hour matrix of Table 3 was then subjected to compatibility screening tests. These tests were performed in closed, heli-arc welded capsules of the containment materials with the reagent- or technical-grade salts plus, in some cases, containment or TCE materials coupons.

Availability and delivery constraints necessitated the use of three capsule designs. Testing of AISI Type 304 and 316 stainless steels was performed in capsules of the following specifications (Figure 1):

- Standard 3/4 inch Schedule 40 welded threaded pipe nipples and end-caps; nipple I.D. = 0.834 inch, O.D. = 1.050 inch, nominal wall thickness = 0.113 inch, nipple height = 4.5 inch; end cap wall thickness (excluding thread) ∿0.100 inch, standard pipe threads, 16 per inch.

Testing of AISI Type 310 stainless steel, Inconel 600, and Inconel 800 was conducted in machined capsule bodies and end-caps as follows (Figure 2):

- Standard 3/4 inch Schedule 40 seamless pipe; I.D. = 0.824 inch, O.D. = 1.050 inch, nominal wall thickness = 0.113 inch; and standard 1-1/8 inch diameter bar stock for machining end-caps (as shown in Figure 2); final capsule height ∿4.5 inch.

In addition, Armco 18SR/Armco 12 SR samples were machined into test capsules as follows:

- Capsule body - Armco 12SR; 1.5 inch TIG welded tubing, I.D. = 1.37 inch, O.D. = 1.50 inch, nominal wall thickness = 0.065 inch, final capsule height 4.5 inch.
- Capsule end-cap - Armco 18SR; machined from 0.040 inch thick plate then fusion welded to Armco 12 SR capsule body. (Figure 3)

The capsules indicated in Table 3 will be sectioned and subjected to the following post-test evaluations:

- Close visual inspection and locating of capsule breaches
  - Cross comparison with pre-test X-rays for location correlation, where possible
- Sectioning and metallographic examination of capsule sections to optically evaluate the nature and extent of containment corrosion in these three areas:
  - Midsalt
  - Meniscus (salt/gas interface)
  - Weld areas
- Mid-salt core sampling and chemical analysis for carbonate content, cation composition (Li, K, Na, Ba, etc.), and relative levels of iron, nickel and chromium (elements indicative of corrosive reaction between salt and containment material)
- Scanning electron microscopy and EDAX analyses to establish Fe, Cr, Ni, etc. profiles in the reaction zone and the bulk metal for selected materials samples.

Preliminary post-test evaluations after 1000 hours of testing indicate the following:

- Stability of both, reagent and technical-grade of carbonates is confirmed;
  - Little or no (1 to 5 wt %) loss of carbonate
  - Little or no loss of cation (Na, Li, K, Ba, etc.) from pre- and post-test Atomic Absorption
  - The stability and corrosion behavior of reagent grades and technical-grade salts were similar.
- The functionality of AISI Type 304, 316, and 310, Inconel 600 and Incoloy 800 has been established as containment materials for carbonates in the 750° to 840°C (1380° to 1540°F) temperature range, while higher alloy content and Al_2O_3 forming materials may be required for containment in the 840° to 950°C (1540° to 1740°F) temperature range.

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Table 1. CANDIDATE ALKALI/ALKALINE EARTH CARBONATE PCM MATERIALS

No.	Salt System	Composition		Literature Melting Point		ΔH_f, Btu/lb	Thermal Conductivity k (ℓ) Btu/hr-°F-ft	Heat Capacity at Melting Point		Density at 25°C, lb/ft³	Discharge Solidification Range		$\bar{Q}$ Btu/hr-ft² mp + 90°F → mp - 90°F	No. of Cycles	Hours at Operational Temperature
		Wt %	Mol %	°C	°F			C_p (s)	C_p (ℓ)		°F →	°F			
								Btu/lb-°F							
1	$BaCO_3$-Na_2CO_3	52.2-41.8	37-63	686	1267	74	--	--	--	--	1323	1314	13,220	36	984
2	K_2CO_3-Na_2CO_3	50-50	44-56	710	1310	70	1.00	0.40	0.37	149.8	1306	1292	11,720	13	336
3	Li_2CO_3	100	100	726	1333	261	1.13	0.627	0.599	131.6	1353	1346	24,290	22	672
4	Na_2CO_3-K_2CO_3	81.3-18.7	85-15	790-737	1454-1360	109				156.9	1454	1360	14,630	38	1032
5	Na_2CO_3	100	100	858	1576	114	1.06	0.239	0.238	157.8	1594	1584	14,480	21	288
6	K_2CO_3	100	100	891	1636	86	1.00	0.363	0.358	151.6	1681	1674	23,000	2	96

Table 2. POTENTIAL THERMAL CONDUCTIVITY ENHANCEMENT MATERIALS

Material	Melting Point, °F (°C)	Thermal Conductivity at 932°F (500°C), Btu/hr-ft-°F	Heat Capacity Btu/lb-°F Room Temp	Materials Cost	
				\$/lb	\$/ft³*
Aluminum	1220 (660)	127	0.220	0.79	134
Copper	1981 (1083)	178	0.092	0.75	417
Iron	2797 (1536)	22	0.110	1.37	673
Molybdenum	4730 (2610)	67	0.061	4.40	2,807
Nickel	2647 (1453)	33	0.120	2.16	1,202
316 Stainless Steel	2478 (1370)	12	0.120	1.27	638
ATJ Graphite	sublimes	45	0.200	4.47	626
Pyrolytic Graphite	sublimes	120	0.200	924.00	130,000
Silicon Carbide	4892 (2700)	50	--	--	--
CS Graphite	sublimes	44	0.200	0.50	68

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* Costs based on 100% of theoretical density.

Table 3. 1000 HOUR COMPATIBILITY TESTING STATUS/POST-TEST EXAMINATION PLAN

No.	Salt System Composition (Wt %)	Grade	Containment Materials (Hours of Operation) 1 S.S. 304^a	2 S.S. 316^a	3 S.S. 310^a	4 Inconel^a 600	5 Incoloy^a 800	6 Armco 18SR/12SR^a (Kanthal Al inside)	7 Alloy HK-40^a sample inside S.S. 310 capsule	TCE Materials (Hours of Operation) 1 Graphite^b P.G. and ATJ	2 Copper^b Solid tube and Reticulated Matix
	OVEN I 750°C	Date Installed	2/8/80	2/8/80	2/27/80	2/8/80	2/8/80	3/27/80	3/14/80	3/14/80	3/14/80
1	52.2 $BaCO_3$-41.8 Na_2CO_3	Reagent	□ 1882	□ 1882	□ 1603	□ 1882	□ 1882				
2	52.2 $BaCO_3$-41.8 Na_2CO_3	Technical	□ 1882	1882	□ 1603	1882	1882	1056		1243	1243
3	50.0 Na_2CO_3-50.0 K_2CO_3	Reagent	□ 1882	□ 1882	□ 1603	□ 1882	□ 1882				
4	50.0 Na_2CO_3-50.0 K_2CO_3	Technical	□ 1882	□ 1882	1603	□ 1603	1603	1056		1243	1243
	OVEN II 840°C										
5	Li_2CO_3	Reagent	□ 1931	□○ 672	□ 1603	□○ 288	□ 1931				
6	Li_2CO_3	Technical	□ 1931	1931	□ 1603	1931	1931	1056	1243	1243	1243
7	81.3 Na_2CO_3-18.7 K_2CO_3	Reagent	□ 1931	□ 1931	□ 1603	□ 1931	□ 1931				
8	81.3 Na_2CO_3-18.7 K_2CO_3	Technical	□ 1931	1931	1603	□ 1931	1931	1056			
	OVEN III 950°C										
9	Na_2CO_3	Reagent	○ 288	○ 288	○ 763	○ 288	□ 816				
10	Na_2CO_3	Technical	○ 552	○ 288	○ 763	○ 288	□ 816	1034	1154	1154	1154
11	K_2CO_3	Reagent	○ 288	○ 288	□ 1490	□ 1803	□ 816				
12	K_2CO_3	Technical	○ 552	816	1490	□ 816	□ 816			1154	1154

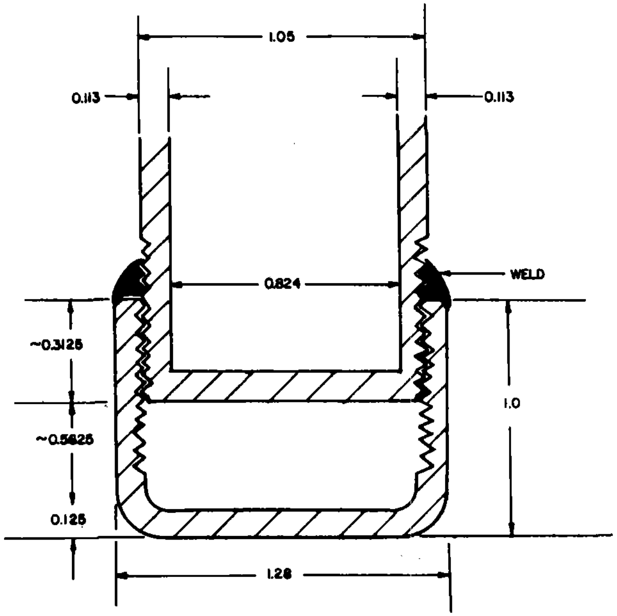
KEY:

○ = Failed Capsule

□ = Capsule to be sectioned and metallographically examined.

a = Welded in air

b = Welded in Argon



NOTE: ALL DIMENSIONS IN INCHES

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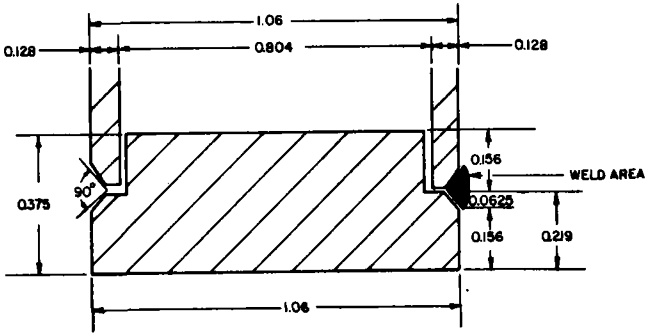
Figure 1. THREADED STANDARD NIPPLE AND END-CAP CAPSULE DESIGN WELD AREA CROSS-SECTION (Used with S.S. 304 and S.S. 316)



NOTE: ALL DIMENSIONS IN INCHES

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Figure 2. MACHINED CAPSULE AND END-CAP DESIGN WELD AREA CROSS-SECTION (Used with S.S. 310, Inconel 600 and Incoloy 800)

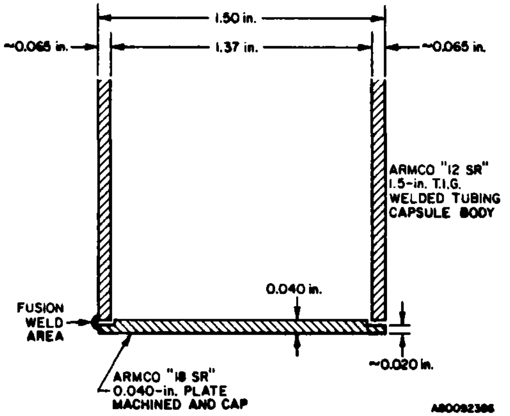

Figure 3. MACHINE ARMCO 12 SR CAPSULE BODY/ ARMCO 18SR END-CAP DESIGN WELD AREA (TIG Fusion Weld) CROSS-SECTION

ACTIVE HEAT EXCHANGE - SYSTEM DEVELOPMENT FOR LATENT HEAT THERMAL ENERGY STORAGE

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Abstract

The objective of this program is to develop an active heat exchange method in a latent heat (salt) thermal energy storage system that prevents a low conductivity solid salt layer from forming on heat transfer surfaces. An evaluation of suitable media with melting points in the temperature range of interest (250 to 400°C) limited the candidates to molten salts from the chloride, hydroxide and nitrate families, based on high storage capacity, good corrosion characteristics and availability in large quantities at reasonable cost. The specific salt recommended for laboratory tests was a choride eutectic (20.5KCL • 24.5NaCL • 55.0$MgCl_2$% by wt.), with a nominal melting point of 385°C.

Various active heat exchange concepts were identified from among three generic categories: scrapers, agitators/vibrators and slurries. The preferred ones were given a more detailed technical evaluation and the economics compared to a passive tube-shell design for a reference application (300 MW_t storage for 6 hours). Test hardware was built for the two most promising concepts: 1) a direct contact heat exchanger in which molten salt droplets are injected into a cooler counterflowing stream of liquid metal carrier fluid (Lead/Bismuth) and 2) a rotating drum scraper in which molten salt is sprayed onto the circumference of a rotating drum, which contains the fluid heat sink in an internal annulus near the surface. A fixed scraper blade removes the solidified salt from the surface which has been nickel plated to decrease adhesion forces.

The test evaluation has been interrupted due to funding limitations resulting from various problems with pumps, plumbing leaks and corrosion failure of electrical heaters. Earlier decisions to select some non-optimum components, which were based on budget limits, proved ill-advised. Plans have been submitted for completing the program after hardware refurbishment.

Introduction

Thermal energy storage is a promising method for extending the steam generating capabilities of both conventional fossil fuel power plants and advanced solar thermal energy conversion systems. Excess thermal energy available from the steam boiler (or concentrating solar collector) can be stored during off-peak demand periods and then used to increase steam capacity during peak load periods. In a solar application, this stored energy would be substituted for the primary source during non-sunlight periods.

Thermal energy can be stored as the heat required to induce a temperature change, a phase transformation (e.g., solid to liquid), or a chemical change in a suitable medium. Using the latent heat of fusion (phase change) is attractive because the heat absorbed per pound of storage material is relatively high, resulting in a more compact system. Molten salts and salt eutectics are particularly attractive as phase change media because of their high weight and volumetric heat storage capabilities, their abundance in nature and as the result of industrial processes, and their low cost per unit storage capability.

A preceding study for NASA-Lewis showed that a latent thermal energy storage system which utilized a conventional passive tube and shell heat exchanger for salt containment was both technically and economically feasible. The study revealed that suitable latent heat media were inexpensive and that a major portion of the cost was related to the passive heat exchange process. The accumulation of salt deposits on discharge tube surfaces, combined with a high thermal resistance of the solid Phase Change Material (PCM) required a large (and costly) heat exchanger surface area. Significant performance and cost benefits can be realized if active heat exchange concepts can be developed which prevent the buildup of a solid salt layer on the heat transfer surfaces.

The overall objective of this program is the development of an active heat exchange process in a latent heat thermal energy storage (TES) system which is suitable for utility applications. These include either conventionally fueled plants or advanced solar central receiver power plants. An effective TES system would be used to supply peak energy requirements with energy stored during the off-peak periods. For conventional power plants this offsets the need to increase the plant boiler capacity, whereas advanced solar power plants require thermal energy storage for buffering during normal operation and as the primary energy source during non-sunlight hours.

Discussion

TES Media Selection - At utility operating temperatures suitable phase change materials are confined to molten salts and salt eutectics. The evaluation of the candidate materials considered the following criteria: melting point, latent heat of fusion, heat storage capacity (kWH_t/unit volume), corrosion characteristics, handling problems, availability and cost. Of the candidate salts considered, three families were found best suited for this TES application: chlorides, hydroxides and nitrates. The specific salts recommended, in order of preference, were as follows:

1. 20.5KCL • 24.5NaCl • 55.0$MgCl_2$, % by weight - A chloride salt eutectic that melts at 385°C (725°F).
2. KOH - Potassium hydroxide, melting point at 360°C (680°F)
3. $NaNO_3$ - Sodium nitrate, melting point at 307° (585°F)

All three salts have good thermal performance, few corrosion problems - which permits the use of less expensive containment materials (e.g., mild steel), and they are available in large quantities at a reasonable cost. The chloride salt eutectic was selected for the demonstration test evaluation since it best fits the steam generating requirement (350°C) of advanced solar power plants.

Heat Exchange Concepts - Two active heat exchange concepts were selected for demonstration hardware development:

- Direct contact heat exchanger
- Rotating drum with fixed scraper

These were chosen from among the various concepts considered (scrapers, agitators, vibrators, slurries) because they exhibited the best combination of low development risk and high cost benefit. Unit cost estimates for the chosen TES concepts as applied to a 300 MW utility application with 6 hr of storage are presented below.

	Unit Cost ($/kWh$_t$)
Passive tube-shell	21
Direct contact HX	16
Rotating drum	16

The development test modules were designed to interface with an intermediate heat transport loop which uses a liquid metal eutectic (44.5Pb/55.5Bi% by wt.) as the fluid. Three separate tank modules are provided: 1) a liquid metal tank which serves as a supply reservoir and contains the pump, 2) a molten salt tank which contains the PCM supply and a pump, and 3) a central heat exchange module within which the heat transfer between the molten salt and liquid metal occurs. All materials were primarily 1020 mild steel, except the plumbing which was stainless steel. A nitrogen gas blanket was used to prevent atmospheric contamination.

Direct Contact Heat Exchanger - The direct contact heat exchange concept is illustrated in Figure 1. Three tank modules are coupled by two separate fluid loops; one for the molten salt, the other for the liquid metal carrier. The salt serves as the thermal energy storage medium, while the liquid metal transfers the stored energy to the eventual heat sink, in this case an air stream. Separate streams of salt and liquid metal, which emanate from their respective tanks, are mixed together in the heat exchange reservoir. Both latent and sensible heat are transferred to the cooler liquid metal by the countercurrent flow of molten salt bubbles which are injected at the bottom of the metal column. As the salt solidifies, it rises to the top of the heat exchange reservoir, where it is directed over the edges, falling to the bottom of the surrounding tank. It is held here until the next charging cycle, when it is melted (by electrical heaters which simulate the heat source) and drained into the molten salt tank. Another discharge cycle can then begin.

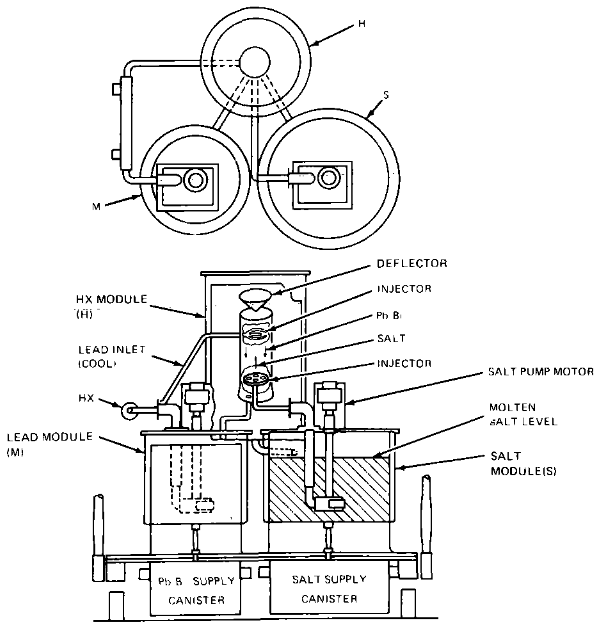

Figure 1 Direct Contact HX Concept

Rotating Drum - The rotating drum concept in Figure 2 is designed to take advantage of all of the hardware (tanks, plumbing, pumps, instrumentation, etc.) used for the direct contact heat exchange concept. Only one-half of the central heat exchange module need be replaced to convert from one system to the other. In this concept, the heat exchange between the molten salt and the liquid metal takes place on the circumference of a rotating hollow steel drum. Molten salt sprays onto the outside surface, while the cooler metal flows through a narrow internal annulus. As heat is removed, the salt solidifies and adheres to the outside surface. Located 270 degrees from the

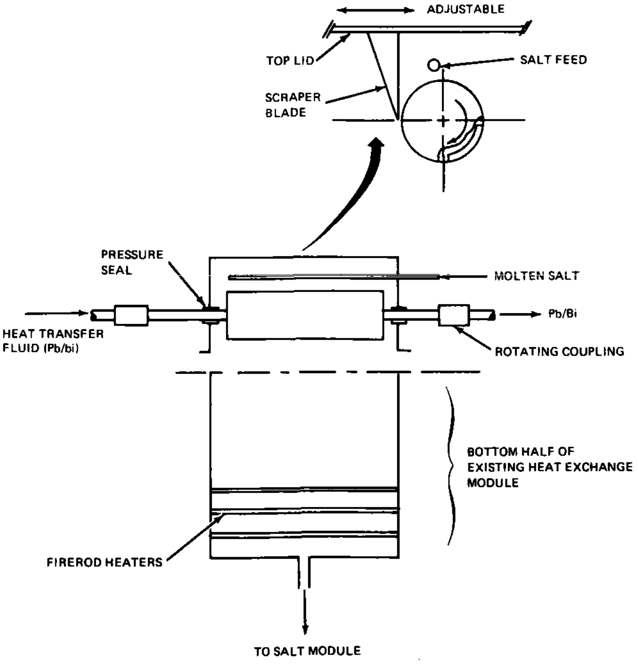

Figure 2 Rotating Drum Heat Exchanger Concept

salt admission point in the direction of rotation, a fixed scraper blade removes the solid salt layer. The electroless nickel plating on the drum minimizes the surface adhesion strength and permits easier scraping.

Test Experience - To date only testing of the direct contact heat exchange concept has been attempted. However, a series of difficulties with the pumps, plumbing and electrical heaters has consumed the budget before testing of the complete system could be accomplished. At this point, the hardware, especially the heaters, needs refurbishment before testing can be resumed. Although definitive test results cannot be reported at this time, our experience might benefit other investigators. A summary of the most significant observations follows.

- In general we found that the size of the test module resulted in slow and difficult repairs since it took days to heat up and cool down.
- Relatively inexpensive air-motor-driven submersible-type pumps were used for which seals had to be provided. Improper seal design resulted in bending of the pump shafts due to differential thermal expansion and necessitated rework to create a much looser than desired fit. Thus, we could not continuously pressurize the system with a nitrogen gas cover blanket, but instead used periodic gas purges. Using a more expensive presealed pump/motor assembly would have been cheaper in the long run.
- Early problems were encountered with swageloc fittings, some of which leaked at operating temperature. The problem was solved by tightening all connections while heating them with an acetylene torch.
- By far the most troublesome of the problems resulted from our decision to use less expensive manual heater controls. Human error during the initial system checkout resulted in over powered band heaters and numerous heater and instrumentation failures. In hindsight, every common heater circuit should have automatic controllers backed up by a direct reading of the sheath temperatures.
- Our experience with the immersion heaters was terrible. Over an effective period of about four weeks operating time, the following failures were experienced: Lead system (4 of 5 failed); Salt system (8 of 8); heat exchanger module (5 of 6). The exact cause of failure has not yet been determined, although it is most likely some combination of corrosion and hydraulic action from the many freeze/melt cycles. A careful post-test inspection is planned prior to refurbishment. These problems indicate that special consideration must be given to methods of heating and cooling that involve immersed tubes.
- After a period of about two weeks the threaded fittings for the immersion heaters on the salt module began to leak salt vapor. (These connections used tapered threads and a high temperature sealant). The escaping vapor, when combined with atmospheric moisture, prove particularly troublesome. All of the terminals on the band heaters in the vicinity of the leaks quickly corroded and caused heater failures, which necessitated several changes to band heaters during the testing. There also was evidence that leaks were coming through the main terminals of the immersion heaters which means that the sheath over the heating element had been broken inside the tank.
- The external salt tank surface in the vicinity of the immersion heaters was badly corroded due to the aforementioned salt leaks. Since the extent of any internal corrosion was unknown, ultrasonic tests to determine the net wall thickness were taken. The results indicated a decrease of 10 mils from the original 1/4 inch thickness, which confirmed that only the external surface was being corroded.
- Over-loading of line heaters occurred due to poor axial heat conduction between heater elements, which were too widely separated. To avoid this problem trace heating should be applied to as much line as possible.
- The use of a thermocouple tree to thermally sense the level of liquid metal and molten salt proved very reliable. These were used as backup to commercial level sensors which were the primary means of level indication in the heat exchange reservoir.
- During the checkout testing it became necessary to change the utility cooling fluid from water to air. This was done to avoid freezing of liquid metal due to nucleate boiling in the water line resulting from excessively high temperature differences.

1980 REPORT ON NRL ENERGY STORAGE PROGRAM

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Abstract

The objective of the project is to develop a means for bulk storage of energy in a form capable of providing demand sensitive steam, heat, or cooling. This paper discusses salt eutectic systems, availability and costs of salts, the progress on the 2 MWht energy storage boiler tank now under construction at NRL, and major elements of storage system costs for this 2 MWht tank which employs a heat transfer fluid. A radiation coupled energy storage tank concept is also discussed.

I. Introduction

The Naval Research Laboratory is in the process of building a 2 MWht energy storage boiler tank. The tank will contain 30 tons of a $MgCl_2$, NaCl, KCl salt eutectic. It will serve as a proof-of-concept demonstration of energy storage in containerized salts. Energy storage is provided as latent heat-of-fusion in the eutectic salt. The tank is energized by 150 kW electrical heaters. It's output is in the form of superheated steam, with usable output rates expected to be as high as 500 kWt. Internal heat transfer is based on evaporation/condensation of m-terphenyl heat transfer fluid.

Initial studies of heat-of-fusion storage began over six years ago at NRL. Containerized salts were considered shortly thereafter. Laboratory studies of corrosion of the salt cans and degradation of the heat transfer fluid were carried out in 1977. Ground breaking for the 2 MWht tank site was in January 1979. Subsequently the site has been prepared to receive the 2 MW energy storage tank and substantial progress has been made on the tank. In addition a major report summarizing the technology of storing energy in containerized salts was prepared. A major purpose of this paper is to summarize the key points of our report, i.e. NRL Memorandum Report 4267, "Energy Storage as Heat-of-Fusion in Containerized Salts", June 27, 1980. A second purpose is to summarize progress during the year on the Energy Storage-Boiler Tank under construction at NRL.

II. Energy Storage In Containerized Salts, Key Elements From Report 4267

Report 4267 addresses the salt fusion storage option for massive energy storage of industrial scale solar power. It examines the adequacy of the salt resource, and provides cost estimates associated with its use. It discusses the technology problems associated with salt storage and presents two solutions to the problem of providing efficient internal heat transfer within the storage devices. The report then focuses on the specific task of thermal storage at 385°C and on the laboratory tests and design efforts that support the construction of the 2 MWht tank. An update on the status of the 2 MWht tank ends the report.

1. Salts and Eutectic Systems

Important considerations relevant to bulk energy storage in containerized salts are the availability, raw material costs, processing costs, and location of deposits of salts. Report 4267 discusses various salt eutectic systems and the problems associated with their use. A list of selected eutectics chosen for bulk availability and cost is the following:

Table 1 **Selected Eutectics**

Composition	Melting Point
NaOH, Na_2CO_3	287°C
$MgCl_2$, NaCl, KCl	385
$MgCl_2$, NaCl	450
$CaCl_2$, NaCl	500
Na_2CO_3, NaCl	638

If any of the above eutectics are to provide important energy storage, they will be required in very large tonnages. The going size of commercial power plants is of the order of 1000 MWe. To provide 24 hours of energy storage to operate such a power plant, assuming 33% thermal conversion efficiency, requires a storage capacity of 72,000 MWht, or 2.6×10^{14}J. The storage capacity of the salt eutectic selected for initial work ($MgCl_2$, NaCl, KCl) is 240 kJ kg^{-1}. Thus to meet the stated storage requirement, requires the use of 1.1×10^6T (metric tons) of salt. One million tons per year is the output of a moderately large coal mine. The point is: material tonnages are large. Use of naturally available substances which require minimum processing is necessary if storage costs are to be acceptable.

Because of the very large tonnages needed raw material availability is a prime consideration. It is expected that, assuming suitable maintenance, thermal energy storage facilities with almost infinite operating life will eventually be developed. Hence, a large size energy storage facility can be thought of as a regional asset, comparable to a dam or pumped hydroelectric facility. Hence, once economic considerations are satisfied, one could reasonably expect steady addition of incremental capacity. A storage addition rate of 72,000 MWht per year could be a reasonable regional rate of development. To meet this need, salt must be made available in large bulk. Known world deposits and production rates of the most abundant salts are listed below:

Table 2 Salt Reserves

Salt	Known World Deposits	1970 or 1971 U.S. Production
KCl	10^{11}T	2.7 x 10^6T yr^{-1}
NaCl	"Virtually Unlimited"	45 x 10^6T yr^{-1}
Na_2CO_2Equiv.	4 x 10^{10}T	2.5 x 10^6T yr^{-1}
$CaCl_2$*	10^9T in Tachyhydrite	
$MgCl_2$**	10^9T in Tachyhydrite	
Na_2SO_4	3 x 10^9T	0.7 x 10^6T yr^{-1}

*"Wells could almost certainly supply domestic needs for at least 100 years."
**"For practical purposes...magnesium compounds in brines and sea water are unlimited, and bedrock resources are large."

Table 3 Breakdown of Salt Costs ($MgCl_2$, NaCl, KCl Eutectic)

Material	Raw Salt Costs 1979 Value (\$ ton^{-1})	Contribution to Eutectic Costs (\$ ton^{-1}eutectic)
NaCl(1)	\$ 9.45	2.3
$MgCl_2$(2)	22.50 (in 35% solution)	12.4
KCl(3)	67.1	13.8
Drying of solution		19.4
Dehydration cost		27.0
Heating, melting cost		8.1
Total cost of salt		83.0

(1) Pacific Salt Co., City of Industry, CA
(2) Great Salt Lake Mineral Co., Salt Lake City, UT
(3) Kerr McGee Chemical, Los Angeles, CA

The $MgCl_2$, NaCl, KCl is ~55.0% $MgCl_2$, 24.5% NaCl, 20.5% KCl by weight.

The cost of the energy storage medium is based both on raw material and processing costs. Transportation is also a major item. Salt supply and processing costs for the particular salts used in the NRL 2 MWht tank are listed in Table 3.

2. Estimated Cost of Energy Storage Boiler Tank

Table 4 addresses the major elements of storage system costs for systems based on $MgCl_2$, NaCl, KCl eutectic combined with m-terphenyl heat transfer fluid.

3. Internal Heat Transfer

Energy storage tanks can be characterized by the methods employed for internal heat transfer. Two methods of accomplishing the transfer of heat into and out of the salt containers have been identified, namely (1) evaporation-condensation of a heat transfer fluid, i.e., the technique used in the home "pressure cooker", and (2) radiation coupling between an extended network of heat pipes and the salt cans, with the heat pipes in turn conductively coupled to the input heat source and the output heat load. The preferred solution depends on energy storage temperature. These two solutions to the internal heat transfer problem in turn lead to two types of energy storage tanks, i.e., the "energy storage boiler tank" and the "radiation coupled energy storage tank". The energy storage boiler tank has been discussed in past papers. The radiation coupled energy storage tank had not previously been described in detail. It will be discussed in the next section. The internal heat transfer methods used in these tanks is described in Table 5.

Table 4
Cost Estimate for Energy Storage Based on $MgCl_2$, NaCl, KCl Eutectic Costs per kWht (\$ 1979)(1)

Item	Proof-of-Concept Tank	At Build-up Rate 1200 MWht per year
Anhydrous Eutectic	16.48	1.37(2)
Containers	9.41	2.20(3)
Heat Transfer Fluid	23.04	3.70(4)
Salt Transportation	1.65	0.49(5)
Containment Vessel	27.50	1.20(6)
Foundation	0.58	0.76(7)
Load Bearing Insulation	0.23	0.04(8)
Loose Insulation	1.23	0.15(9)
Piping-Including Boiler, Superheater	5.49	0.24(10)
Pump for Heat Transfer Fluid	2.03	0.05(11)
Feedwater Pump	0.46	0.02(12)
TOTAL of Big Items	88.10	10.22
Allowance for Misc. and Construction, (30% of above)	26.43	3.07
TOTAL	114.53 \$ kWht^{-}(13)	13.29 \$ kWht^{-1}

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(1)All costs based on eutectic heat-of fusion measurement 240 kJ kg^{-1} (Appendix C).

(2)Based on quotes for raw salts with processing costs estimated as per Appendix B. Rossborough estimate is 6.1 \$ kWht^{-1}.

(3)Based on 1975 can prices of the Freund Can Co., inflated 10% per year. See Appendix G.

(4)Based on m-terphenyl fractionated within tank from a starting fluid of therminal 88, Appendix F. Initial cost only.

(5)1500 miles. Cost inflated 10% per year from 1976 quote.

(6)Based on use of 66' tanks providing 444 MWht storage and weighing 241 tons. Cost of steel and fabrication estimated at 1200 \$ ton^{-1}.

(7)7324 tons of salt + 241 tons steel => 4422 lbs. ft^{-2} based on slab 2 feet thick of sufficient area to reduce ground loading to 1000 lb. ft^{-2}. Cost of doubly reinforced concrete taken at \$300 per cu. yd.

(8)Based on 24" of Foamglas, Pittsburgh Corning, Pittsburgh, PA.

(9)Based on 40" of Dacotherm sodium silicate insulation, Diamond-Shamrock, Cleveland, OH.

(10)Ratio of piping cost to tank cost assumed same as for proof-of-concept tank.

(11)Three pumps (500 gpm each @ 100' head) with 20 hp motors, Lawrence Pump and Engine Co., Lawrence, MA.

(12)Two triplex pumps plus relief valve including motors, F.E. Meyers, Ashland, OH.

(13)Actual cost several times this value due to expensive site preparations, development costs and costs associated with electrical heater input system.

Table 5
Heat Transfer: Energy Storage Boiler Tank and Radiation Coupled Energy Storage Tank

Item	Energy Storage Boiler Tank	Radiation Coupled Energy Storage Tank
Input heat exchanger	Boiling of heat transfer liquid, or conduction to forced-circulation heat transfer liquid followed by flash evaporation.	Conduction to lower ends of potassium heat pipe, possibly through liquid metal intermediary.
Store input heat transfer loop	Transport of vapor of heat transport fluid driven by weak pressure gradients in pressurized tank. Loop closed by liquid return under gravity.	Transport of potassium vapor driven by pressure gradients within heat pipe tubes, followed by condensation of potassium vapor on heat pipe walls, followed by liquid return driven by surface tension gradients on tube walls ± gravity.
Storage heat exchanger	(input) Condensation of vapor or heat transfer fluid on salt can surfaces. (output) Evaporation of liquid heat transfer fluid from salt can surfaces. Liquid resupplied by pumped circulation loop.	(input) Radiation from heat pipe tubes to salt can surfaces. (output) Radiation from salt can walls to heat pipe tubes.
Store output heat transport loop	Transport of vapor of heat transfer fluid driven by weak pressure gradients in pressurized tank. Loop closed by liquid return under gravity.	Transport of potassium vapor driven by pressure gradients within heat pipe tubes, followed by condensation, followed by liquid return driven by surface tension gradients on tube walls ± gravity.
Boiler-superheater heat exchanger	(input) Condensation of vapor of heat transfer fluid on boiler and superheater tubes. (steam output) Conduction to boiling water or flowing steam.	(input) Conduction from heat pipe tubes to boiler and/or superheater tubes, possibly through liquid metal intermediary. (steam output) Conduction to boiling water or flowing steam.

4. Description of Radiation Coupled Energy Storage Tank

For energy storage at higher temperature, use of radiation for heat transfer between salt cans and a network of heat pipes is a practical means of carrying heat to and from the salt cans. This approach requires a large area of heat pipe surface. The aggregate heat pipe surface, however, can be a factor of 10 or less than the surface area of the salt cans. The concept is shown in Figure 1. The importance of the concept is that it allows salt containers to be stacked in large, unpressurized buildings, permitting buildup of a very large storage capability. It promises to be especially effective for energy storage at temperatures above 450°C and storage periods of greater than 1 day.

III. Progress on Energy Storage Boiler Tank

The site preparation for the 2 MWht energy storage boiler tank was completed in January 1980. Detailed design of such items as the pressure containment vessel, boiler, terphenyl circulation system, water circulation system, baskets to hold salt cans, etc., have been completed. A description of the boiler and the other subsystems is given in Report 4267. Major components such as the terphenyl pump, feedwater pump, insulation, heaters, and control parts have been received. The pressure containment vessel has been 80% fabricated. A prototype of the baskets to hold the salt cans has been fabricated.

Heat transfer tests are planned to begin in March 1981. It is planned to install the salts in August 1981 with energy storage tests to begin shortly thereafter.

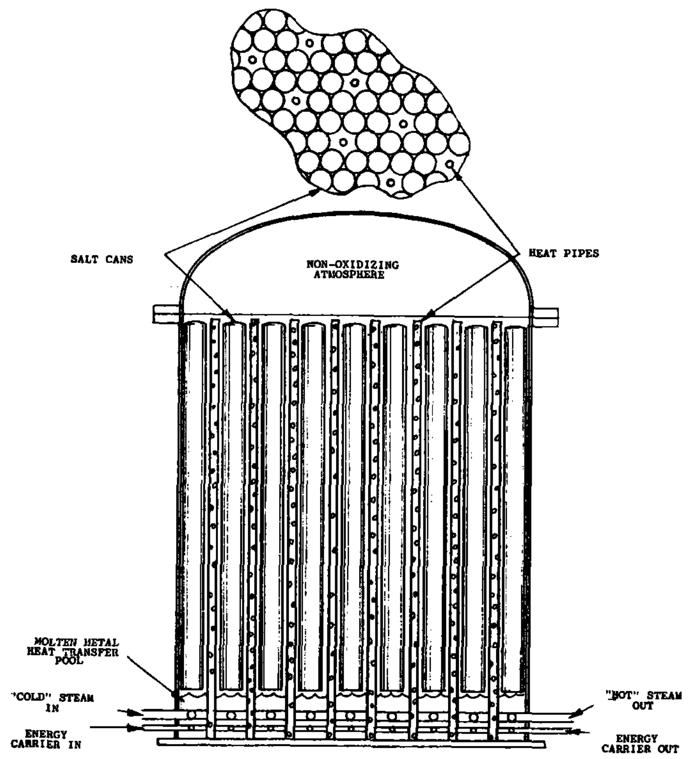

Fig. 1 - Radiation coupled energy storage tank. Energy is stored as latent heat-of-fusion in containerized molten salts. The salt containers are closed-off pipes filled with salt, and largely fill the containment vessel. They are permitted to breathe to accomodate salt volume changes during cycling. Heat is delivered, and removed from, the salt containers by radiation coupling to a network of alkali metal vapor heat pipes. Heat transfer between energy input pipes and the alkali metal heat pipes is by conduction through molten metal coupled interfaces. Heat transfer between alkali metal heat pipes and the energy output boiler/superheater is also by conduction through molten metal coupled interfaces. The radiation coupled energy storage superheater tank operates at ambient pressure and can be engineered to provide enormous storage capacity in factory size building structures.

HEAT STORAGE IN ALLOY TRANSFORMATIONS

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Abstract

Heat storage has been approached from four directions.

1. Calorimetric measurements of heats of eutectic transformation and heat capacities of solid and liquid mixtures determined the maximum heat storage capability. New eutectics have been found and measured. This work is being written for publication.
2. Volume changes during transformation and thermal expansion below and above the transformation temperature have been measured by an X-ray absorption measurement. A radioactive X-ray emitter and improvements of the furnace simplify the procedure. The measurements are nearly completed.
3. The use of graphite and carbides, successful bulk containers, as coatings to protect steels against attack by the heat storage alloys must be developed in future research.
4. Heat flow models for simple heat exchanger geometries show the advantage of alloys over salts for fast storage.

1. Thermal Properties of Alloy Eutectics
(Diana Farkas)

Binary, ternary and quaternary eutectic alloys of the relatively inexpensive elements Al, Mg, Si, P, Cu, Zn have been identified that have heat storage densities on a mass or volume basis that compare favorably with other phase change materials (PCMs) between about 450 and 950°C. Good alloys are available for almost any narrow interval in that temperature range; for some intervals the eutectic alloys are the best PCMs available. Table 1 summarizes our measurements. The most promising alloys are underlined for each temperature interval.

The alloys have thermal conductivities that are one to two orders of magnitude more favorable than those of the competing salts. Heat flow model calculations suggest potentially large benefits from this property if containment materials also possess good thermal conductivities.

2. Volume Change During Transformation

Measurements in progress show that the volume change during eutectic melting for some of the alloys is about 5 pct. or less, compared with changes exceeding 25 pct. for some of the salts. Table 2 summarizes our recent results on Al, Al-12 at. pct. Si and Al-17 at. pct. Cu.

3. Containment
(Nikhil Nagaswami)

The laboratory work on calorimetry and volume change was conducted successfully in graphite vessels. None of the alloys reacted in a detectable way except those containing Ca. Only the Ca-containing alloy Si-0.35 Mg-0.15 Ca was among the better performers. Graphite appears to be chemically stable for the other alloys. It has a moderately good directionally-averaged thermal conductivity. It retains its strength to high temperatures. The nuclear industry has extensive experience with graphite structures. However, graphite is susceptible to oxidation, its conductivity properties and mechanical properties are highly anisotropic, and the structures cannot be fabricated by convention methods and in conventional geometries for heat exchangers.

Silicon carbide is being tried as a structural material in many advanced energy systems. Studies in progress seem to be demonstrating compatibility with the eutectic alloys in Table 1. The material also resists high temperature oxidation. Its strength at low and high temperatures is greater than that of graphite, in fact, it is very strong. Brittleness is a potential hazard that may be overcome by designs that keep the carbide members in compression. The remaining difficulty is the difficulty of joining.

Conventional high temperature alloys, such as stainless steels, that have good oxidation resistance and that can be fabricated by welding and brazing react with components in the alloy PCMs to form intermetallic phases. Some of these phases have high growth rates. Many are brittle. Often their specific volumes are appreciably greater than the volumes of the reactants. Work is just beginning to study some of these reaction rates to prepare a basis for the development of coatings that protect the containment alloys from attack by the PCM alloys. Protection requires the formation of a more stable phase, essentially insoluble in the reactants, that has a very slow growth rate under operating conditions.

4. Modeling Heat Transfer from a Phase-Change Storage Material

(Dr. S. İ. Güçeri, Michael Labdon)

A more refined and versatile numerical model was to be developed for use in analyzing the phase-change problem in more than one dimension. Presently, the numerical method is completed using a novel approach for determining the two-dimensional melt-line location and temperature distributions within a cylinder of phase-change material.

This method is applicable to problems involving insulated and constant-temperature boundary conditions, as well as those subject to time-varying convection and heat flux boundary conditions. Temperature-dependent properties, time-varying fluid temperatures, and arbitrary initial temperature distributions can also be handled.

The two dimensional phase change problem in cylindrical coordinates is given by:

Field equations:

$$\nabla^2 T_s = \frac{1}{\alpha_s} \frac{dT_s}{dt} \; ; \; R_o < \gamma < S$$

$$\nabla^2 T_\ell = \frac{1}{\alpha_\ell} \frac{dT_\ell}{dt} \; ; \; S < \gamma < R_\infty$$

Interface conditions:

$$\left[1 + \left(\frac{\partial s}{\partial z} \right)^2 \right] \left[k_s \frac{dT_s}{d\gamma} \bigg|_s - k_\ell \frac{dT_\ell}{d\gamma} \bigg|_s \right] = \rho L \frac{dS}{dt} \; ; \; \gamma = S$$

$$T_s = T_\ell = T_m \qquad ; \; \gamma = S$$

where R_o is the fluid pipe radius, R_∞ is the outer radius of the solution domain and $s(r,z)$ is the two dimensional melt front location. The subscripts s and ℓ refer to the solid and liquid regions.

The novelty of the approach arises from two aspects. First, an explicit-type, finite-difference routine monitors the heat conduction for the regions two nodes away from the interface, while Taylor-Series expansions of the temperature are made within the two-node regions. This permits direct calculation of the temperature gradients on either side of the melt front and hence its speed of propagation. Second, the two-dimensionality of the meltline propagation is mathematically decomposed to unidimensional movement along a primary coordinate axis, which facilitates the analysis.

An example of the output from this routine is presented in the accompanying figures. The melt-front locations along the axis of an internally convected pipe is shown for the solidification of a phase-change material initially at the fusion temperature. Figure 1 shows the behavior for the representative metal alloy Al-Si, whereas Figure 2 depicts that of the representative salt $7CaF_2/54KF/39NaF$.

This powerful routine is presently undergoing one additional modification by incorporating a two-dimensional Taylor-Series expansion about the interface in lieu of the one-dimensional type used.

This relatively minor change (programming wise), will yield a smoother behavior of the temperature distribution near the interface and reduce both the analytical and computational complexity presently encountered.

Essentially, this new method is viable, and will be used to contrast the thermal performance of the previously designed solar receivers. Design optimization and cost summaries will also result.

Table 1. Thermal Properties of Selected Metal Eutectics

Alloy (Mole Fractions)	Eutectic Temperature (°K)	Maximum Heat Storage Capacity in kJ/kg		Heat Capacity kJ/kg-°K
		Calculated	Measured*	
Mg-0.24Zn-0.05Si	608	260		
Mg-0.29Zn	616	230	210	1.04s 1.511
Mg-0.14Zn-0.14Ca	673	405		- -
Al-0.35Mg-0.06Zn	720	406	310	1.73s 1.621
Al-0.375Mg	724	376	310	
Mg-0.13Cu-0.08Zn	725	408	253	- -
Al-0.17Cu-0.16Mg	779	406	360	1.09s 1.181
Mg-0.105Ca	790	431	269	- -
Al-0.175Cu	821	359	353	1.11s 1.111
Al-0.126Si-0.051Mg	833	549	545	1.39s 1.211
Mg_2Cu	841	398	243	- -
Al-0.31Cu-0.07Si	844	561	423	- -
Al-0.12Si	852	571	515	1.49s 1.271
$MgZn_2$	861	259	220	- -
Zn-0.4Cu-0.15Mg	978	313		
Cu-0.157P	987			
*Cu-0.25P-0.14Zn	993		368	
Cu-0.42Mg	995	235		
*Si-0.35Cu-0.28Mg	1023	892	422	
*Cu-0.17Zn-0.15Si	1038		125	
Cu-0.29Si	1076	308	196	
*Cu-0.13Si-0.17P	1093		92	
Cu-0.49Ca	1106		25	
*Si-0.45Mg-0.07Zn	1207		310	
Si-0.471Mg	1219	1212	805	

*By Alan Riechman and Diana Farkas

Table 2. Density Changes During Melting for Al and Two Al-Eutectic Alloys. Linear (Solid) and Volumetric (Liquid) Expansion Coefficients.*

Material	Temp. °C	Density kg/m^3	$\frac{\Delta V}{V_s}$	Linear Expansion Coeff. (Solid), K^{-1}	Volume Expansion Coeff. (Liquid), K^{-1}
Al	20(s) 660(s) 660(l) 760(l)	2690 2558 2377 2343	0.072	2.77×10^{-5} (20 to 660°C)	9×10^{-5} (660 to 760°C)
Al-17 at. pct. Cu	20(s) 548(s) 548(l) 748(l)	3506 3424 3258 3186	0.051	1.5×10^{-5} (20 to 548°C)	1.1×10^{-4} (548 to 748°C)
Al-12 at. pct. Si	20(s) 579(s) 579(l) 779(l)	2626 2553 2445 2382	0.048	1.7×10^{-5} (20 to 579°C)	1.3×10^{-5} (579 to 679°C)

*Measured by Andrew Harrison and Silvia Balart

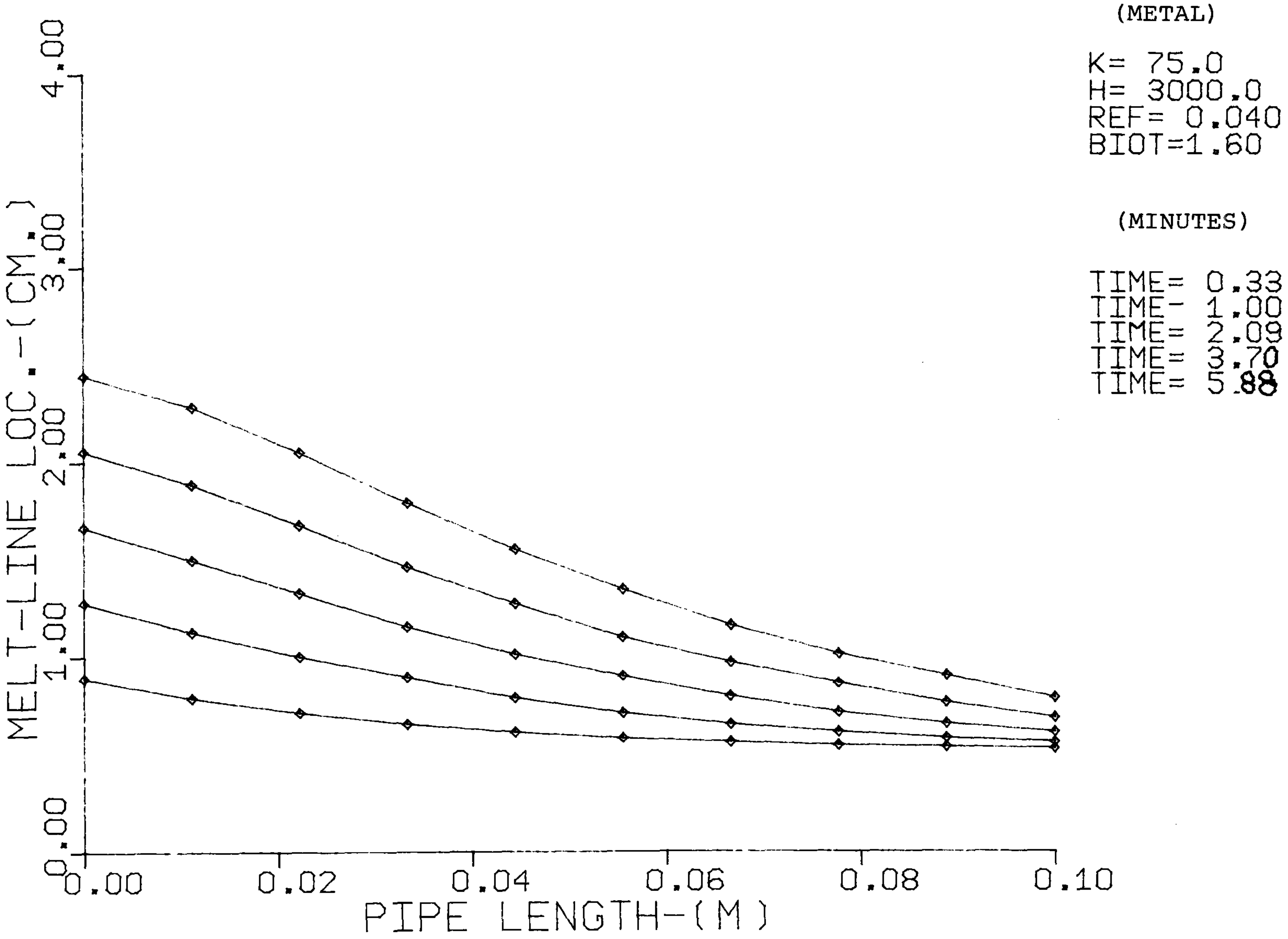
(METAL)
K= 75.0
H= 3000.0
REF= 0.040
BIOT=1.60
(MINUTES)
TIME= 0.33
TIME- 1.00
TIME= 2.09
TIME= 3.70
TIME= 5.88
MELT-LINE LOC.-(CM.)
0.00
1.00
2.00
3.00
4.00
PIPE LENGTH-(M)
0.00
0.02
0.04
0.06
0.08
0.10

Figure 1

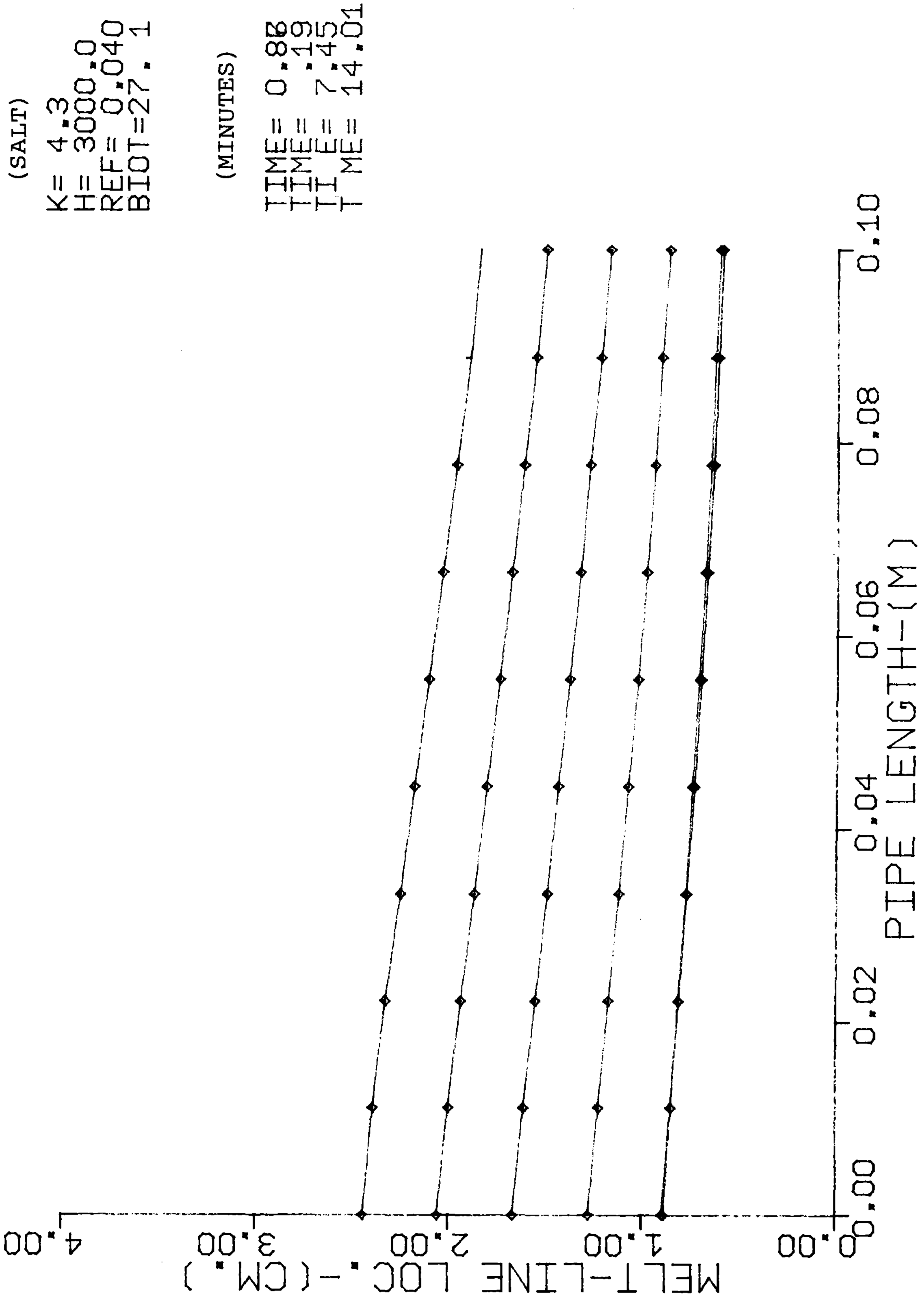
(SALT)
K= 4.3
H= 3000.0
REF= 0.040
BIOT=27. 1
(MINUTES)
TIME= 0.88
TIME= .19
TI E= 7.45
T ME= 14.01
PIPE LENGTH-(M)
MELT-LINE LOC.-(CM.)
0.00
0.02
0.04
0.06
0.08
0.10
1.00
2.00
3.00
4.00

Figure 2

THERMAL ENERGY STORAGE FOR RESIDENTIAL ENERGY CONSERVATION

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Abstract

The potential for conservation of oil and gas was evaluated for thermal energy storage applications involving waste heat recovery and passive solar systems for houses that have gas- or oil-fired furnaces. A waste heat recovery device, using pebbles as the TES medium, increases furnace seasonal efficiency to 95%. Passive solar system performance was estimated from work sponsored by the Department of Energy. Potential market sizes and penetrations were evaluated by region to determine national oil and gas savings. The total oil and gas savings, for the year 2000, were estimated to be 0.22 quads/year for the furnace waste heat recovery device and 0.10 quads/year for passive solar systems installed in houses heated by gas or oil furnaces.

Introduction

Waste heat recovery for residential furnaces and increased thermal capacitance in residential structures were studied for potential conservation of gas and oil due to improved performance of gas- and oil-fired furnaces.

The system developed for waste heat recovery for residential furnaces is termed the "pebble bed TES device". The device consists of a procelainized metal bin, filled with pebbles, that is connected to a furnace by metal ducting. System controls alternately direct flue gases, rinse air, and recovery air through the packed pebble bed to first recover heat from the hot flue gases and then to supply this energy to the residence. The theoretical sesaonal efficiency for a furnace using this device is 95%. A more conservative value of 90% was used for savings estimates in this study. The pebble bed TES device has the potential to meet and exceed the new federal standards covering furnaces for 1986. Installation of this device with new furnaces could be an effective means of complying with the proposed standards. This device can also upgrade existing furnaces to make them high efficiency units.

Potential gas and oil savings from increased thermal capacitance in residential structures were evaluated in three areas:

1) The use of solar radiation (passive solar systems) to heat a residence.
2) Advantageous use of diurnal temperature swings above and below the house thermostat setting to reduce heating fuel consumption.
3) Extension of the on-off cycle time of residential furnaces to decrease off-cycle losses.

The savings in area 2 were determined to be very low and not cost-effective. The savings in area 3 were slightly higher but did not approach being cost-effective. The only cost effective use of increased thermal capacitance was for passive solar systems. The evaluation of passive solar systems was a change from the original scope.

The potential for gas and oil savings in the year 2000 was estimated to be:

		Quads per Year	
		Gas	Oil
Pebble Bed TES Device	-	0.18	0.04
Passive Solar Heating	-	0.075	0.026

Pebble Bed TES Device

The operation of this device is described extensively in the report delivered to Oak Ridge National Laboratory. A schematic diagram of this device is shown in Figure 1. The control status, flow rates, and temperatures for the three cycle phases are shown in Table 1. Although Figure 1 depicts a forced air furnace, the pebble bed TES device will also work with a gravity flow furnace.

The timing of the phases for each cycle is determined by temperatures in the pebble bed. The optimum configuration of the pebble bin and the optimum temperature(s) for switching from phase to phase have not been determined. The configuration and values shown in Table 1 and Figure 1 are reasonable first-cut assumptions.

The thermoswitches labeled 5 (5a) and 6 (6a) could be similar to the furnace plenum switches now used to switch off furnace fans. Switch 5 initiates the change from charge to rinse phase. Table 1 lists the changeover temperature as 100°F. The rinse phase ends and the recovery phase begins when the temperature front at 100°F reaches switch 6. The recovery phase ends and one cycle is completed when the temperature front at 80°F reaches switch 5. If the house thermostat is still demanding heat, a new cycle will begin. Switches 5a and 6a are redundant overheat switches set at 200°F.

The valve/switch combinations (1, 2, 3, and 4) are operated by static pressure differences created by the fans. The switch portion serves as an indicator that the valve is closed, and as an override, in case of malfunction.

TES in Residential Structures (Passive Solar Systems)

Some simple rules of thumb have been developed for TES in passive solar heating designs[1]. These rules were developed for initial concept design by builders and designers. The rules are as follows:

- TES for a mass wall should be 0.6 x SSF pounds of water or 3 x SSF pounds of masonry for each square foot of south glazing. (SSF is the solar savings fraction in percent.)
- If the TES is not directly irradiated, but is in the same room that receives the sunlight, three times as much mass is needed.

- If the TES is not in a room that receives sunlight, and the TES is not irradiated but is insulated from the ambient, about four times as much TES is required. For these last two cases, if masonry is used, it is not effective beyond a depth of 4-6 inches from the surface.

These rules of thumb were based on a study of the sensitivity curves of the SSF for varying TES capacities over the range of 20 percent to 80 percent SSF for several climates. Presently, Reference 1 contains no rule-of-thumb guidelines for phase change materials (PCM's) as the TES medium in passive solar systems.

Procedure for Estimating Gas and Oil Savings

Data concerning housing and furnaces were collected which showed the present use of furnaces in new and existing residential construction (References 2, 3, and 4). A projection of the gas and oil furnace populations in single-family houses through the year 2000 is given in Table 2.

Energy consumption data for gas and oil heating equipment are found in References 4 and 5. Reference 4 contains a breakdown of gas consumption by region, and this information was used to estimate regional gas consumption of residential gas furnaces. Regional oil consumption percentages were estimated by comparing regional gas consumption with the number of gas heating units and extending these comparisons to the regional number of oil heating units. The breakdown of regional fuel consumption for gas and oil furnaces is given in Table 3.

Pebble Bed Device

A projection of the number of houses which would install the pebble bed TES device is given by region in Table 4. The penetration of the pebble bed TES device as a gas and oil conservation method in the market represented by the 34 million homes in the year 2000 with gas- or oil-fired furances is assumed to follow a standard penetration pattern. For this pattern, the first seven years (1985-1992) are assumed to be the period of education, discovery, and production buildup, with 2 percent (overall) of this market reached by the end of this period. An additional 13 percent (overall) of the market is reached by the year 2000. The real growth potential lies after the year 2000, when perhaps 65 percent of all gas and oil furnaces could have a pebble bed TES device installed by the year 2015. However, such a projection is too far term and was not tabulated in this study. Table 5 shows the expected oil and gas savings per year resulting from installations of the pebble bed TES device. Existing seasonal efficiencies used for this report are given in Table 6.

Passive Solar Systems

A projection of the number of houses with gas- or oil-fired furnaces that will install passive solar systems is presented in Table 7. The penetration of the potential market is assumed to be 4 percent by 1990 and 20 percent (overall) by the year 2000. As with the pebble bed TES device, real growth potential lies beyond the year 2000 with perhaps 60 percent of this market reached by the year 2010. The market is restricted by solar access (shading) and to houses with gas- or oil-fired furnaces. Table 8 is a breakdown by region which shows the effect of these two conditions. The total market is only 14 million homes by the year 2000. In the period 1995-2000, it is likely that the effects of solar-conscious design will begin to be felt, since a significant number of houses built in that period will be designed with solar access in mind.

Table 9 shows the expected oil and gas savings per year resulting from passive solar installations. These savings are determined by using a regional SSF, shown in Table 10, together with the percentage of gas- or oil-fired furnaces in that region.

Results

The pebble bed TES device offers a means for retrofitting standard furnaces to become high seasonal efficiency furnaces (greater than 90 percent). The present population of 22 million gas and 5 million oil furnaces is a large market for retrofit. Increasing the seasonal efficiency from 60 to 90 percent allows annual fuel savings of 33 percent. An increase from 80 to 90 percent allows annual savings of 11 percent.

The TES device already has the potential to meet and exceed the proposed standards for seasonal efficiencies for gas and oil furnaces in 1986, as published by DOE in the June 30, 1980 Federal Register. Competing technologies, such as pulse combustion for gas, may have similar benefits for conserving energy. A performance comparison study should be funded to determine the cost effectiveness of several of these systems.

The results of this study show that the pebble bed TES device has a potential gas and oil savings of 0.21 quads per year in the year 2000.

TES in residential structures was found to be very beneficial when used as part of a passive solar heating system. The use of TES in structures to reduce furnace cycling does not appear to be justified by itself, although it could be considered a very small additional benefit for residences with passive solar heating systems that have gas- or oil-fired furnaces for auxiliary heat.

While the use of common building materials for TES in passive solar systems can be reasonably well analyzed by a designer, the use of advanced materials, such as PCM's, for this purpose could not benefit from a similar analysis at this time. A program for study of PCM's for use as TES in passive solar systems should be started. Effective designs, design criteria, and expected performance should all be studied, but effective designs may imply development of special concepts for containment or dispersion of the PCM's in residential structures. Effective designs would also imply compatibility with existing building practices and techniques.

Passive solar heating systems are known already to be effective in conserving heating energy, such as that of gas- or oil-fired furnaces. While these systems will probably have more impact on electrical heating systems' energy consumption for the next ten years, significant gas and oil savings of 0.10 quads per year are projected for the year 2000.

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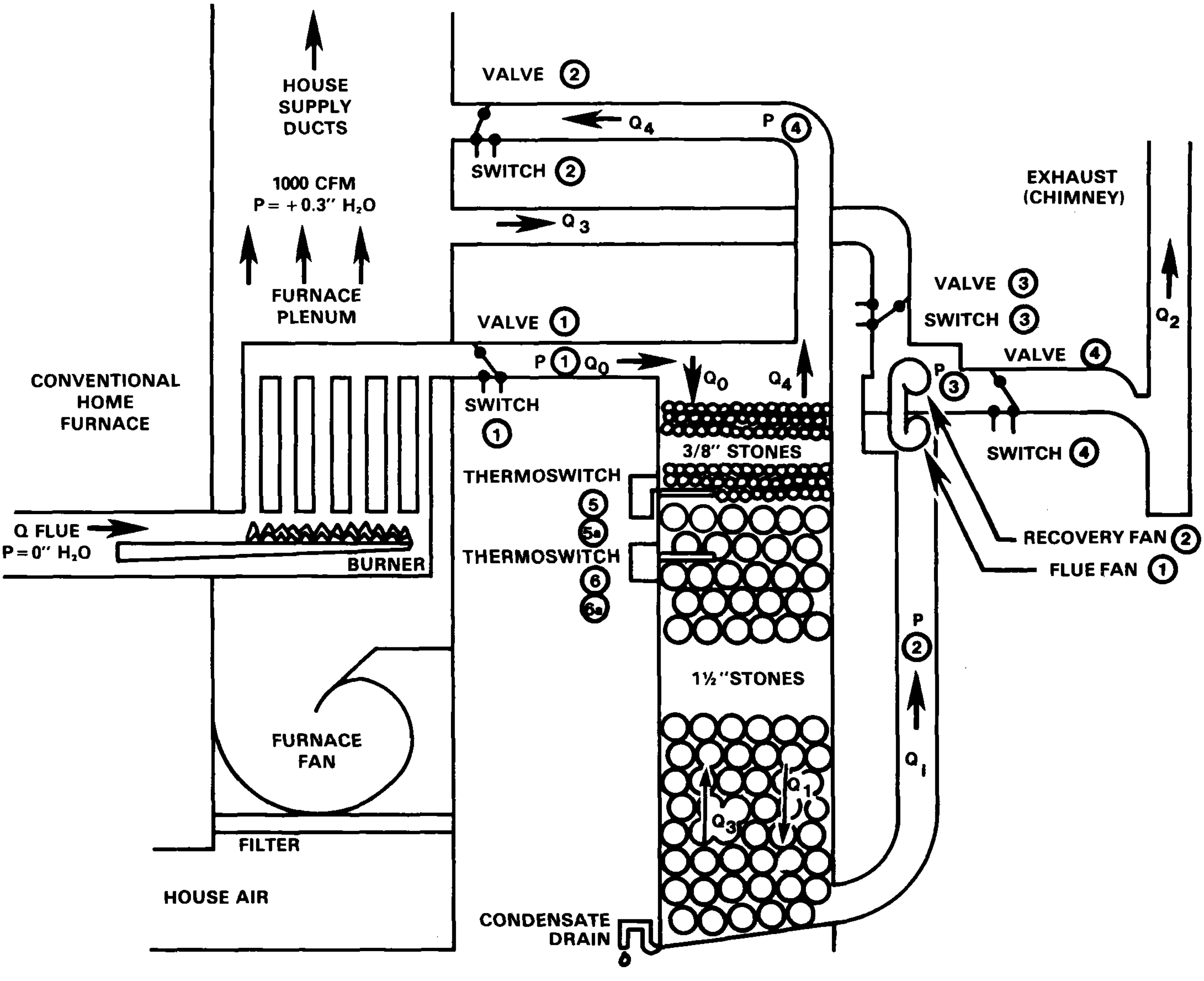

Figure 1. Pebble Bed TES System for Residential Furnaces

Table 1. TES System Cycle Phases—120,000 Btuh Furnace

FUNCTION	FURNACE BURNER	FLUE FAN 1	FURNACE FAN	RECOVERY FAN 2	FLOW RATES AND STATES						VALVE 1 AND SWITCH 1	VALVE 2 AND SWITCH 2	VALVE 3 AND SWITCH 3	VALVE 4 AND SWITCH 4	THERMO SWITCH 5 AND 5a	THERMO SWITCH 6 AND T6a	PRESSURES			
					Q FLUE	Q_0	Q_1	Q_2	Q_3	Q_4							P1	P2	P3	P4
STORAGE CHARGE PHASE	ON	OFF	ON	OFF	28SCFM AIR @60°F	30SCFM 300-700°F CO_2+N_2 +H_2O	29SCFM 70-90°F CO_2+ N_2	29SCFM 70-90°F CO_2+ N_2	0	0	OPEN	CLOSED	CLOSED	OPEN	T5 OPEN @T<100°F T5a CLOSED T<200°F OPEN T>200°F	OPEN @ T<100°F T6aCLOSED T<200°F OPEN T>200°F	−.01" H_2O	−.28" H_2O	+0" TO +.25" H_2O	−.01" H_2O
RINSE PHASE	OFF	ON	ON	OFF	28SCFM @60°F	28SCFM @180°F 60°F AIR	28SCFM @60°F AIR	28SCFM @60°F AIR	0	0	OPEN	CLOSED	CLOSED	OPEN	T5 CLOSED @T>100°F	T6 OPEN @T<100°F	−.01" H_2O	−.28" H_2O	+.25" H_2O	−.01" H_2O
RECOVERY PHASE	OFF	OFF	ON	ON	0	0	−25 TO −50 SCFM AIR	0	25 TO 50 SCFM AIR 80°F	25 TO 50 SCFM AIR 100°F—400°F	CLOSED	OPEN	OPEN	CLOSED	T5 CLOSED @T<100°F OPENS @T>80°F	T6 CLOSED @T>100°F OPENS @T<80°F	+.3" H_2O	+.55" TO 1.3" H_2O	+.3" H_2O	+.3" H_2O

Table 2. Gas- and Oil-Fired Furnace Populations (millions)

	TOTAL		REGION							
			N'EAST		N.CENTRAL		SOUTH		WEST	
YEAR	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL
1980	22.27	5.27	2.67	1.74	9.13	1.74	5.57	1.37	4.90	0.42
1981	22.67	5.27	2.72	1.74	9.29	1.74	5.67	1.37	4.99	0.42
1983	23.18	5.39	2.78	1.78	9.50	1.78	5.80	1.40	5.10	0.43
1985	23.73	5.39	2.85	1.78	9.73	1.78	5.93	1.40	5.22	0.43
1990	25.35	5.61	3.04	1.85	10.39	1.85	6.34	1.46	5.58	0.45
1995	27.06	5.82	3.25	1.92	11.09	1.92	6.77	1.51	5.95	0.47
2000	28.06	6.12	3.37	2.02	11.50	2.02	7.02	1.59	6.17	0.49

Table 3. Gas- and Oil-Fired Furnace Consumption (quads/yr)

	TOTAL		REGION							
			N'EAST		N.CENTRAL		SOUTH		WEST	
YEAR	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL
1980	2.20	0.82	0.38	0.28	1.14	0.35	0.34	0.13	0.34	0.06
1981	2.24	0.82	0.39	0.28	1.16	0.35	0.35	0.13	0.35	0.06
1983	2.29	0.84	0.40	0.29	1.19	0.36	0.35	0.13	0.35	0.06
1985	2.34	0.84	0.41	0.29	1.21	0.36	0.36	0.13	0.36	0.06
1990	2.50	0.87	0.43	0.30	1.30	0.37	0.39	0.14	0.39	0,06
1995	2.67	0.91	0.46	0.31	1.38	0.39	0.41	0.14	0.41	0.07
2000	2.77	0.96	0.48	0.33	1.44	0.41	0.43	0.15	0.43	0.07

Table 4. Pebble Bed TES Devices Installed (thousands)

	TOTAL		REGION							
			N'EAST		N. CENTRAL		SOUTH		WEST	
YEAR	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL
1990	380	80	80	30	250	40	20	4	40	6
1995	2200	460	450	180	1450	220	100	20	200	40
2000	4300	920	900	360	2800	450	200	40	400	70

Table 5. Expected Gas and Oil Savings for the Pebble Bed TES Device (Quads/yr)

	TOTAL		REGION							
			N'EAST		N. CENTRAL		SOUTH		WEST	
YEAR	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL
1990	.015	.003	.004	.001	.010	.002	—	—	.001	—
1995	.089	.020	.021	.007	.060	.011	.003	.001	.005	.001
2000	*.176	*.038	.043	.014	.117	.022	.005	.001	.011	.001

*EQUIVALENT TO 31.7 AND 6.8 MILLION BARRELS OF OIL PER YEAR FOR GAS AND OIL RESPECTIVELY.

Table 6. Regional Seasonal Efficiencies of Gas- and Oil-Fired Furnaces (percent)

FURNACE FUEL	REGION			
	N'EAST	N. CENTRAL	SOUTH	WEST
GAS	60	60	53	56
OIL	68	68	56	62

Table 7. Passive Solar Systems Installed in Houses with Gas- or Oil-Fired Furnaces (thousands)

YEAR	TOTAL		REGION							
			N'EAST		N. CENTRAL		SOUTH		WEST	
	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL
1990	400	100	50	30	160	40	60	10	130	20
1995	1100	230	150	70	450	90	150	20	350	50
2000	2300	500	320	150	950	200	300	40	730	110

Table 8. Combined Effect of Solar Access and Furnace Populations on the Passive Solar Retrofit Market for Houses with Gas- or Oil-Fired Furnaces

REGION	ASSUMED HOUSING POPULATION WITH ADEQUATE SOLAR ACCESS (%)	HEATING SYSTEM POPULATION THAT IS GAS OR OIL FIRED FURNACES (%)		MARKET SHARE OF ALL HOUSES IN THE U.S. (%)	
		GAS	OIL	GAS	OIL
N'EAST	30	5.1	3.4	1.5	1.0
N. CENTRAL	35	17.9	3.4	6.3	1.2
SOUTH	40	11.1	2.7	4.4	1.1
WEST	50	9.6	0.9	4.8	0.4
TOTAL		43.7	10.4	17.0	3.7

Table 9. Expected Gas and Oil Savings from Passive Solar Installations in Houses with Gas- or Oil-Fired Furnaces (quads/yr)

YEAR	TOTAL		REGION							
			N'EAST		N. CENTRAL		SOUTH		WEST	
	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL	GAS	OIL
1990	.010	.003	.001	—	.005	.002	.001	—	.003	.001
1995	.032	.010	.004	.002	.016	.005	.003	—	.009	.003
2000	*.075	*.026	.009	.005	.039	.013	.006	.001	.021	.007

*EQUIVALENT TO 13.5 AND 4.7 MILLION BARRELS OF OIL PER YEAR FOR GAS AND OIL RESPECTIVELY.

Table 10. Regional Solar Savings Fractions (SSF's) for the Average Passive Solar Installation—New and Retrofit Combined (percent)

YEAR	REGION			
	N'EAST	N. CENTRAL	SOUTH	WEST
1990	17	26	27	35
1995	18	28	29	37
2000	20	33	33	42

SOLAR THERMAL POWER STORAGE APPLICATIONS LEAD LABORATORY OVERVIEW*

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Abstract

This paper presents an overview of activities for the applications elements of the Thermal Energy Storage for Solar Thermal Applications (TESSTA) program. The TESSTA program which was initiated in FY80 is organized through a work breakdown structure which includes the development of thermal storage technologies matched to solar thermal power system requirements for several near-term applications. The status of the technology development activities ongoing in FY80 is presented here along with plans for FY81.

General Program Description

The Thermal Energy Storage for Solar Thermal Applications (TESSTA) program was initiated in FY80. The program provides for thermal energy storage technology development in direct support of solar thermal power applications. The program concentrates on storage subsystem development in the FY80 to 85 time period with emphasis on the more near-term solar thermal power system applications.

The overall objective of this storage development program is to develop general solar thermal energy storage technologies that provide:

- Second-generation storage subsystems offering cost/performance improvements over the first-generation storage subsystems currently being developed for solar thermal power applications.
- First-generation storage subsystems for those solar thermal applications that presently have no storage subsystems under development.
- A technology base to support storage subsystem development for future solar thermal power applications.

This paper describes the implementation of the first two objectives. Implementation of these objectives, which are application oriented, has been delegated by DOE/STOR to Sandia National Laboratories (SNL). Implementation of the technology base objective, which is the responsibility of the Solar Energy Research Institute (SERI), is not described here.

Applications Program Description

The applications portion of the TESSTA program is organized through a work breakdown structure which includes the development of thermal storage technologies matched to solar thermal power system requirements for several near-term applications. Solar thermal power systems include troughs, dishes and central receivers with working fluids at various operating conditions. Storage development for central receivers and generic storage development are directed by Sandia National Laboratories Livermore (SNLL), who also performs overall program management and coordination functions. Storage development for trough and dish collectors is directed by Sandia National Laboratories Albuquerque (SNLA) and Jet Propulsion Laboratory (JPL), respectively. Based on current direction of the Division of Solar Thermal Energy Systems (STES) the early portion of the program is stressing storage for repowering/industrial retrofit, total energy, and small community systems applications.

The basic TESSTA program development flow shown in Figure 1 consists of three phases: storage concept development - concept feasibility and lab experiments, storage subsystem development, and system applications including new projects or retrofits. The plan for accomplishing this development has been divided into seven major elements according to the tasks outlined in Figure 2. The first element represents generic activities required to support program management functions while the remaining elements are keyed to development for system applications summarized in Figure 3** and Table I. Several tasks have been further divided into subtasks which represent specific concepts or applications being pursued.

Technology Development Status

The status of the FY80 development activities and planned FY81 development for each of the major program focused elements is described below.

Storage for Water/Steam Cooled Collector/Receivers

During FY80 storage development was initiated for saturated steam receivers for industrial retrofit applications and superheated steam receivers for Barstow retrofit and repowering applications. A competitive procurement resulted in contract awards to Combustion Engineering and Babcock and Wilcox for storage concept development studies. These studies will be completed in early FY81. Consistent with the applications priorities of the STES program and the status of the technology development one or both of these concepts will be selected during FY81 for storage subsystem development.

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*This work was supported by the Department of Energy under contract DOE AN-35, PACE 35-AL-10

**The solar interface operating conditions and candidate applications in this figure are representative cases only. For example, water/steam collector/ receivers at various operating conditions are under consideration for the repowering/ industrial retrofit system application.

Storage for Molten Salt Cooled Sensible Heat Collector/Receivers

This task provides for the development of a storage subsystem for a repowering application. Concept development of internally insulated thermal storage containment was completed in early FY80. The purpose of this program which was conducted by Martin Marietta was to define a cost effective thermal storage system for a solar central receiver power system using molten nitrate salt stored in internally insulated carbon steel tanks at temperatures up to 566°C (1050°F).

Molten nitrate salt storage subsystem development was initiated in FY80. A competitive procurement resulted in a contract award to Martin Marietta for the design, construction, testing, and evaluation of a molten salt subsystem research experiment. This study will be completed in mid-FY82.

During FY80 several materials studies were performed to resolve technical issues for molten nitrate salt storage systems. SNLL conducted experiments and analyses to study the thermal stability of molten nitrate salts in order to understand the factors affecting salt decomposition. A contract was awarded to EIC Corporation via a competitive procurement to develop a thorough understanding of the interactions of molten $NaNO_3$-KNO_3 mixtures with water vapor and carbon dioxide in the air. The results of this study will help to determine whether an open, closed, or breathing system is needed for storage. The results of these chemistry studies, which will be completed FY81, will be evaluated to identify any need for a study of techniques for regeneration of the salt.

Materials studies were also initiated to evaluate the corrosion behavior of high temperature structural alloys in molten nitrate salts. These include: 1) thermal convection loops tests of both closed (at Oak Ridge National Laboratory) and open (at SNLL) systems to determine if thermal gradient mass transfer phenomena affect the corrosion behavior of three alloys, SS 304, SS 316, and Incoloy 800; 2) electrochemical analyses. The thermal convection loop tests will be completed in FY81. At that time the need for forced convection loop tests of these alloys or thermal convection loop tests of alternative alloy-salt combinations will be assessed. The electrochemical studies performed at SNLL in FY80 emphasized the development of species specific indicator electrodes which can serve as on line salt monitors. In FY81 these will be used to study and identify chemical species present in nitrate melts. A contract with the University of New York at Buffalo was initiated in the third quarter of FY80. The purpose is to study the effects of temperature, oxygen, and impurities on the salt melt and the formation of a passivating film on Incoloy 800. This work will continue through FY81.

In FY80 the development of equipment to measure viscosity, surface tension, and density over a temperature range of 25-900°C (77-1652°F) and a pressure range of 1 to 10 atmospheres was completed at SNLL. Preliminary data on the viscosity and density of molten $NaNO_3$-KNO_3 mixtures were obtained. During FY80 heat capacity measurements were also performed on $NaNO_3$ and KNO_3 at SNLL, and a competitive procurement resulted in a contract award to Norwegian Institute of Technology for thermal conductivity measurements of molten nitrate salts. In FY81 the thermophysical property measurements will be completed except for thermal conductivity. The latter will be completed in FY82.

Storage for Liquid Metal Cooled Sensible Heat Collector/Receivers

The objective of this task is to develop a storage subsystem for an IEA retrofit application. In FY79 Energy Systems Group (ESG) of Rockwell International performed a conceptual design of an air/rock thermocline storage system as part of the Advanced Central Receiver Program. This system has potential for low cost but requires experimental verification. Prior to the consideration of any contracted large-scale development effort SNLL is performing laboratory tests to study the effect of thermal cycling on rock strength. The preliminary data show little evidence of rock fracture when thermally cycled (approximately 600 cycles) from 316°C (600°F) to 593°C (1100°F) while under a mechanical load. Additional tests are being performed to allow a greater number of samples to be simultaneously tested.

Storage for Gas Cooled Sensible Heat Collector/Receivers

This task addresses the development of a storage subsystem for a EPRI/DOE hybrid Brayton retrofit project. The air/rock storage concept proposed for liquid metal cooled receivers may also be applicable to gas cooled receivers. This concept has the potential for very low media cost and for low pressure systems very low containment costs. During FY80 preliminary studies were performed to investigate thermal cycling of rocks. In FY81 the air/rock storage concept development will focus on air/rock heat transfer studies needed to establish the concept feasibility. This work is being coordinated with activities described under storage for liquid metal cooled receivers.

Storage for Organic or Silicone Fluid Cooled Sensible Heat Collector/Receivers

The objective of this task is to provide support for and advanced alternatives to storage subsystems under development for midtemperature solar thermal applications, such as irrigation, total energy and industrial retrofit. The task includes analyses and testing of organic fluid single and dual media storage systems leading to the preparation of a design handbook. The task also provides for the development of a second generation latent heat storage subsystem for a Shenandoah midtemperature solar thermal application.

Studies performed in FY80 include fabrication and preliminary testing of a single media thermocline system at the Sandia Mid-Temperature Solar Test Facility (MSTF). This testing will continue through FY81. A contract was also awarded in FY80 to the University of California, Berkeley (UCB) to provide generic thermocline analyses and laboratory testing to predict thermocline performance as a function of time under various operational modes.

In FY81 this work may be extended to correlate the results with the single media thermocline data obtained at the MSTF. Design, fabrication, and testing of a dual media system may be initiated in FY82 pending an assessment of the technology development at the end of FY81.

The latent heat storage concept development activity for this task was coordinated with Task 2 through issuance of a single RFP in FY80 for storage concept development. Under this activity the applicability of the second generation latent heat storage concepts identified for saturated steam receivers to organic or silicone fluid sensible heat receivers is being assessed. With the current program funding priorities latent heat storage subsystem development for organic or silicone fluid receivers will depend on storage development activities for saturated steam receivers. A separate storage subsystem development is not planned at this time.

Dish Mounted Latent Heat Buffer Storage

The objective of this task is the development of dish mounted latent heat storage subsystems for three small community system applications. Power conversion cycles under consideration include Rankine, Brayton, and Stirling operating at temperatures of 427°C (800°F), 816°C (1500°F), and 816°C (1500°F), respectively. During FY80 contracts were awarded to Ford Aerospace and Communications, Garrett AiResearch, and General Electric for storage requirements definition and SRE design studies for concepts using these cycles. The studies will be completed in FY81 and the most promising will be selected for storage subsystem development.

During FY80 materials studies to investigate storage media chemistry and containment material corrosion were begun. These studies include salts, such as $KCl\text{-}MgCl_2$ in contact with SS321 or alloy steel, for the 427°C (800°F) application, and $NaF\text{-}MgF_2$ or Na-NaCl in contact with SS321 for the 816°C (1500°F) applications. These studies will be completed in FY81. A new activity planned for FY81 is the thermophysical property measurements of these latent heat salts.

During FY80 JPL developed a computer model to predict the transient thermal behavior of a paraboloidal dish receiver integrated with latent heat thermal storage and a power conversion unit. The model demonstrated a need for improved heat transfer of the latent heat storage media. Analyses and experiments will therefore be performed in FY81 on heat transfer enhancement techniques. These techniques will be integrated into containment designs in early FY82 in order to provide a low cost, low weight dish mounted latent heat storage system.

TABLE I

DESCRIPTION OF PROJECT APPLICATIONS

NAME	LOCATION	SIZE	STORAGE TECHNOLOGY	STATUS
BARSTOW	BARSTOW, CA	10 MW_e	OIL/ROCK THERMOCLINE	UNDER CONSTRUCTION
REPOWERING/ INDUSTRIAL RETROFIT	TBD	TBD	TBD	CONCEPTUAL DESIGNS PERFORMED ON SEVEN REPOWERING AND SIX INDUSTRIAL APPLICATIONS. SEVERAL PROJECTS MAY BE SELECTED FOR DEMONSTRATION
IEA	ALMERIA, SPAIN	0.5 MW_e	LIQUID METAL WITH EXTERNAL INSULATION	UNDER CONSTRUCTION
EPRI/DOE HYBRID	TBD	TBD	TBD	CONCEPTUAL DESIGN TO BEGIN IN 1981
SHENANDOAH	SHENANDOAH, GA	0.4 MW_e ELECTRIC, 2.6 MW_t PEAK THERMAL	SILICONE OIL THERMOCLINE	UNDER CONSTRUCTION
SMALL COMMUNITY	TBD	1 MW_e	TBD	SITE SELECTION UNDERWAY

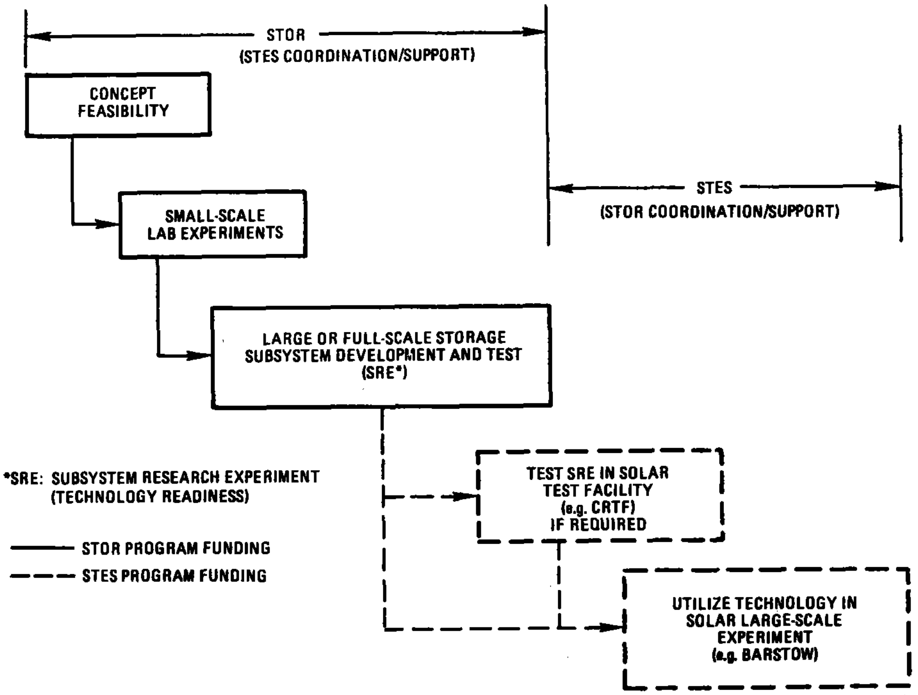

Figure 1 - Program Development Flow

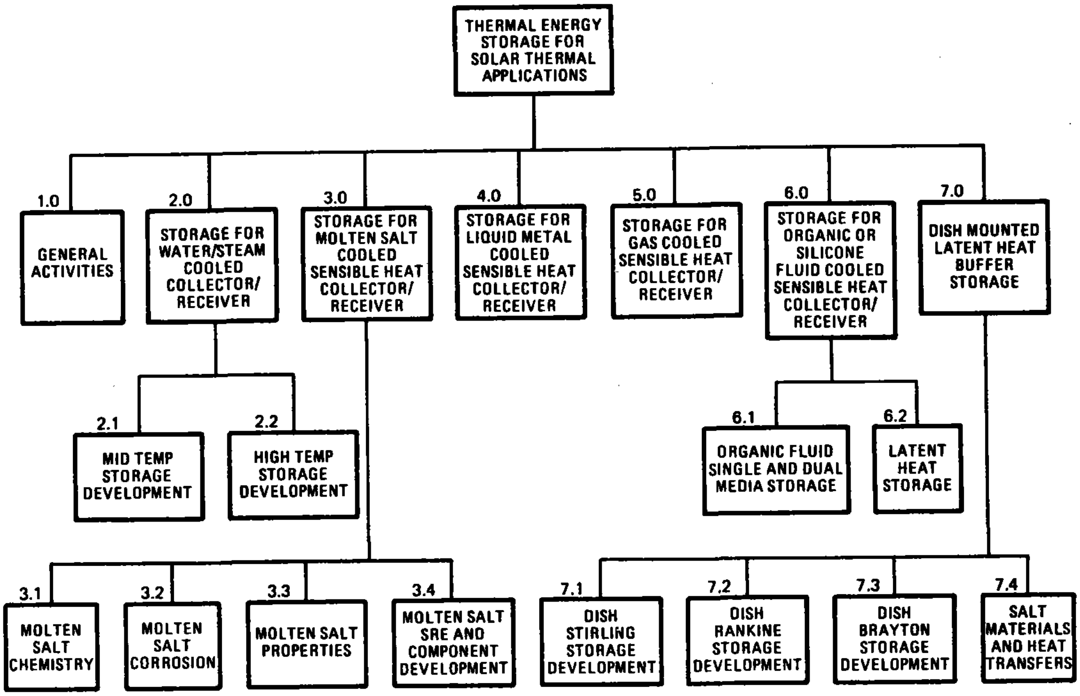

Figure 2 - Task Outline

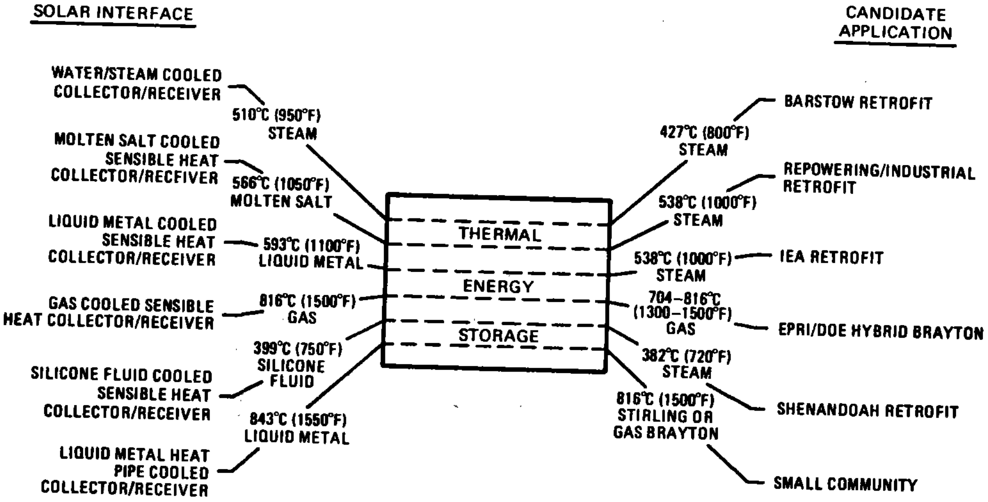

Figure 3 - Focused Elements

MOLTEN NITRATE SALT MATERIALS STUDIES*

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Abstract

This paper presents an overview of the experimental programs underway in support of the Thermal Energy Storage for Solar Thermal Applications (TESSTA) program. The experimental programs are concentrating on molten nitrate salts which have been proposed as heat transfer and energy storage medium. The experimental programs involve corrosion, decomposition, physical properties, and environmental cracking. Summaries of each project and how they impact central receiver applications are presented.

Introduction

Recognizing thermal energy storage as potentially critical to the successful commercialization of solar thermal power systems, the Department of Energy (DOE) has established a comprehensive and aggresive thermal energy storage technology development program. Molten nitrate salts have been proposed for use as primary heat transfer and thermal energy storage media in some solar thermal power applications. Nitrate salts are of interest because they are abundant, readily available and inexpensive, and have excellent thermal properties and low vapor pressures. However, salt physical properties, corrosive behavior, and environmental effects are not well-known over the temperature range of interest, 350° to 600°C. In addition, while molten nitrates have performed satisfactorily for many years as a heat transfer fluid and as a heat treatment bath medium, solar applications place more rigorous demands on the salt.

The salt composition of greatest interest is drawsalt, nominally a 50-50 molar mixture of $NaNO_3$ and KNO_3 with a melting point to 220°C. Several technical uncertainties have been identified, and must be resolved before nitrate based solar plants can be commercialized. Research programs at Sandia National Laboratories (SNL), universities, and industrial suppliers have been implemented to resolve these technical issues. Areas of investigation include corrosion, salt decomposition, thermophysical properties studies, and environmental cracking. Experimental programs to address the above areas and recent results are described here.

Experimental Programs

Corrosion

One of the chief concerns in building anything is how long it will last. Obviously, the corrosion behavior of the molten nitrate salts and their container materials are an important consideration in estimating lifetimes. Although there is a large amount of industrial experience with molten nitrate salts, most is at lower temperatures. Therefore, an experimental program was developed to address the corrosion behavior with metal alloys that could conceivably be used to contain the salt.

The first experiments in this area involved screening croloy alloys (2 to 9 percent chromium) in static immersion tests. The tests involved suspending the alloys in a molten nitrate salt bath for about 100 days at 500°C. Results from this work showed a decreasing amount of oxidation and spalling of the alloy as the chromium content increased. The conclusion drawn from the immersion tests was that higher chromium content and higher strength alloys would be required for molten salt containment.

Following the static immersion tests three alloys were selected for study in molten salt convection loops. The alloys were Incoloy 800 (I800), 304 stainless steel, and 316 stainless steel. Convection loops of each alloy have been built at SNL and Oak Ridge National Laboratory (ORNL). A schematic of the loops is shown in Figure 1. The temperature range of the salt in the loops is 350° to 600°C with a salt flow rate of about 0.5 cm sec^{-1}. Metal coupons were suspended in the hot and cold legs of each loop. The coupons are used to evaluate the corrosion behavior of the alloys in molten nitrate salts and to ascertain if thermal gradient mass transfer phenomena significantly affect corrosion behavior. The SNL program differs from the ORNL in only one respect. The SNL convection loops operate open to the atmosphere whereas the ORNL loops operate with an argon cover gas. The results to date are summarized in Table 1.

Some general comments about the results can be made:

1. Below 600°C corrosion is relatively benign although samples lose weight due to chromium depletion. At temperatures about 600°C, corrosion and depletion rates are several times faster. Figures 2 and 3 illustrate these points. Further experiments are required to clarify the temperature limit for acceptable corrosion rates.
2. There is no thermal gradient mass transport of chromium. Once the chromium is leached from the alloy it remains in the salt and does not precipitate in the cold leg of the loop.
3. Weldments behave similarly to the base metal.
4. Although the data from ORNL are not extensive, preliminary results indicate similar corrosion rates between the open or breathing loops (SNL) and those employing an inert cover gas (ORNL).

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*This work was supported by the Department of Energy under contract DOE AN-35, PACE 35-AL-10

Table 1

Status of Molten Nitrate Salt Convection Loops

Loop Material	Hours of Operation	Weight Change at 600°C	Nitrite wgt. %
		SNL	
304SS	8500	1 mg cm^{-2}	3-4
316SS	5500	1 mg cm^{-2}	3-4
I800	4000	1 mg cm^{-2}	3-4
		ORNL	
316SS	1500	0.2 mg cm^{-2}	2

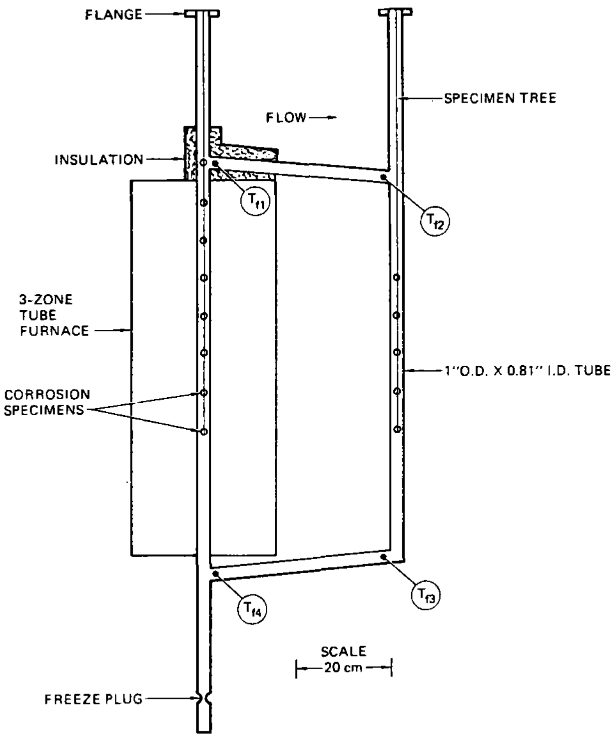

Figure 1. Schematic of Molten Nitrate Salt Convection Loops

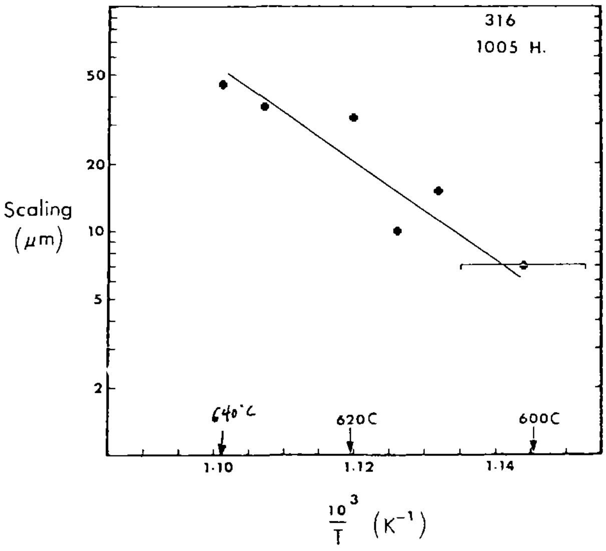

Figure 2. Amount of Oxide Scaling vs. Temperature on 316SS Coupons in a Molten Nitrate Salt for 1005 Hours.

In an effort to better understand corrosion mechanisms in I800 a contract has been placed with the State University of New York at Buffalo. The objective of this project is to develop an understanding of the phenomena ascribed to Incoloy 800 that inhibits the corrosion of the metal by molten nitrates. Available experimental evidence indicates that the formation of thin passivating oxide layers is responsible for the negligible corrosion rates of certain structural alloys in molten nitrates. However, nothing is known about either the kinetics or temperature nor the effect of oxygen partial pressure on these processes is understood. A thorough appreciation of these effects is critical because this passivating film will be subjected to disruptive forces developed during the heating and cooling cycles experienced in solar receiver and thermal storage applications. It is the purpose of this program to develop a thorough understanding of the corrosion mechanism of Incoloy 800, as a representative structural alloy, and of the mechanism of formation of these passivating films so that conditions leading to catastrophic failure of this protective layer can be avoided.

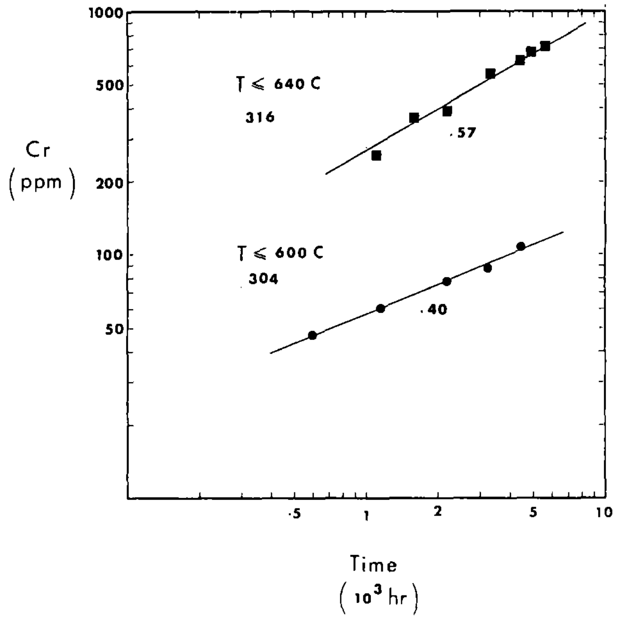

Figure 3. Amount of Chromium Leaching as a Function of Time in 304SS and 316SS Molten Nitrate Salt Convection Loops.

The final experimental program in the corrosion area is one at SNL. The objectives of this project are to identify the various chemical species present in nitrate melts and develop an understanding of the relationship between the concentration of these species and such variables as temperature and composition of the gas phase. It is intended that these data will provide a foundation for a fundamental understanding of corrosion processes in molten nitrates. Appropriate electrochemical techniques are being used to accomplish these objectives.

A combination of literature surveys and screening studies have identified the electrode system Pb, $PbO/ZrO_2(Y_2O_3)$ as being responsive to the oxide ion in molten nitrates. Extensive tests of this electrode have been completed. They have shown that this electrode will respond in a rapid, predictable and reproducible manner to the oxide ion concentration in $NaNO_3$-KNO_3 melts. There is a linear relationship between the electrode potential and temperature over the temperature range, 330°-410°C (626°-770°F).

An electrochemical cell and appropriate electrodes have been fabricated and appropriate instrumentation assembled for the study of chemical species in nitrate melts. Cyclic voltammetry has been chosen as the experimental technique that will be used in these studies. Current emphasis in on the NO_2^- ion. Peaks corresponding to the NO_2^-/NO_2 couple have been found at +0.425 V vs. $Ag/AgNO_3$, and +0.325 V for the reduction step at 350°C (662°F). The peak separation of 0.10 V is in reasonable agreement with the theoretical value of 0.118 V. There is a linear relationship between NO_2^- concentration and peak current up to at least 4×10^{-2} molal. From these data, the intrinsic NO_2^- concentration resulting from the thermal decomposition of NO_3^-, at 350°C (662°F) in an inert atmosphere is $\sim 5 \times 10^{-3}$ molal. How this intrinsic NO_2^- concentration changes with temperature and atmosphere is now under study.

Salt Decomposition

It is recognized that nitrate salts, when heated, can degrade by numerous reactions. Decomposition reactions produce nitrites and oxides while the decomposition products and/or the nitrates react with components of the atmosphere to produce hydroxides and carbonates. The extent to which these degradation reactions impact the use of salts in energy systems has not been determined with certainty. Studies are currently being conducted at SNL and EIC Corporation to understand the thermal decomposition and reaction mechanisms and kinetics for salt interactions with CO_2 and H_2O. The production of nitrites, hydroxides, and carbonates may seriously affect salt physical properties such as melting point, thermal conductivity, heat capacity, viscosity, etc. Results from these experiments will be used to assess the need for a salt regeneration or purification subsystem in a solar thermal power system.

A thermal microbalance and a mass spectrometer (TGA/MS) system has been designed and built to study the decomposition of nitrate salts. The TGA/MS system has been successfully tested for operating with experiments at 1 atm pressure and in vacuum.

Experiments with $NaNO_3$ and $(Na,K)NO_3$ have been performed with the TGA/MS. The salts decompose linearly with time and the rates increase with temperature. The rate of decomposition appears to be proportional to the surface to volume ratio of the salt. The extent of the weight losses indicate that as the salts decompose to metal oxides, some of the oxides volatilize. The gas analyses show that O_2, NO, and N_2 are decomposition products at 400°C (752°F) in vacuum. In addition to these gases, NO_2 appears to be a decomposition product at 600°C (1112°F) in vacuum. The gas analyses support that multiple reactions are occurring over the temperature range of interest.

Due to the low viscosity and low surface energies of the nitrate salts, they have a strong propensity to spread, cover and creep out of any container. This wetting behavior interfered with the accuracy of the chemical analyses for the screening tests and with the measurement of the surface area of the salt in the kinetic investigations. No container material or crucible configuration could be found to alleviate this problem. A possible solution to this problem for kinetic studies involves the use of adherent salt films on gold substrates.

In another study, researchers at EIC Corporation of Newton, Massachusetts are examing drawsalt behavior in the presence of CO_2 and/or H_2O. By using electrochemical techniques they hope to elucidate the mechanisms and rates of formation of carbonates and hydroxides.

Thermophysical Properties

Data such as viscosity, surface tension, density, heat capacity, and thermal conductivity are needed from 350° to 600°C. These data are required by the designers and engineers of solar thermal power systems in order to size hardware and for thermal modeling of the system. Experiments to determine these properties of drawsalt are in progress. Thermophysical properties of drawsalt plus impurities such as nitrite, carbonate, and hyroxide are also being measured. These latter results will impact the need for a salt regeneration or purification system in a solar thermal power system.

Viscosity, Surface Tension, and Density. These properties have been measured using a single instrument. The instrument allows the measurement of the viscosity, as the damping of a harmonic oscillator, and the surface tension, by a plate detachment method, on the same sample and follows changes in viscosity and surface tension with changes in temperature and atmospheric composition. Measurements can be made over a temperature range of 25° to 900°C (77° to 1652°F), a pressure range of 1 to 10 atmospheres, and in a variety of atmospheric compositions.

The viscosity of the equimolar $NaNO_3$-KNO_3 mixture has been measured over the temperature range 275°C-600°C (527° to 1112°F) in both argon and oxygen. It varied from 3.8 cp to 1.0 cp over this temperature range. Over the same temperature range the surface tension is a linear function of the temperature and can be represented by the equation:

$$\gamma = 133.78 - 6.4 \times 10^{-2}T$$

The density of the salt was measured using a buoyancy technique. Between 300° to 600°C (572° to 1112°F) in argon the density can be approximated by:

$$\rho = 2.086 - 6.28 \times 10^{-4}T$$

However, if the melt is held for 72 hours at 600°C there is a slight decrease in density due to the presence of about 7 wt% NO_2^-, caused by the thermal decomposition of NO_3^-. In this case:

$$\rho = 2.062 - 6.11 \times 10^{-4}T$$

Heat Capacity. Heat capacity measurements are being made using Perkin-Elmer differential scanning calorimeter, DSC-2. Measurements of $NaNO_3$, KNO_3, and mixtures of $NaNO_3$-KNO_3 up to 557°C (1070°F) are being made. In addition, the effect of nitrite impurity on the heat capacity of the nitrates will be determined. To date measurements have been made on $NaNO_3$ (77° to 477°C), KNO_3 (77° to 527°C), 50/50 molar mixture of $NaNO_3$ and KNO_3 (77° to 347°C), and 64/36 molar mixture of $NaNO_3$ and KNO_3 (277° to 377°C). Measurements beyond the upper temperatures mentioned above have been impossible because of the tendancy of the salts to creep out of the sample capsules. Methods to prevent this and make the measurements to higher temperatures are under investigation. Preliminary results show the heat capacity decreasing with temperature above the melting point on all the systems studied.

Thermal Conductivity. The objective is to measure the thermal conductivity of molten $NaNO_3$-KNO_3 mixtures, to determine the effect of impurities upon the thermal conductivity of these mixtures, and to use these data to construct a predictive model for the thermal conductivity. The thermal conductivity of the following uncontaminated mixtures of molten nitrate salts will be measured over the temperature range, 350°-600°C (662°-1112°F).

a. $50KNO_3$-$50\ NaNO_3$ (molar ratio)
b. $60KNO_3$-$40NaNO_3$
c. $40KNO_3$-$60NaNO_3$
d. $45KNO_3$-$45NaNO_3$-$10KNO_2$

The effect on the thermal conductivity of small additions of CO_3^{-2}, and OH^- will be determined for each salt listed above. The suggested maximum additions are contaminants are:

a. $CO_3^=$ (5 wt%)
b. OH^- (0.1 wt%)

A competitive procurement has resulted in a contract award to the Norwegian Institute of Technology in Trondheim, Norway. Work is just underway.

Environmental Cracking

These experiments are underway to determine the effects of molten nitrate salts on creep ductility and fracture morphology of high temperature alloys. The tensile specimens are Incoloy 800 (.04%C) tubes filled with drawsalt. Constant load creep tests have been performed at temperatures between 600° and 670°C (1112° and 1238°F). Preliminary findings in specimens tested to fracture ($\varepsilon_F \simeq 30\%$) indicate that extensive subsurface cracking occurs on both the air and salt sides of the tube wall to about an equal degree. The fracture is mixed mode, with approximately 30% of the frature surface being intergranular and the balance ductile rupture.

In contrast to general corrosion studies in unstressed coupons in convection loops, surface corrosion of the tube walls below the fracture surface appears to be rapid at these temperatures, with about one mil of corrosion product forming on the salt exposed surfaces during the relatively short exposure time.

Additional work is planned in this area using slow strain rate and corrosion fatigue tests. These experiments are intended to study the behavior of Incoloy 800 in a molten salt environment under mechanical stresses.

Impact of Experimental Programs

The information derived from the above experimental studies will impact decision points set by DOE for the development of thermal storage technologies matched to solar thermal power system requirements for several near-term central receiver applications such as the repowering/industrial retrofit program. This program has two applications: repowering of existing electrical power generating plant and retrofitting of existing industrial process heat plants.

The experimental program has already provided information to the advanced central receiver program and will impact the storage subsystem research experiment to be started very soon. Figures 4 and 5 detail how the experimental program fits the needs of the central receiver applications. Conceptual designs for the cogeneration of electricity and heat have recently been selected for contract negotiation by DOE. Two of the designs call for molten salts to store energy. The experimental programs described above will also impact the cogeneration designs. In summary, the molten nitrate salt experimental program has been designed to meet the needs of the designers and engineers of near-term central receiver applications in a timely fashion.

Acknowledgements

The experimental program at SNL involves many individuals. They are: D. A. Nissen, C. M. Kramer, R. W. Bradshaw, and S. H. Goods. Their inputs to this report are greatfully acknowledged.

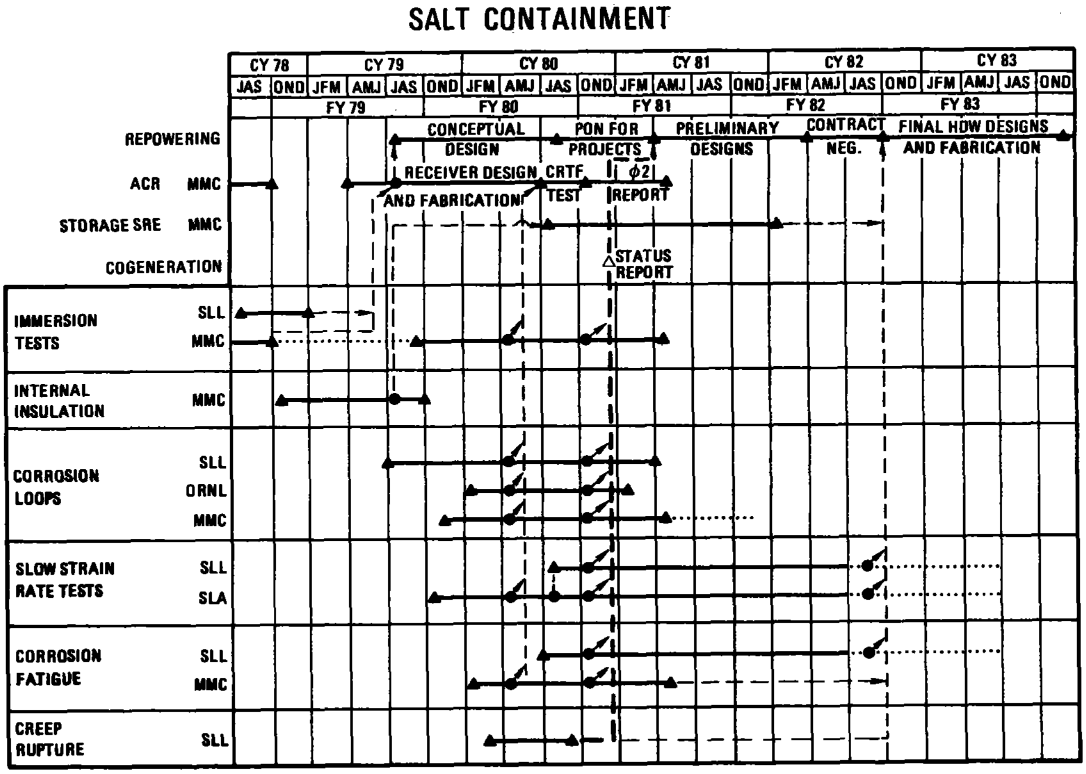

Figure 4. Summary of Experimental Molten Nitrate Salt Containment Program and its Impact on Solar Applications

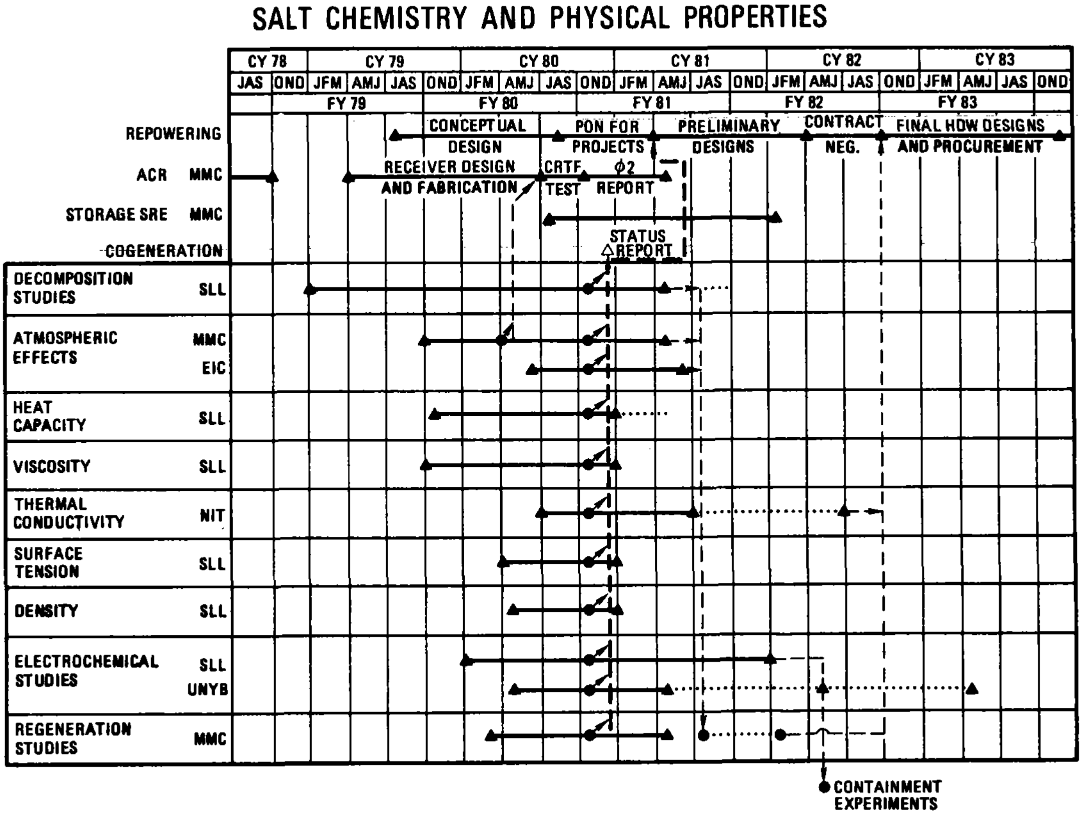

Figure 5. Summary of Experimental Molten Nitrate Salt Chemistry and Physical Properties Program and its Impact on Solar Applications

MOLTEN NITRATE SALT CHEMISTRY STUDIES

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Abstract

The contract is concerned with determining and quantifying the interaction of water and carbon dioxide in air with molten alkali nitrates in the temperature range 300-600°C. Electroanalytical methods involving voltammetry, chronopotentiometry and chronoamperometry at both rotating and stationary electrodes have been established to investigate this molten nitrate chemistry. The preliminary results show that water is reversibly removed from the melt up to 350°C. The activation energy associated with the water mass transfer coefficient is 4.4 kcal mol^{-1}. The reduction of water and the oxidation of carbonate and nitrite ions are complex electrochemical processes. In the case of the latter two reactions, because the products are gaseous, fast scan cyclic voltammetry and high current density chronopotentiometry will be necessary to avoid disturbances of the diffusion layer at high solute concentrations to enable the electroanalysis to be rigorous.

Objectives

The objective of this program is to provide a thorough understanding of the interactions of molten potassium nitrate, sodium nitrate, and their binary mixtures with water and carbon dioxide in the air. These studies will complement ongoing work at Sandia into the development of molten nitrate mixtures for application as heat transfer and sensible heat storage media in large solar energy power systems. The results of these studies will help to determine whether an open, closed or breathing system is needed in salt storage.

Background

Recently the molten nitrates of sodium and potassium have become potential candidates for thermal storage media in solar thermal applications.[1] This proposed application will involve handling many thousands of tonnes of salt in the liquid phase at temperatures between 300-600°C. The chemical reactivity of such solvents is of paramount importance in such an undertaking, particularly since these liquids would be exposed to variable atmospheric conditions. Interactions with atmospheric components are of importance particularly with respect to the oxygen, water and carbon dioxide content of the atmosphere. The likelihood of interaction between these atmosphere components and the liquid nitrates is small at lower temperatures (<300°C for the binary mixture $NaKNO_3$). However, the long term temperature cycling, the need for higher temperatures, 400-600°C, and the use of metallic containers will most certainly lead to decomposition of the nitrate.[2] The presence of atmospheric oxygen, carbon dioxide and water will certainly moderate the reaction pathways available.[3-5] Thus the characterization of the reactions involving water and carbon dioxide with these nitrate melts under aerial conditions is of prime importance. A number of anionic species may result from these interactions, for example, $CO_3^{=}$, OH^-, O^{2-}, O_2^{2-}, O_2^-, etc.

These species have received particular attention especially with regard to their electro-oxidative behavior.[6-9] Several workers have established half wave potentials, diffusion coefficients, and n values albeit over a limited temperature range which suggest that electroanalytical techniques could be successfully used to study the formation of these species as well as the direct behavior of water, carbon dioxide, and oxygen in the nitrate melts.

In the table are summarized some of the species and their electroanalytical properties.[10] The low concentrations of water, carbon dioxide, oxygen, etc., suggest that the monitoring of these species and their degradation products might best be achieved by in situ electroanalytical techniques in the molten nitrates. It is clear from the table that the rotating disc electrode, cyclic voltammetry and chronopotentiometry offer rapid dynamic means by which the low concentrations of reactants (and products) can be monitored quantitatively as a function of controlled gas pressure/atmosphere and temperature.

Although the use of a rotating disc electrode in molten salts is difficult, the combination of this procedure with one of the other two offers some unique advantages. The primary advantage arises because the particular concentration of the electroactive species may be measured directly from a pair of measurements. This is because the particular relationship (reversible process) which describes the limiting current density at the disc (the Levich equation)[11]

$$i_L = B \times n \times D^{2/3} \times \nu^{-1/6} \times \omega^{1/2} \times C_{OX} \times A \quad (1)$$

contains the diffusion coefficient raised to a power different from that contained in say the Sand equation (chronopotentiometry)[12]

$$i\tau^{1/2} = G\, D^{1/2}\, C_{OX} A \quad (2)$$

or the Randles-Sevcik equation of cyclic voltammetry[13]

$$i_p = K\, n^{3/2}\, D^{1/2}\, C_{OX} A V^{1/2} \quad (3)$$

Therefore, taking the ratio of (2) and (3) or (4) which give

$$\frac{i_L}{i_p} = \frac{B'\, D^{1/6}}{K'\, n^{1/2}} \quad \text{or} \quad \frac{i_L}{i\tau^{1/2}} = \frac{B'\, D^{1/6}}{G} \quad (4)$$

Thus if these ratios are measured experimentally, D can be found and hence C_{OX} calculated from (1)-(3).

ELECTROCHEMICAL DATA RELATING TO OXIDIC AND OTHER SPECIES IN NITRATES ($NaNO_3$-KNO_3)

Species	E(V)[*]	$10^5 D$ $cm^2 sec^{-1}$	Temp. (°K)	Method	Reference
NO_2^-	$E_{\tau/4}^{NO_2/NO_2^-} = -0.44$	5.2[**]	571	Chronopotentiometry	6
	$E_{1/2} = -0.44$	0.525	502	Rotating Disc Electrode	24
		2.4 ± 0.7	523	Chronopotentiometry	
H_2O	$E_{1/2} = -1.19$	1.9	502	Rotating Disc Electrode	23
O_2^-	$E_{1/2}^{O_2/O_2^-} = -0.74$	0.475	502	Rotating Disc Electrode	19
O_2^{2-}	$E_{1/2}^{O_2/O_2^{2-}} = -1.28$	0.31	502	Rotating Disc Electrode	19
OH^-	$E^{O_2H_2O/OH^-} = -0.495$	-	502	Potentiometry	4
O_2	$E_{1/2}^{O_2H_2O/OH^-} = -0.65$	31[†]	520[††]	Rotating Disc Electrode	25
Cl^-	$E_p = -0.27$	0.152	423	Linear Sweep Voltammetry Hg	26
	$E_{1/2} = -0.212$	0.691	518	Pulse Polarography Hg	27

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[*] Versus 0.07 molal Ag^+/Ag reference electrode.

[**] The large discrepancy here may arise from the inadvertent presence of oxidic species which in the chronopotentiometric method consume current leading to τ being enhanced, hence resulting in D being too large cf. RDE technique.

[†] This based on (a) K_H 4.8×10^{-6} mol $kg^{-1}atm^{-1}$ and using wet oxygen.[20]

[††] Measured over the temperature range 525-575°K.

This approach offers considerable advantage where pilot ion/standard addition cannot be made as in the case of gaseous solutes. Furthermore, rotating disc electrode measurement enables the easy separation of limiting currents when more than one electroactive species is present. Zambonin's work illustrates the successful use of this method in difficult experimental conditions.[14]

The proposed electroanalytical techniques are sensitive, powerful methods of in situ analysis in molten nitrates. The quality of the solvent may therefore present a problem, unless adequate purification procedures are adopted to prepare and standardize these solvents. Careful heating/vacuum procedures followed by NO_2 gas bubbling and filtration are necessary to produce solvents of acceptable purity.[10] Although the way in which such solvents behave thermally is not known, some thermal decomposition studies of nitrate melts have been reported in the literature.[15,16] Thus background measurements are being made over a range of temperatures to assess the thermal decomposition prior to the introduction of air, water or carbon dioxide. Nitrite[17] and oxide[7] are commonly observed products of the degradation and are often reported even when the salts have been carefully treated under inert atmosphere. The presence of oxygen in the atmosphere in contact with these salts can result in further reactions. Some studies have reportedly prepared nitrite-free melts ($<10^{-4}$M NO_2^-) at low temperature, <280°C, and in such cases Zambonin and co-workers[17,18] have studied manometrically the solubility of gases such as O_2, CO_2, H_2, and water vapor in the binary melt over the temperature range 225-300°C. These measurements will be extended (using the electrochemical approach outlined above) and additionally detect any interactive behavior in these systems. The presence of wet air rather than an inert atmosphere will certainly moderate the behavior reported in the earlier measurements. Jordan and Zambonin[19] reported that the chemistry of oxide ion in nitrate melts was affected not only by the presence of oxygen but also by the container material such as Pyrex glass which tended to buffer the oxide content of the melt as well as introduce silicate moieties into the system.[20] Subsequently, there has been considerable controversy[21,22] concerning the nature and stability of species such as oxide, peroxide, superoxide ions, resulting in a detailed effort by several groups to understand the complex chemistry of oxygen under wet and dry conditions. It is not opportune here to discuss the detailed chemistry, but it is sufficient to point out that the chemistry likely to be involved in the use of these salts under air must be well understood before introducing water and/or carbon dioxide. Careful delineation of the base-line condition of the solvent under inert conditions, how this changes under air, and the subsequent behavior of H_2O/CO_2 containing air will be studied.

The data for water solubility in sodium nitrate-potassium nitrate mixtures have been found to obey Henry's law for water vapor pressures below about 30 mm.[23] The Henrian constant K_H (mol $kg^{-1}mm^{-1}$) is related to temperature by

$$\log K_H = \frac{1.862 \times 10^3}{T} - 6.735 \qquad T\ 500°K \rightarrow 567°K \qquad (5)$$

Thus at a water vapor pressure of 20 mm at 500°K, water has a molar solubility of 37×10^{-3} moles ℓ^{-1}. Fortunately the concentration decreases with increasing temperature and extrapolation of equation (5) to 800°K gives 1.5 x 10^{-3} mole ℓ^{-1}, at the same partial pressure of water. These figures already show that water solubility in the molten nitrate medium chosen for thermal storage applications must be characterized. (A molten nitrate at an intermediate temperature <800°K could contain $\sim$1 tonne of water distributed within the 20 x 10^3 tonnes of molten salt; rapid evolution of this vapor could be extremely undesirable!)

On the other hand, the carbon dioxide solubility may be less of a problem since the Henrian coefficient is some 100X smaller.[17]

These observations assume that no interaction occurs between water, carbon dioxide, and the molten nitrate at the higher temperatures. Furthermore, the data reported were for solutions in the absence of air, i.e., under inert nitrogen or argon atmospheres, and at low temperatures. The interaction of solute species (H_2O or CO_2 or both), air, molten nitrate and high temperature (370°K to 800°K) are now being investigated implicitly. The electrochemical approach will provide a powerful method to study the behavior of molten nitrates exposed to atmospheric conditions in the range of temperature required by their use in thermal storage applications.

Technical Achievements

The electroanalytical procedures using cyclic voltammetry, chronopotentiometry and chronoamperometry and differential pulse polarography have been set up using the PAR 174A polarographic analyzer and PAR 175 signal generator. The data is recorded on a PAR 4102 signal processor or the Bascom-Turner 8000 series microprocessor controlled X-Y recorder. Software to process these data is being developed.

A procedure for the purification and characterization of the individual sodium and potassium nitrate melts and their binary mixture involving vacuum drying and treatment with NO_2 gas has been developed and is being evaluated using cyclic voltammetry.

Preliminary measurements have been made to obtain information on the behavior of water, carbon dioxide, and potential decomposition products such as nitrite, carbonate, and hydroxide ions in the binary nitrate mixture. The cyclic voltammetric results obtained on the low temperature behavior of water showed a well defined reduction peak (responsive to the presence of different water concentrations) close to the cathodic limit of the solvent. An analysis of the peak characteristics show that the reduction is not a simple diffusion controlled process. Nevertheless, from the peak current density it is possible to obtain an activation energy which was 4.4 kcal typical for diffusional processes involving ionic species in molten nitrates. Experiments were carried out at 300°C to examine the rate of absorption and desorption of water by the melt. It was observed that argon, carbon dioxide, or oxygen saturated with water at a vapor pressure of 19.6 mm took approximately 3 min to saturate the nitrate melt with the bubbler below the surface of the melt and 90 min when the bubbler was about 2-3 cm above the melt. (The gas flow rate was $\sim$200 ml min^{-1} and the surface area $\sim$28 cm^2.) On the other hand, water was completely removed by bubbling dry argon through the melt for 20 min. These results show that water may be reversibly removed from the nitrate melt.

The behavior of nitrite and carbonate ions is less well resolved. For example, the solubility of the carbonate ions is very much less than that of nitrite ions, and the apparent rate of carbonate dissolution is also small. Because the products of electrooxidation of carbonate and nitrite are thought to be gaseous,

$$NO_2^- \rightleftarrows NO_2(g) + e \qquad (6)$$

and

$$CO_3^= \rightleftarrows CO_2 + \tfrac{1}{2}O_2 + 2e \qquad (7)$$

fast scan voltammetry or high current density chronopotentiometry may be required for electroanalysis to prevent disturbance of the diffusion layer and hence invalidation of the simple reversible conditions especially at higher concentrations to enable the electroanalysis to be rigorous.

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MASS-TRANSFER CHARACTERISTICS OF NITRATE-BASED SALT MIXTURES*

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Abstract

Molten eutectic $NaNO_3$-KNO_3 is being circulated in three thermal-convection loops constructed of alloy 800 and types 304L and 316 stainless steel. The loops are operated at a maximum salt temperature of 595°C and a salt temperature differential of 235°C. Corrosion specimens contained within each loop are withdrawn for periodic determinations of weight and microstructural changes. Salt samples are analyzed at selected intervals to monitor changes in the composition of the salt. Controlled potential voltammetry is also used to follow changes in the oxidation potential of the salt. Preliminary results indicate low corrosion rates for the austenitic stainless steels in flowing $NaNO_3$-KNO_3. Corrosion rate data from these tests will be used to develop a kinetic model for the mass transfer of Cr, Ni, and Fe as a function of temperature gradient along the salt flow path.

I. Introduction

A eutectic salt mixture composed of 60 wt % $NaNO_3$-40 wt % KNO_3 (draw salt) has been proposed[1] for use in solar thermal power systems as both a solar receiver working fluid and a thermal energy storage medium. Since the feasibility of such a system depends in part on the compatibility of structural alloys with draw salt, experiments are currently under way at Oak Ridge National Laboratory (ORNL) to study the mass transfer characteristics of alloy 800 and types 304 and 316 stainless steel in slowly flowing draw salt under an impressed temperature gradient. The tests are being conducted in closed loop systems and, as such, are complementary to similar experiments being performed at Sandia Livermore Laboratory (SLL) since their salt loops are open to the ambient atmosphere.

II. Experimental Procedures

The test device used for these corrosion studies is shown schematically in Fig. 1. Natural circulation of test salt is induced in a closed loop by controlling the temperature around the loop and thus causing convective flow. Salt samples can be extracted and corrosion coupons can be removed and re-inserted without affecting temperature and chemical conditions in the loop. The loops are controlled at a maximum temperature of 595°C (at a point just below the large surge tank, see Fig. 1) with a minimum temperature of approximately 360°C at the bottom of the cold leg. The resulting salt flow velocity is about 4 mm/s.

Three loops were constructed; each was fabricated from a different alloy thereby resulting in loops of types 304L and 316 stainless steel and alloy 800. Tubing for these loops is in the size range 1.9–2.5 cm OD with wall thicknesses 0.2–0.3 cm. Insert specimens are approximately 1.9 × 0.8 × 0.1 cm. In any given loop test the insert specimens and tubing are of the same nominal compositions, although in the case of 304 stainless steel both normal and low carbon grades are being tested.

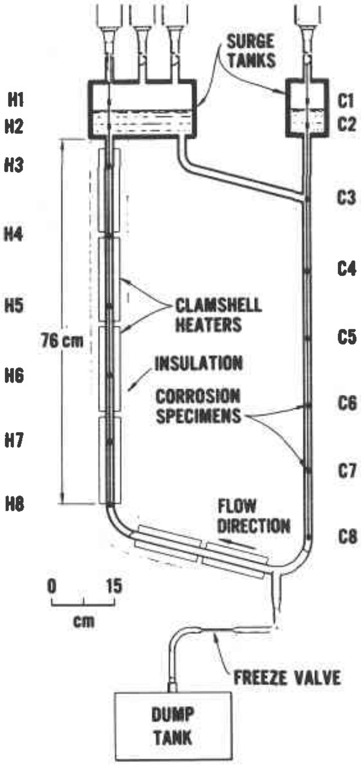

Fig. 1. Thermal-convection loop used in salt studies.

Controlled potential voltammetry is used to monitor electrochemical changes in the loop salt. Current is measured as a function of impressed voltage between iridium electrodes placed in the hot leg surge tank. A typical current-voltage scan of the draw salt in the type 304L stainless steel loop is shown in Fig. 2. In general, any significant change in the constituents of the salt will produce a change in the shape of the current-voltage curve. Additionally, changes in the oxidation potential of the salt can be gotten by noting the change in the voltage required to obtain a given current.

The draw salt was obtained from SLL and was subsequently outgassed and purged with argon to remove H_2O. When the loop was filled with salt and the temperature raised above approximately 520°C, the pressure above the salt rapidly increased. Analysis of this gas showed it to be mainly oxygen, which is a product of the thermal decomposition of $NaNO_3$-KNO_3.[1] Subsequently, care was taken to maintain this pressure by only using oxygen as a cover gas during sampling procedures.

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†Operated by Union Carbide Corp. for the Dept. of Energy under Contract W-7405-eng-26.

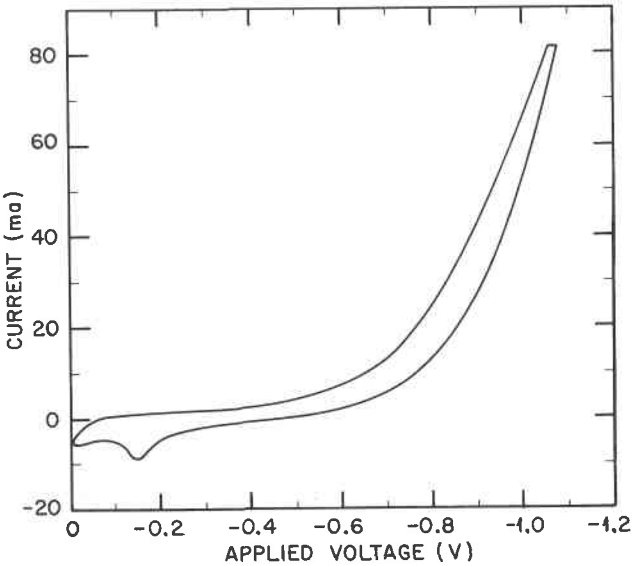

Fig. 2. Typical current-applied voltage scan of the draw salt in the type 304L stainless steel loop.

III. Status of Current Studies

Weight changes have been recorded for the first 1500 h for the three candidate alloys. These results indicate that the short-time corrosion rate of types 304, 304L, and 316 stainless steel in naturally circulating draw salt are quite small (<4 mg/m^2-h) compared to rates measured under similar conditions in HTS salt (53 wt % KNO_3, 40 wt % $NaNO_2$, 7 wt % $NaNO_3$).[3] Data currently being taken at longer exposure times (up to 4500 h) will be used to establish the time dependence of the corrosion processes and will allow comparisons with other oxidizing environments, such as steam and air.

A micrograph of type 316 stainless steel exposed for 1500 h at 595°C is shown in Fig. 3. The duplex oxide layer which has formed on the specimen surface is quite similar to layers seen on types 304 and 316 stainless steel exposed in atmospheric draw salt loops operated at SLL.[2] Scales on the SLL specimens consisted of an outer zone of Fe_3O_4 and an underlying spinel layer containing Cr in addition to Fe. Microprobe analysis and x-ray diffraction of these layers on types 304, 304L, and 316 stainless steel and alloy 800 are currently being performed.

It is apparent that two competing processes are operative in the hot zone of the draw salt-type 316 stainless steel loop: oxidation and dissolution. The oxidation is clearly seen from the micrograph of Fig. 3 while the occurrence of dissolution is evident from measured weight losses and analysis of the salt. Such a salt analysis has been done for the type 316 stainless steel system and the results are given in Table 1. Note that significant dissolution of Cr has occurred.

As shown by the data in Table 1, the nitrite concentration of the draw salt increased to about 2 wt % from its initial concentration of 0.05 wt %. This is consistent with the thermal decomposition reaction

$$(Na,K)NO_3 \rightleftarrows (Na,K)NO_2 + 1/2O_2$$

which is also responsible for the increase in the oxygen pressure over the loop mentioned earlier. The ratio of nitrite to nitrate ions in the salt fixes its oxidation potential and, as such, is a key parameter in analyzing any differences between our experiments in closed systems, where the oxygen activity is controlled by corrosion reactions, and the SLL tests which are performed with the salt in contact with air. Controlled potential voltammetry and chemical analyses of loop salt samples are being used to monitor any changes in the oxidation potential of the salt in the three operating loops.

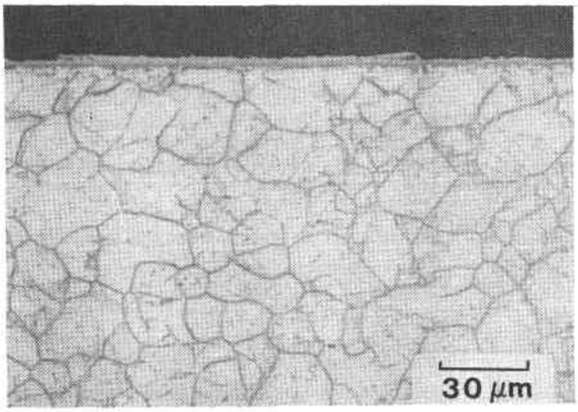

Fig. 3. Cross-section of type 316 stainless steel exposed to circulating draw salt for 1500 h at 595°C.

Table 1. Compositions of Partherm 430 Draw Salt ($NaNO_3$-KNO_3) in As-Received Condition and After 1150 h of Circulation in the Type 316 Stainless Steel Loop

Exposure (h)	Concentration in Salt				
	NO_3^- (wt %)	NO_2^- (wt %)	Cr (wt ppm)	Ni (wt ppm)	Fe (wt ppm)
0	65.5	0.05	3.8	1.5	21
1150	64.4	1.93	63.0	1.4	14

IV. Summary

1. Thermal-convection loops of types 304L and 316 stainless steel and alloy 800 are circulating draw salt ($NaNO_3$-KNO_3) between 595 and 360°C. These are closed systems in which the oxygen activity is controlled by reactions between the salt and its containment material.

2. Preliminary results have indicated relatively low short-term corrosion rates for types 304, 304L, and 316 stainless steel in draw salt. After 1500 h of exposure, specimen surfaces were covered by a continuous oxide layer, but significant Cr dissolution from the steels had also occurred.

3. Analyses of loop salt samples and in-situ controlled potential voltammetry are being used to determine the nitrite to nitrate ratio of the circulating salt as a function of salt decomposition and corrosion product generation.

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CORROSION BEHAVIOR OF ALLOYS

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Abstract

The objectives of this work involves studies in molten nitrates at temperatures in the 450-550°C range to obtain information which will ultimately permit an understanding of the corrosion behavior of structural alloys, such as Incoloy 800, that will be employed in thermal loops in solar power systems. This work has just gotten underway; initial activity will involve studies of species expected to exist in these melts from corrosion of structural alloys, i.e., iron, nickel and chromium.

I. Introduction

While a very large body of information exists on molten nitrates at temperatures in the 200-300°C range, little experimental work has been performed at temperatures significantly above these values[1-4]. Work has been performed to establish the existence and possible equilibria of different species in this melt[3], and the stability range of the melt[5-7]. Gurovich[8] and Bough[9] have reported some data on the corrosion of several metals, in the melt at 500°C, but gave no quantitative description of the reaction products. Metallic iron has been studied in $LiNO_3$-KNO_3[9] and in $NaNO_3$-KNO_3 eutectic[10,11]. In fused $NaNO_3$-KNO_3 the metal acquires an oxide film, (Fe_3O_4), on immersion in the melt; anodization gives rise to a formation of Fe_2O_3. Potentiodynamic studies confirmed the oxide films[2,12-13]. Voltammetric studies indicated that the rate of formation of NO_2^- in the melt was the same as the rate of formation of Fe_3O_4[14] during iron corrosion. A study of mild steel has been performed by Baraka et al.[15,16] in the same eutectic in the 250-450°C range. Their experimental data revealed the formation of a passivating film consisting mainly of Fe_3O_4. The growth of the oxide film proceeds according to a parabolic law, at a rate depending on the temperature of the melt. The same authors[17-19] found that the addition of halides and acidic oxides increased the corrosion of steel while the basic oxides had, in general, a retarding effect. However, above 400°C, basic oxides appeared to increase the corrosion. The corrosion rate also increases with increase in temperature.

Elemental chromium does not appear to have been studied in this melt[2], but some studies of ionic species of this metal in solution have been performed. Thus, dichromate solutions were considered stable in the absence of heavy metals[20]. The cathodic reduction of $Cr_2O_7^=$ is complex; its products are the oxide Cr_2O_3, the soluble chromite CrO_2^- and chromate ions. CrO_3 added to fused KNO_3 has been studied[21].

Nickel metal reacts with the melt, yielding a passivating film of the oxide NiO[11,22]; upon anodization, the proportion of soluble Ni(II) varies with the current density[23].

On the other hand, studies of corrosion behavior of stainless steel are rather scarce in the $NaNO_3$-KNO_3 melt[11,24]. Most studies have been done in $LiNO_3$-$NaNO_3$-KNO_3 mixture by weight gain methods[25-27], but nothing is known about either the kinetics or mechanism of the processes or the stability of the species that are formed in the solution. Water intrusion into nitrate-nitrite salt mixture does not cause serious corrosion effects, but the corrosion results from the presence of impurities such as Na_2O which reacts with water to form NaOH. The latter compound is known to aggravate corrosion in stainless steel systems, especially with respect to intergranular effects[26].

II. Experimental Plan

In our work, current-potential polarization curves will be obtained for each pure metal (iron-nickel-chromium) to establish the range of potentials where passivation/dissolution occurs, and at the same time to obtain information about the nature of the species formed during this process (passivating film, ions in solution, etc.). These experiments will be done in the 450-550°C temperature range. The effects of impurities like nitrite, hydroxide and chloride will be investigated.

After establishing the behavior of each individual metal in particular, studies on Incoloy 800 alloy will be carried out. This study will include steady and non-steady electrochemical methods and spectrophoto-metric techniques.

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STATUS REPORT OF THERMOCLINE THERMAL ENERGY STORAGE STUDIES AT SANDIA NATIONAL LABORATORIES

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Abstract

Sandia National Laboratories is evaluating the thermocline thermal energy storage concept to fulfill the needs of solar thermal energy systems. The motivation for studying the thermocline concept is based not only on the first law of thermodynamics (efficiency), but also on the second law, which takes availability into account. A 1200 gallon engineering prototype tank has been constructed and is currently undergoing testing. Detailed small-scale laboratory experiments which focus on component development and computer code verification have been initiated. Complementary analytical modeling, both one- and two-dimensional, is also underway. The objective of this work is to determine whether thermocline storage is feasible and, if it is, to determine maximum expected performance, in both an engineering and economic sense.

I. Introduction

To fully realize the potential of solar thermal technology , thermal energy storage (TES) becomes a necessity. Sandia National Laboratories, Albuquerque (SNLA) is evaluating the thermocline TES concept to fulfill the needs of solar thermal systems.

Thermocline TES uses the system working fluid to store the thermal energy in a single well-insulated tank. Use is made of natural buoyant forces and the extremely slow diffusive properties of liquids to keep the hot upper layer from the cold lower fluid layer.

The attractive characteristic of thermocline storage is that theory shows it has the potential of being a very efficient storage concept. Often when a claim is made concerning the efficiency of a storage system, the claim is based on the first law of thermodynamics (i.e. an energy balance). Availability and the second law of thermodynamics are not taken into account. However, if one examines TES systems from a second law standpoint, one fact is clear: the more heat that is transferred across a surface area with finite temperature differences, the lower is its overall second law efficiency. Thus the thermocline concept which has one phase that never transfers heat to other media will exhibit a large theoretical second law efficiency.

Thermocline storage is also economically attractive. A single-tank thermocline system consists of a tank filled with the system working fluid and two flow diffusers. With such a simple system, control, initial cost and maintenance cost could be minimal.

The objective of the thermocline project at SNLA is to determine the feasibility of thermocline TES from a theoretical, operational, and economic standpoint. This will be done by testing an engineering prototype (1200 gallon) storage tank, small-scale laboratory test programs, and development of analytical computer models.

II. Prior Development Work

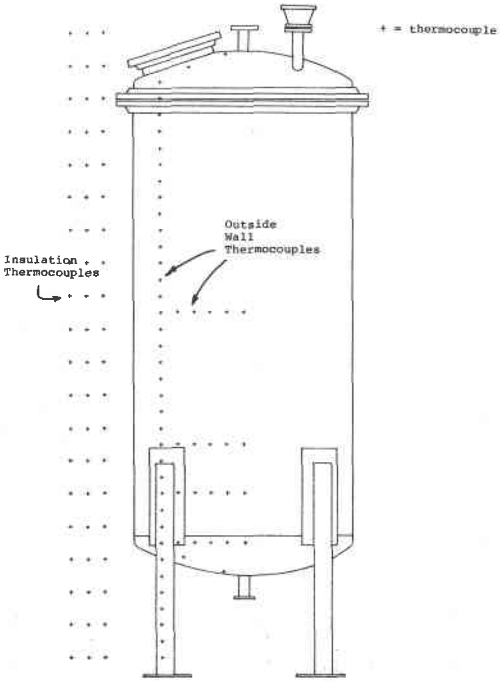
Single media thermocline storage systems have been installed in solar thermal energy systems employing parabolic troughs as the energy collection subsystem. Such thermoclines are at Sandia National Laboratories, Albuquerque (SNLA), Willard, New Mexico, and Coolidge, Arizona.[1,2] The results from tests of these thermocline systems have indicated that a well-designed flow diffuser is imperative to establishing a sharp thermocline. In these first-generation tanks, the width of the thermocline region is typically 20% or more of the entire tank height. It appears that current diffuser designs do not prevent mixing of the hot and cold fluid layers; indeed, some designs promote mixing. A further source of thermocline degradation in tanks with thick conducting walls is thermal conduction from the hot to the cold layers along the conducting wall.[1] A third source of degradation is the diffusion of heat from the hot layer to the cold layer at the thermocline interface. Research at SNLA is currently being conducted to evaluate and minimize these second law inefficiencies that result in thermocline degradation.

III ENGINEERING PROTOTYPE TANK

Design

A 1200 gallon engineering prototype storage tank has been designed and installed at the Midtemperature Solar Test Facility (MSTF) located at SNLA. The oil storage tank design was constrained to be representative of standard commercial ASTM fabrication techniques and be compatible with a single media thermocline storage test program. A sketch of the thermocline tank is shown in Figure 1. The tank has a removable top so that devices such as floating diaphrams, improved diffusers, etc. may be placed in the tank. Personnel access to the tank is through a manhole located on the upper head. Nine ports were also built into the upper head for instrumentation access. The center port is used for fluid entry. The tank is constructed of 3/16 inch mild steel plate and is supported on four stainless steel legs. Stainless steel was chosen for the leg material because of its low thermal conductivity.

FIGURE 1. THERMOCLINE TANK SHOW EXTERNAL INSTRUMENTATION



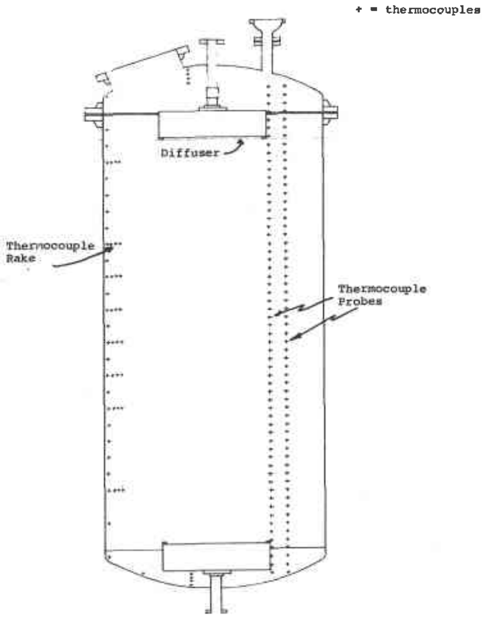
Insulation

The side wall of the engineering prototype tank was insulated with sixteen inches of fiberglass insulation. The insulation was applied in four inch thick batts. A skirt was applied to the bottom of the tank and filled with the fiberglass insulation. At the top of the tank, an aluminum jacket used to protect the side wall insulation was extended upward above the upper head of the tank, and the resulting space was filled with fiberglass insulation. The tank was mounted on two inches of Johns-Manville Marinite^{R} insulation to prevent a direct thermal short of the tank legs to the concrete pad.

Instrumentation

A primary goal of the instrumentation on the engineering prototype was to provide accurate radial and axial temperature profiles of the tank. This has been accomplished, as shown in Figure 2, by using two vertical probes of sixty thermocouples each in conjunction with thermocouples just inside and outside the tank wall. In addition, thermocouples were placed between the four-inch layers of the batt insulation to define the temperature profile out to ambient conditions. At the inside wall, thermocouple rakes (see Figure 3) were installed at eight locations (see Figure 2) to indicate the possible presence of a boundary layer. At twenty-five locations in the tank the radial temperature profile is defined from near center of the tank to the outside of the wall by four thermocouples. At thirteen of these locations the profile is extended through the insulation (see Figure 1). Knowledge of these temperature profiles allows integration of the thermal energy content of the tank and serves as a guide to knowing when thermal equilibrium has been achieved.

FIGURE 2. INTERNAL INSTRUMENTATION OF THERMOCLINE TANK



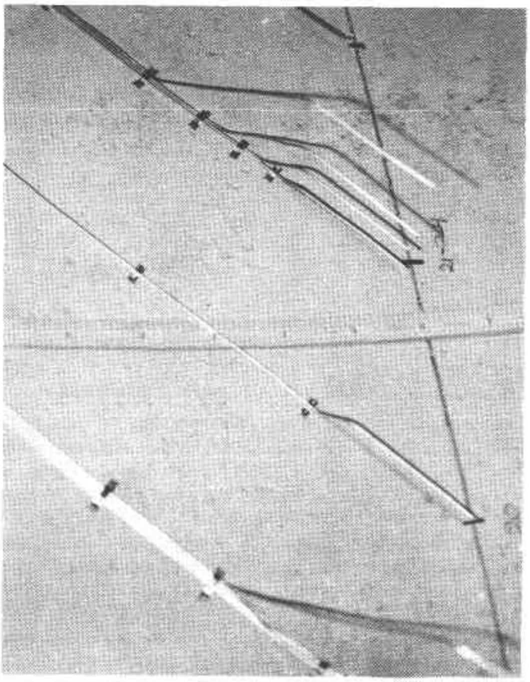
The first series of tests scheduled will determine the heat loss characteristics of the tank. To perform a heat loss test, fluid at a constant temperature is circulated through the tank. The fluid temperature drop is monitored as it moves from the inlet to the outlet of the tank. Since this temperature drop is small (typically less than 5^{o}F), sensitive resistance temperature devices (RTD) are used. The two RTD's, one each at the inlet and outlet of the tank, were calibrated by the SNLA standards laboratory prior to installation.

Fluid flow entering and leaving the thermocline tank is measured using turbine flowmeters. A flowmeter is placed both at the top and bottom of the tank to provide redundancy.

As indicated on Figure 1, thermocouples are also attached to the tank legs to monitor heat loss due to conduction down the legs. Previous experience with hot oil storage tanks in the MSTF has indicated that heat loss through the legs can be an important mechanism.

All data collection is performed using the MSTF data acquisition computer system. This system allows constant monitoring of up to 290 data channels with a scanning time of approximately 20 seconds.

Figure 3 Thermocouple Rakes on Inside Tank Wall



Status of Testing

Instrumentation checkout has been completed and preliminary tests designed to determine steady-state, constant temperature heat loss measurements are underway. Small-scale laboratory tests have determined that the current diffuser design consisting of a wire mesh diverting screen is inadequate and will require replacement prior to starting thermocline stability testing.

IV ANALYTICAL INVESTIGATION

Analytical models are being developed to investigate the thermocline behavior and to correlate the experimental data. The three sources of thermocline degradation which require consideration in the modelling effort are thermal losses at the walls of the tank, diffusion of heat from the hot layer to the cold layer at the thermocline interface and mixing caused by the charging or discharging process.

The diffusion of heat between layers is a small effect.[4] When the tank is charging/discharging fluid at a reasonable flow rate, mixing at the inlet and outlet is the main source of thermocline degradation, while diffusion and wall losses are a secondary concern as long as the tank is well-insulated. On the other hand, if a thermocline exists and the tank is in a static mode (no fluid flow), natural convection heat transfer induced by thermal conduction at the walls is a prime concern. Thus, depending upon whether the tank is in dynamic or static mode, attention may be focused on either the inlet/outlet conditions or the tank walls.

Rahm and Walin[5,6,7,8]developed an analytical solution which applies during charging/discharging operation. A one-dimensional boundary layer model which includes heat loss at the walls is used and unlike other models, is applicable to any geometry. Rahm and Walin's analysis has been extended by SNLA to thermoclines in cylinders (the usual geometry for thermocline tanks) assuming either a cooling or heating wall.

Experimental results by Rahm and Walin in some stably stratified situations indicate that the method can be very accurate. Their thermocline data, however, is insufficient for direct verification of the method for application to thermoclines. Thus, SNLA is performing small-scale laboratory experiments to verify the Rahm-Walin approach.

When the thermocline tank is in a static mode, thermal losses from the walls become the primary cause of degradation. Hess and Miller[9,10] have thoroughly investigated this aspect of thermoclines and Miller has developed a computer model capable of predicting thermocline degradation with a conducting wall. Hess performed well-designed experiments and confirmed the model's accuracy. The computer model solves the two-dimensional Navier-Stokes equations coupled to the energy equation. The computer model for the prediction of static thermoclines has been obtained, and is in the process of being placed on the SNLA computer system.

V LABORATORY INVESTIGATION

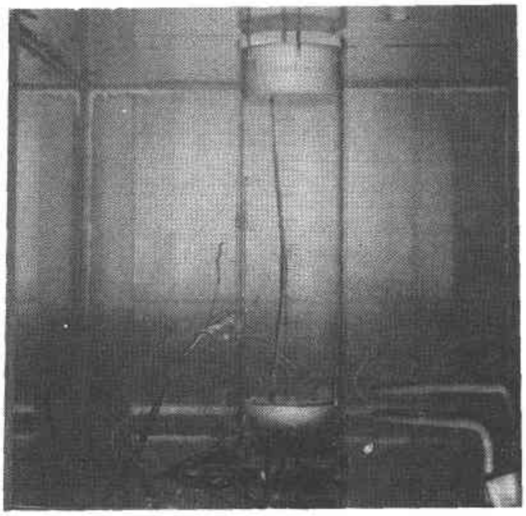
The engineering prototype thermocline tank will provide information concerning subsystem operation and control as well as overall performance data as a result of the extensive instrumentation. However, as is usual with such a large system, changing parameters and hardware is time-consuming and expensive. Thus, small-scale laboratory investigations are currently underway to complement the prototype tank testing and support the development of analytical tools. These investigations examine certain aspects of the thermocline phenomenon in detail.

One of the most important factors contributing towards thermocline efficiency during charging and discharging is the ability of the flow diffusers at the inlet and outlet to minimize turbulence and mixing. To focus on this important thermocline component, an experiment has been constructed to investigate diffusers designs. A diffuser design with diverter plates has been constructed and is presently being installed in a small-scale glass tank. Flowmeters will measure flow rate in and out of the tank, and dye injection techniques will provide qualitative and quantitative data on the performance of the diffuser. This prototype diffuser and the entire experimental facility are designed so that flow configuration may be easily changed to facilitate optimization of the diffuser design. One design consideration is that the diffuser should have the shortest possible axial length to maximize the useful storage capacity of the tank. Low pressure drop through the diffuser is desirable also.

Since the flow through the diffuser is extremely complex, parallel analytical work on the diffuser design is not contemplated.

Another small-scale experiment is being conducted to investigate the applicability of the one-dimensional analytical method of Rahm and Walin (see Figure 4). The experiment consists of a small, plastic closed tank instrumented with 34 thermocouples. The tank will be filled with water at room temperature and then immersed in a hot water bath. This process will cause a thermocline to form at the top of the tank which will then commence to travel down to the tank bottom. If experiment confirms the Rahm-Walin theory, then the associated computer program will be modified to account more accurately for the thermal losses associated with a highly conducting wall.

Figure 4 Ram and Walin Test Tank



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EXPERIMENTAL AND THEORETICAL STUDY OF THERMOCLINE DEGRADATION†

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Abstract

A brief review is given of a research program investigating the basic fluid mechanics and heat transfer aspects of thermocline behavior in energy storage systems. The research consists of a three-pronged effort. Theoretical and numerical analyses are developed the results of which are to be compared with a laboratory-scale experiment. The experiment and theoretical approaches are described. The present status of the research program is outlined and anticipated accomplishments demarcated.

I. Introduction

A thermocline energy storage system is based on the notion that a hot fluid layer will remain stably stratified over a colder one. In practice, the realization of such a condition is difficult. Poor diffuser design, heat conduction through the fluid storage medium and along container walls, thermal losses to the surroundings, buoyancy driven motions and transition from laminar to turbulent flow along vertical walls in contact with the fluid medium, all contribute to the mixing of the hot and cold fluid layers. Henceforth such mixing will be referred to here as thermocline degradation.

If cost-efficient thermocline energy storage systems are to become a practical reality, the characteristics of the fundamental processes governing their behavior must be understood and, whenever possible, made predictable.

Prediction capabilities in the form of computer encoded calculation procedures are useful tools for design purposes provided they can be used with confidence over a meaningful range of system variables (operating conditions). Such calculation procedures may be based on numerical schemes solving finite difference forms of complete transport equations or may be based on closed form (analytic) solutions of approximated transport equations. Regardless of the path followed, either route must be tested and evaluated against a standard which, in this work, is a laboratory-scale experiment.

In addition to serving as a test for model guidance, development and final evaluation, the experiment is expected to provide valuable information on the question of transition to turbulence and its influence on thermocline degradation. This information will be of use for extending the calculation approaches mentioned above to turbulent flow regime at a later date.

Whereas due consideration has been given to the question of modeling thermocline storage systems and related flows[1-4] little corresponding experimental information is available[5-7]. To this author's knowledge there is no existing body of experimental data sufficiently detailed to guide the present program of research and possible future work focusing on the problems of instability and transition to turbulent flow in thermocline systems.

II. The Experiment

The experiment is a laboratory-scale mode of a 2-D thermocline storage system. Due to size and material properties limitations it does not provide geometrical and dynamical similarity with currently contemplated life-scale systems. Thus, for example, a typical value of Grashof number in the experiment is $Gr \simeq 10^7$ while that of a real system is $10^{10} \lesssim Gr \lesssim 10^{12}$. Whereas this and similar constraints pose obvious limitations on the "practical" use of measurements derived from the experiment, the data is of value for the quantitative validation of the calculation models. In addition, it is permissible to use the laboratory-scale measurements to anticipate the general qualitative behavior, and perhaps some specific characteristics, of life-scale thermocline systems.

The test section of the experimental apparatus is shown in Figures 1-a and b. Figure 1-a gives the dimensions of the system while Figure 1-b is a picture of the finished test section. The construction material is transparent Plexiglass to allow flow visualization. It should be noted that three aspect ratios (height/width) can be set in the test section corresponding to H/W = 2, 1 and 1/2. The aspect ratio is varied by placing the test section side walls within appropriately spaced grooves machined into the surrounding walls of the test section. Rubber O-ring seals are placed along the periphery of the side wall (plates) to prevent leakage. The bottom wall is fixed to the test section but the top is removable allowing access to the interior for positioning side walls at the desired locations. A rubber gasket is used to seal the top wall of the test section.

Both top and bottom walls of the test section have circular plastic PVC pipe sections attached to them which act as diffusers. The pipe sections have regularly spaced 1/4" holes through which the fluid medium (water) will be made to flow from constant head tanks. The size of the holes and their positions were determined by reference to available literature on the subject[8]. Screens were placed over the pipe sections to improve diffusion of the incoming flow.

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Two Dayton 4500W electrical water heaters will provide hot water to the constant head tanks respectively. The final temperature of the water in the constant head tanks will be monitored to within ± 0.5°C by Chromalox immersion heaters controlled by a circuit in which the sensing element is Fenwall bimettalic switch. The water level in the tanks will be controlled by constant level floats. The water will flow through 1" CPCV tubing from the head tanks to the test section. During the course of an experimental run only one head tank will be used; the high temperature tank (∿ 70°C) for simulating "charging" of the thermocline system, or the low temperature tank (∿ 30°C) to simulate "discharging" of the system.

Preliminary analysis shows that the 1/2" Plexiglass walls of the test section are thick enough to be considered adiabatic for practical purposes. Two series of experiments will be conducted. In one series the side walls in the test section will be made of Plexiglass to simulate adiabatic wall conditions. In a second series, the walls will be made of copper to investigate the effects on the thermocline of heat conduction along the side walls and thermal losses to the environment. Air at room temperature will be made to circulate past the side walls of the test section, along their outer surface. The air will enter and exit through slots provided at the end walls of the test section (see Figure 1).

Temperature will be measured by means of 24 gauge copper-constantan thermocouples. Measurements will be made as a function of time with the help of an Autodata Nine at ten locations on one side wall and ten locations in the symmetry plane of the flow. The temperature measurement technique has been developed, in part, in reference 9.

Flow visualization will be performed by injecting dye and/or particles at various locations in the flow. Among the possible coloration techniques, that described in ^{10} looks particularly promising. Since the flow moves slowly (∿ 0.5 in/min) it should be possible to make fairly accurate quantitative determinations of velocity. Recordings will be made on 35 mm. film and, possibly, video tape.

Flow through the thermocline will be controlled by needle valves and measured by rotameters to within ± 2% of maximum velocity. Thermocouples positioned at the inlet and exit points in the test section will allow temperature to be monitored continuously at these positions.

III. Numerical Calculations

Appropriate transport equations describing a 2-D thermocline energy storage system are given by:

Continuity

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} = 0 \qquad (1)$$

Momentum (x coordinate aligned with direction of gravity, g_x).

$$\rho(\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y}) = - \frac{\partial p}{\partial x}$$

$$- (\frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y}) + \rho g_x \qquad (2)$$

$$\rho(\frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y}) = - \frac{\partial p}{\partial y}$$

$$- (\frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y}) \qquad (3)$$

Energy

$$\rho c_p(\frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y}) = - (\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y}) \qquad (4)$$

In the above equations the τ's and q's are components of the shear stress tensor and conduction flux vector respectively. In addition to the conservation equations it is necessary to prescribe empirical expressions for the physical properties of the fluid medium.

Equations 1-4 together with the physical property auxiliary relations and appropriate boundary conditions are solved by means of the calculation scheme described in reference 11. The calculation scheme - denoted as REBUFFS for Recirculating Buoyant and Forced Flows Solver - derives its parentage from the TEACH - 2E family of codes developed at Imperial College[12]. It has been extended to include time dependent effects and large variations in density (which cannot be modeled using the Boussinesq approximation). In addition to reference 11, references 13-14 may also be consulted for information pertaining to the calculation scheme.

Among the conditions to be set as boundary conditions it will be necessary to specify the magnitude and sense of the inlet velocity distribution, the initial temperature distribution and the temperature or heat flux conditions at the various walls. In practice advantage is taken of the symmetry plane condition to calculate half of the entire flow domain. No-slip velocity conditions are imposed at all walls. The influence of the diffuser geometry can be modeled approximately on the rectangular grid.

Calculations are presently being performed for the case of a "charging" thermocline with all walls adiabatic. Because of its relative simplicity this has been chosen as the first test case. Boundary conditions will subsequently be imposed which include thermal losses through side walls to the environment. Both "charging" and "discharging" modes will be studied separately, and in connection with a cycle where the sense of the flow is reversed.

The results obtained to date are preliminary in nature and, therefore, are not provided here. However, they suggest that it will be costly to predict the velocity and temperature fields of an evolving thermocline with adequate resolution in space and time for engineering purposes.

IV. Analytical Model

The constraint imposed by costly numerical calculations can be circumvented, in part, by solving analytically, a simpler version of the thermocline problem which retains the dominant heat transfer characteristics of this flow. Thus, for example, while buoyancy-driven motions may arise in a thermocline energy storage system through thermal losses to the environment and heat conduction along the container walls, for aspect ratios H/W < "some value determined experimentally", the effect could be confined mostly to near-wall regions. In this case, it should be possible to "lump" buoyant effects into an "effective" eddy diffusivity within the context of a simple 1-D transient flow analysis.

However, a more persuasive case for simpler modelling can be set forth by arguing that if in the laboratory-scale experiment and in life-sized systems it is found that diffuser design, buoyant effects and thermal losses to the environment make thermocline systems unattractive as storage devices then these effects should be designed-out of the system. Complicated calculation approaches and laborious experimentation will show just how badly thermoclines are degraded by the effects mentioned above. If, as is expected, it is found that these effects seriously influence the cost-efficient performance of thermocline systems it behoves the design engineer to find solutions to these problems; by improving diffuser design and considering possible ways for insulating the inside walls of the fluid medium container. Such changes, fortunately for the theoretist, are in the sense of making the problem simpler to treat through an analytical approach. Improved diffuser design and the elimination of buoyant effects will tend to make the flow one-dimensional. However, as will be shown below, thermal losses to the environment can still be accounted for in a 1-D approach.

The energy equation appropriate for a 1-D transient laminar flow analysis of an idealized thermocline energy storage system (with u positive), corresponding to a "discharging" condition, is given by:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c_p} \frac{\partial^2 T}{\partial x^2} - v_x \frac{\partial T}{\partial x} - \frac{\left[\frac{\delta_i}{k_i} + \frac{\delta_\omega}{k_\omega} + \frac{1}{h_s}\right]^{-1} (T - T_s)}{\rho c_p W} \qquad (5)$$

In words, this equation says that the time rate of change of temperature at a position x and time t in the flow is governed by heat conduction and convection in the flow direction (first two terms on the r.h.s. of equation (5)) and thermal losses to the surroundings (third term on the r.h.s. of equation (5)). In the last term losses are dictated by the conduction properties of a possible insulation material, the metal wall and the surrounding environment (air). Recognizing that there are characteristic parameters in this system a dimensionless form of equation (5) is given by:

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial \eta^2} - Pe \frac{\partial \theta}{\partial \eta} - Nu \frac{H}{W} [\theta - \theta_s] \qquad (6)$$

where Pe and Nu are the Peclet and Nusselt numbers respectively, H is the height of the thermocline and W its width.

Equation (6) can be solved by the method of separation of variables $^{15-17}$. The solutions (which depend on the type of boundary conditions imposed) involve a considerable amount of algebra which is not given here. The final general result may be written:

$$\theta(\eta,\tau) = \theta_{ss}(\eta) + \phi\,(\eta,\tau) \qquad (7)$$

where $\theta_{ss}(\eta)$ is the steady state solution of Equation (6).

A fairly involved* computer code is being programmed which encompasses all cases of interest to this study. However, by comparison to the numerical calculation approach of the previous section the present code should be considerably faster to execute and require much less storage.

Calculations using the analysis outlined above will probably be available by mid-October. A decision as to the usefulness of this modeling approach must await its relative evaluation with corresponding experimental measurements and numerical calculations.

V. Status of Research Program

Experiment

The experimental test section has been constructed. It is being assembled with the remainder of the apparatus and should be ready for testing by the end of August 1980. Final runs including variations of the different parameters of interest to this work should take place September-November 1980.

Numerical Calculations

The calculation code is presently being used to predict one test case (described in the main text) by means of which various code-related parameters such as time step-size, under-relaxation factors, number of tridiagonal matrix sweeps etc. may be optimized. When this condition is attained several cases corresponding to various experimental conditions will be predicted on intermediately refined grids.

Analytical Model

This has been completed and is presently being encoded to predict the various experimental test cases; albeit with the simplifications that this modeling approach includes.

Calculations from the numerical and analytical approaches should have been completed by November 1980. Their relative evaluation and their evaluation with respect to the experiment will be performed at that time.

VI. Summary

It is believed that the experimental and calculation approaches being investigated in this work will be of significant value for determining the performance of life-scale thermoclines and, hence, their potential as energy storage systems. Quite apart from the eventual fate of such systems, the study offers the unique opportunity to investigate transition and turbulent flow (induced by buoyancy driven instabilities) of a stratified flow adjacent to a thermally conducting vertical surface.

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* In the sense that the logic required to deal with all possible boundary and initial conditions with one algorithm is complex.

VII. Acknowledgements

The authors thank Mr. W. Winters for his continued interest in the research program. We wish to acknowledge frequent and stimulating discussions held with Dr. P. LeQuere (CNRS, France) in relation to the numerical calculation approach. Likewise, thanks are due to Professor L. Month for her valuable contribution to the theoretical analysis conducted in this work. We are grateful to the U.C. Berkeley Mechanical Engineering Department for the construction of the experimental test section. Finally, thanks go to Ms. L. Petersen for the typing of this manuscript.

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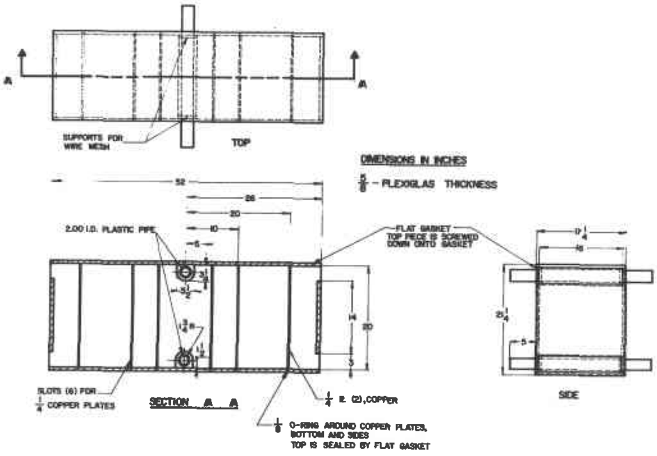

Fig. 1-a: Dimensions of thermocline test section.

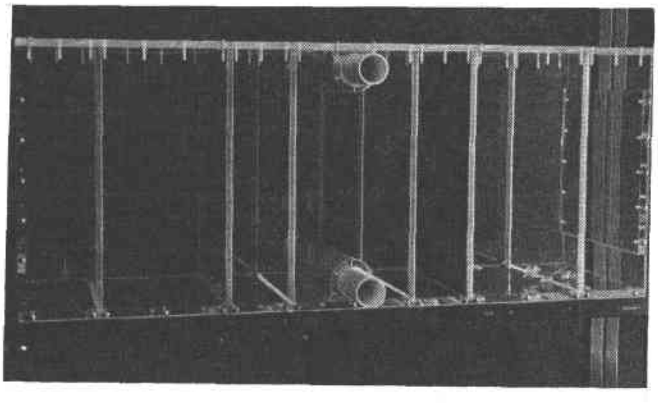

Fig. 1-b: Photograph of fabricated test section.

DISH-MOUNTED LATENT HEAT BUFFER STORAGE*

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ABSTRACT

A parabolic dish solar thermal power plant comprises a field of parabolic dish power modules. Each module is composed of a two-axis tracking parabolic dish concentrator, which reflects insolation into the aperture of a cavity receiver at the focal point of the dish. The heat generated by the solar flux entering the receiver is removed by a heat transfer fluid and is used to drive a small heat engine/generator mounted adjacent to the receiver. Since thermal buffer storage can improve upon system performance, a task is being conducted in support of the Thermal Energy Storage for Solar Thermal Applications Program (TESSTA). The objective of this task is to develop appropriate dish-mounted latent heat storage subsystems for Rankine, Brayton, and Stirling engines operating at 427°C, 816°C, and 816°C, respectively. This paper describes the effort completed during FY 1980 concerning storage requirements definition, conceptual design, media stability and compatibility tests, and thermal performance analyses.

I. INTRODUCTION

As a first step toward commercialization of the modular point-focusing distributed receiver solar thermal electric system, the U.S. Department of Energy is planning a series of experiments to help establish their technical, operational, and economic aspects. In these experiments small heat engines with attached electrical generators will be mounted adjacent to the receivers located at the focal point of each parabolic dish concentrator. The power conversion system requirements are the following:

1. Rankine cycle - 15 kW_e organic engine, operating at ~427°C
2. Brayton cycle - 18 kW_e open cycle Brayton engine, operating at ~816°C
3. Stirling cycle - 15 kW_e kinematic Stirling engine, operating at ~816°C

Since insolation varies with diurnal and seasonal cycles as well as with local cloud cover, the thermal energy entering the receiver is subject to corresponding time-dependent fluctuations. The heat removed from the receiver also fluctuates. These fluctuations, especially rapid fluctuations due to cloud cover, can be attenuated by incorporating latent heat buffer storage. The addition of thermal storage to receivers is referred to as "thermal buffering" since it provides a buffer between the variations in solar flux and the heat delivered to the heat engine. This buffering reduces engine part-load operation, improves efficiency, and alleviates control requirements. Buffer storage also reduces engine start/stop cycles (resulting from cloud cover), which is an important factor in extending engine life.

The degree of attenuation or buffering provided by the receiver depends upon its thermal inertia, heat flow paths, and control logic. Each power conversion unit requires a different amount of thermal buffering to handle variations in short-term insolation. Hence, a task was initiated during FY 1980 in support of the TESSTA Program to define the requirements for latent heat thermal energy buffer storage subsystems and for subsystem research experiments for point-focusing distributed receivers equipped with Rankine, Brayton, and Stirling power conversion cycles. The storage requirement definition includes thermodynamic and economic performance analyses to determine the need for thermal energy buffer storage and, if necessary, to identify optimum size and candidate storage concepts which meet specified cost and weight goals and to develop specific component and subsystem hardware.

II. PROJECT EFFORTS

The task described above comprises both in-house and contracted efforts as shown in Table 1.

Table 1. Development of Latent Heat Buffer Storage

Activity	Effort Mode
PCM selection, containment	In-House
Subsystem requirements, design, development, and research experiment (SRE)	Contracted
Solidification control and heat transfer enhancement	In-House and Contracted
Heat transfer computer code	In-House
Material corrosion tests	In-House

Task activities are briefly described below.

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*The program described in this paper is managed by the Jet Propulsion Laboratory, California Institute of Technology, for the U.S. Department of Energy through an agreement with NASA. The NASA Lewis Research Center supports the program in the area of power conversion.

PCM Selection and Containment

Table 2 shows the PCM (phase change material) candidate containment combinations which have been selected for detailed investigation on the basis of their applicability as dish-mounted latent heat buffer storage media.

Several mixtures of alkali-alkali halides and alkaline earth-alkaline earth halides form two stratified, immiscible molten phases in which one phase is rich in metal and the other in salt concentration. By using the lower melting, lighter metal-rich phase as the heat transfer medium and salt-rich denser phase as the phase change material for thermal energy storage, undesirable solidification on the heat transfer surface may be prevented. These mixtures offer the following advantages:

1. The salt crystals formed in the energy discharge period will precipitate and avoid the blockage of heat transfer.
2. The heat conductivities of solid and melt can be increased by the addition of a small fraction of metal.
3. The monotectic temperature is constant and spans over a wide range of concentration which provides a degree of freedom for the system design.
4. The metal itself may function like a getter metal to "get" the impurities and inhibit corrosion.

For buffer storage applications, the Na-NaCl mixture has been selected because of its monotectic temperature of ~ 795°C as shown in Figure 1.

Subsystem Requirements, Design, and Development

The major objectives of this effort are the following: (1) identify the requirements for latent heat thermal energy buffer storage subsystems for point-focusing distributed receivers equipped with Rankine, Brayton, and Stirling power conversion cycles; (2) design, fabricate, plan, conduct, and analyze subsystem research experiment requirements for the development of attractive receiver-integrated thermal energy buffer storage subsystems; and (3) explore and identify concepts, methods of fabrication, materials, and subsystem integration techniques which will permit reduction in weight, cost, and energy loss associated with thermal energy storage subsystems.

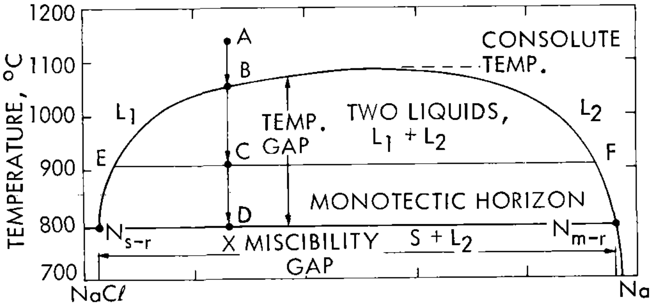


Figure 1. Sodium and Sodium Chloride Phase Diagram

Table 3 shows the details of the three industrial contracts awarded during FY 1980. The following tasks have been identified for the contracted effort.

1. Thermal Buffer Storage Requirement. Dynamic performance, cost, weight, control, and structural design characteristics of the dish-mounted heat engine in the absence and presence of a buffer storage system will be generated to explore the utilization opportunity, advantages, and the required capacities of latent heat thermal energy buffer storage. The thermodynamic and economic performance of the integral system with and without buffer storage will be established by simulating the behavior of the system under time-varying insolation and meteorological conditions of a specified geographical location over an entire year.

2. Parametric Evaluation. System integration and trade-off studies for various buffer storage options, which are different in concept, material, and capacity, will be performed to quantitatively assess the technical and economic advantages of the conceptual designs of latent heat thermal energy buffer storage. Three conceptual designs

Table 2. Selected PCM Candidate Containment Combinations

Application/ Temperature	Salt Composition (By Weight)	Melting Point	Containment Material
Organic Rankine	61 KCl-39 $MgCl_2$	435°C	SS 316 & 321
Brayton, Stirling	66.9 NaF-33.1 MgF_2	813°C	SS 316, 321, and 430
Brayton, Stirling	75 NaCl-25 Na	795°C	SS 316, 321, and 430
Brayton, Stirling	100 NaCl	802°C	9 Cr/1 Mo alloy steel

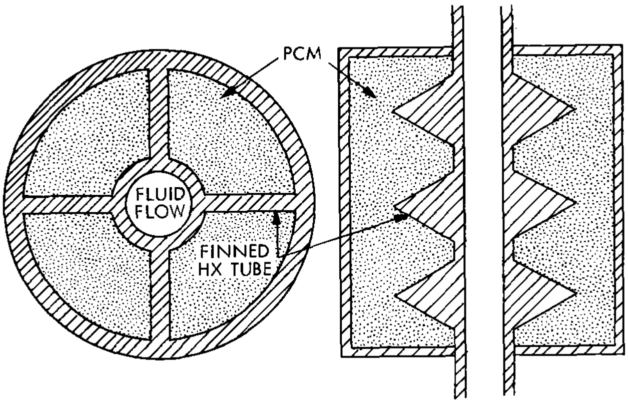
of the receiver/buffer storage/engine integral system will be developed which will meet the receiver/buffer storage cost goal of \$10-15/kW (1980 dollars) and a total weight goal of 680 kg at the dish focal point.

3. Development Requirements. Development requirements including system analyses, materials, components, fabrication, assembly, testing, and control required to carry the conceptual designs into successful hardware demonstration and eventual mass production will be identified.

4. Subscale Experiment Design. A detailed subscale experiment design will be performed from one of the three conceptual designs developed. The subscale experiment design will include drawings of sufficient detail for complete fabrication and testing, fabrication costs and schedule, required instrumentation and test plan, material lists, and test data to be collected and associated costs.

Solidification Control and Heat Transfer Enhancement

In a latent heat storage system, the heat transfer area required for a given quantity of heat depends strongly upon thermal conductance, particularly near the heat transfer walls where solidification occurs. High heat transfer rates (resulting in reduced heat transfer areas) and the corresponding energy storage system costs can be achieved if suitable techniques are developed for the solidification control of the latent heat materials. Such techniques include active and passive control of the buildup of solids on the heat transfer surface and bulk additives as conductivity parameters. Since the present thrust is on the development of dish-mounted, receiver-integrated thermal energy buffer storage systems, no active control techniques such as scraping, agitation, or electromagnetic field application are considered. The emphasis is on passive techniques such as wall configurations and surface coatings along with the addition of bulk additives as conductivity promoters. The following tasks are being conducted to determine experimentally (1) the effects of PCM containment wall geometry and configuration, including concave and convex external and internal surfaces; (2) thermal conductivity enhancing additives; and (3) various types of surface finishing and coating of heat exchanger surfaces on PCM solidification. Attractive solidification control options will be identified which will promote heat transfer in a distributed dish receiver integrated latent heat thermal energy buffer storage system as shown in Figure 2.



- RADIAL FINS
- AXIAL FINS
- METAL MATRIX AND WOOL
- MINI HEAT PIPES
- SURFACE COATING
- BULK ADDITIVES

Figure 2. Concepts for Solidification Control

Heat Transfer Computer Code

A computer program called High Temperature Energy Storage (HTES) has been developed and assembled to simulate a parabolic dish receiver which has latent heat buffer storage. The model predicts the performance of the dish-mounted receiver under varying solar flux, ambient temperatures, varying amounts of latent heat buffer storage, and different thermal control techniques. The program handles the receiver/thermal energy buffer storage system on a nodal basis, and hence is capable of yielding local receiver and receiver coolant temperature variations for the transient simulation. Various designs of receiver/thermal energy buffer storage combinations can be easily modeled to identify

Table 3. Requirements Contracts

System	Application	Contractor (Start Date)	Receiver	Engine
Dish Rankine	Small Community Solar Thermal Experiment, grid connected	Ford Aerospace and Communications Corporation, Newport Beach, CA (4-28-80)	1) Direct heated metal shell 2) Sodium pool	Barber-Nichols Organic Rankine
Dish Brayton	Isolated Load, Engineering Systems Experiment	Garrett AiResearch Manufacturing Company of California, Torrance, CA (9-29-80)	1) Plate fin	TBD
Dish Stirling	Advanced Solar Thermal Power Systems	General Electric, Cincinnati, OH (4-2-80)	1) Heat pipe 2) Direct heated	P-40 United Stirling

attractive concepts. A typical output of the program is shown in Figure 3. The computer results yielded the following conclusions:

1. PCM thermal conductivity and interface thermal resistance are critical factors affecting the performance of a thermal energy buffer storage subsystem. These factors will affect receiver cavity temperature, subsystem heat extraction rates, thermal lag, and subsystem thermal efficiency. The effects worsen as storage capacity increases.
2. By heat transfer enhancement of PCM (such as the use of bulk additives, mini heat pipes, metallic meshes, screens or other materials) and by the increase of contact area with PCM, thermal resistance problems can be alleviated significantly.
3. The results indicate that in certain configurations without heat transfer enhancement the subsystem will not work satisfactorily.
4. The results also show that the fluid inlet conditions (temperature and flow rate) can affect the transient behavior of the subsystem. Hence, fluid flow control is an important aspect of latent heat buffer storage designs.

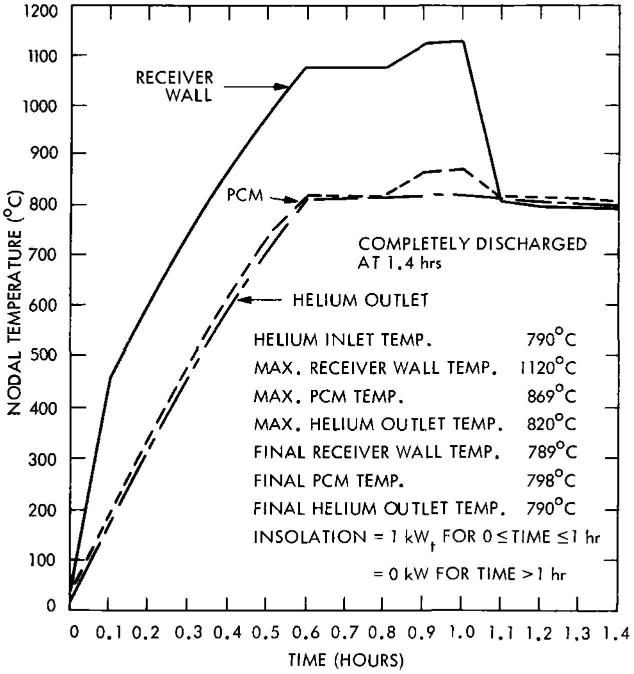


Figure 3. Effect of 4.0 kg of PCM Storage (NaF_2 - MgF_2)

Material Corrosion Tests

Containment materials and corrosion experiments are being conducted under thermal cycling conditions to characterize molten-salt corrosion behavior. Both capsule and free convection loop experiments are planned to obtain realistic corrosion data. The specific experiments are as follows:

1. Capsule Tests (see Figure 4)
    - a) Salts to be Tested
        - i) 69.8 NaF/MgF_2 in SS 316, 321, and 430
        - ii) 75 NaCl/Na in SS 316, 321, and 430
        - iii) NaCl in 9 Cr, 1 Mo, and SS 430
    - b) Conditions
        - i) High purity
        - ii) High purity + gettering (Zirconium)
        - iii) Commercial purity
        - iv) Commercial purity + gettering (Zirconium)
    - c) Test Times: 500, 2000, and 8000 hours
    - d) Capsule Description
        - i) Total number of capsules = 108
        - ii) Most capsules to contain a tensile sample
        - iii) Four tensile samples outside the capules for each time and temperature
        - iv) Weight changes on tensile sample
        - v) Vacuum test atmosphere
    - e) Special Capsules
        - i) One commercial purity + getter capsule will be tested in a tube furnace with N_2 flowing as cover gas to obtain rapid temperature cycling. Each of these capsules will be instrumented with a thermowell.
        - ii) One thermowell capsule will be included in each group of samples to assure full melting and solidification of the test salt.

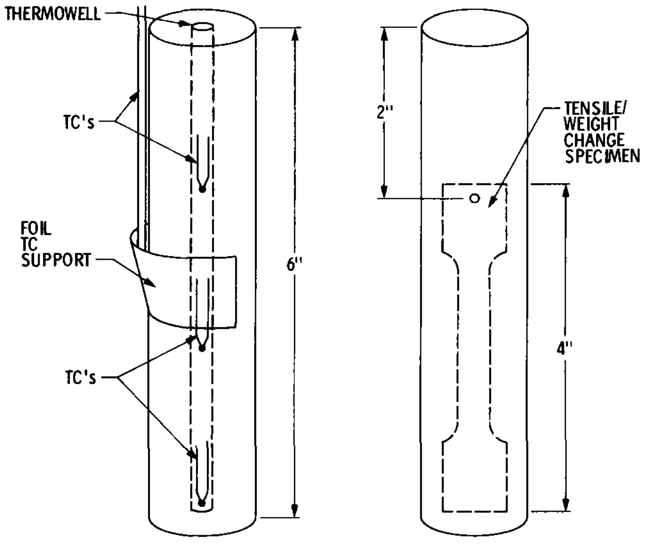


Figure 4. Test Capsules

2. Thermal Circulation Loop Tests (see Figure 5)
    a) 8 loops
    b) Each to be commercial purity salt + getter
    c) Test time = 8000 hours
    d) Each loop to contain 8 tensile samples, 4 in the hot vertical leg and 4 in the cold vertical leg.

Material corrosion experiments, scheduled to be completed by the end of March 1982, are expected to yield the following results:

1. Maximum corrosion to be expected in system
2. Model of corrosion mechanism to allow projection of data to longer times
3. Mechanical property changes of containment material
4. Separation of material aging effects and salt corrosion effects
5. Demonstration of less expensive containment material using less critical material (Cr and Ni)

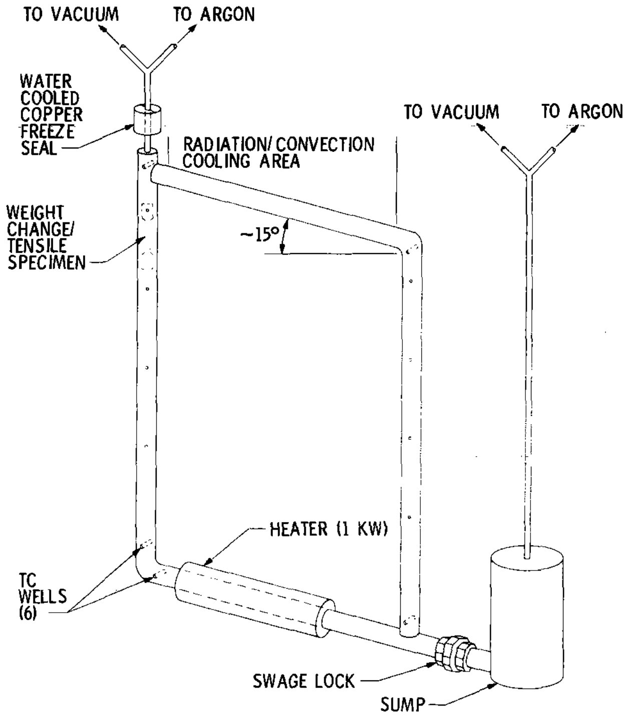


Figure 5. Thermal Convection Loop

STORAGE REQUIREMENTS DEFINITION AND SRE DESIGN FOR DISH STIRLING SYSTEMS

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Abstract

A direct dish Stirling solar receiver (DSSR) and a heat pipe solar receiver with TES (HPSR) are described for which the cost effectiveness and thermal performance are being analyzed, minute by minute, over one year of solar insolation. Using existing designs of these two receivers, parametric performance and cost studies are underway to determine the influences of adding varying amounts of TES to the DSSR and of providing fossil fuel combustion and of varying the levels of TES in the HPSR. The thermal modeling of the two receivers has been completed and the criteria and programming for the economic analysis have been documented. After completing the parametric analysis, alternative design concepts for TES in both systems will be developed, subscale research experiments (SRE) will be suggested, TES development needs will be identified and recommendations will be made for future experimental and analytical efforts.

I. Introduction

Analytical and design work is currently underway to assess the performance capabilities and future development avenues for the use of latent heat in two types of solar receivers. These receivers are intended for use at the focal point of a two axis, tracking parabolic concentrator and delivering power to a Stirling engine-generator system capable of producing about 25 kW_e. For both of these systems the system definition, cost and performance characteristics are to be documented and the utilization opportunity and economic performance are to be determined over a one year period of solar operation. The systems are to be operated as each system was originally developed or with the addition of varying amounts of latent heat TES or of a fossil fuel combustor burning natural gas. Additional solar receiver design modifications are to be conceived as TES configurations of at least two types. These concepts may serve as the basis for future design effort if they appear advantageous. An evaluation of the development efforts, schedule and costs necessary to further advance the more promising TES concepts is required and recommendations are to be made for two types of SRE to explore the technical feasibility and economic merits of these concepts in later efforts.

II. System Descriptions

Two types of solar receivers are being studied. The first involves a dish Stirling solar receiver (DSSR), shown in Figure 1, which is being developed by Advanco Corporation. It features a conical copper plate solar heat exchanger protected from oxidation on the surface by means of oxidation resistant alloys; the Stirling engine heat exchanger tubes are contained within and external to the cone. Solar heat is applied directly to the Stirling engine through the copper cone. Fossil fuel heat is applied to the back surface of the cone and to those HX tubes internal to the cone. The system is operated continuously with a minimum of 10 percent power input through the combustor. As solar insolation changes, the heat supply to the engine is provided by modu-

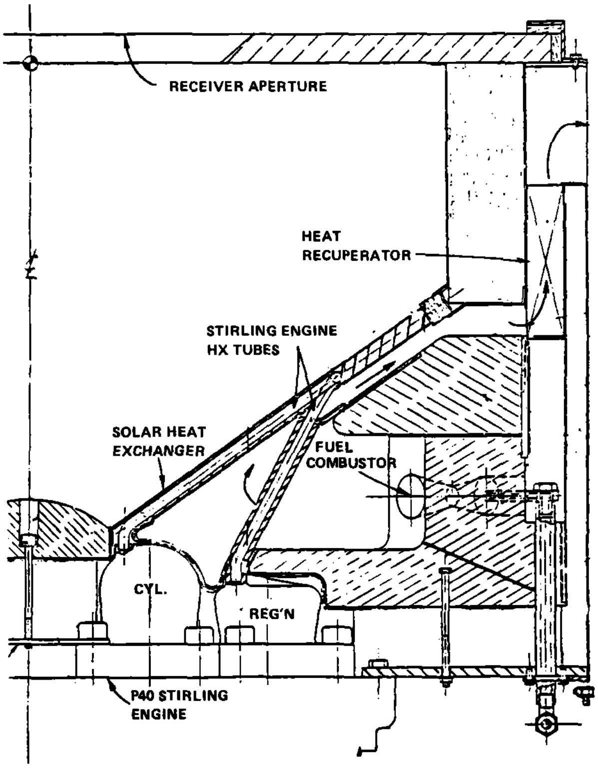

Figure 1. Advanco Dish Stirling Solar Receiver (DSSR)

lating the combustor power. While no TES is provided in the original design, the present study considers the addition of limited amounts of TES along the surface of the cone or by other means. Concepts envisioned, but not yet defined, include heat transfer from the TES to the cone by conduction or by radiation.

Key design factors necessary to the performance and economic analysis over a one year solar insolation period are shown in Table 1.

Table 1. Receiver Performance and Operational Data for DSSR Baseline Design

Concentrator Diam.		9.77 m
Active Concentrator Area		74.0 m^2
Concentrator Efficiency		0.9259
Focal Plane Power		68.5 kW_t
Aperture Diam.		20 cm
Intercept Factor		0.99
Solar Power Input, Rated (at 1 KW/m^2 insolation)		67.8 kW_t
Receiver Losses		
Reflection	0.49 KW_t	
Reradiation	3.4 kW_t	
Convection	3.06 kW_t	
Conduction	1.00 kW_t	
Total Receiver Losses		8.16 kW_t
Receiver Efficiency		0.879
Max. Power Output		59.6 kW_t
Min./Nominal/Max. HX Surface Temp. (at Design Point)		1630/1735/1845°F

COMBUSTOR	
Minimum Required Combustor Power (10% Turndown)	6.6 kW_t
Maximum Required Combustor Power to Engine	66.2 kW_t
Combustor Efficiency	0.575 expt'l
Operating Mode	Variable Turndown
STIRLING ENGINE/GENERATOR	
Engine Thermal Power	66.2 kW_t
Engine Efficiency	0.396
- 150 ATM He	
- 1800 RPM	
- 1500°F	
Engine Power at Above Conditions	26.2 kW_s
Generator Efficiency	0.93
Generator Output	24.4 kW_e

The second type of solar receiver is the heat pipe solar receiver with TES (HPSR) shown in Figure 2. The solar insolation is absorbed on fourteen thermal diode sodium heat pipes which supply heat to a near-isothermal secondary heat pipe. This heat pipe contains (1) sodium fluoride-magnesium fluoride eutectic TES salt in metal containers and (2) the Stirling engine heat exchanger tubes. Temperature differences influence the pressure of the sodium vapor in contact with liquid sodium on the heat source surfaces and provide rapid heat transfer at a low ΔT to the engine, to the TES and from the TES. Large TES surface areas are available for efficient heat transfer to and from the TES. A fossil fuel combustor also can be added to the outer shell of the secondary heat pipe to provide supplemental power, if needed.

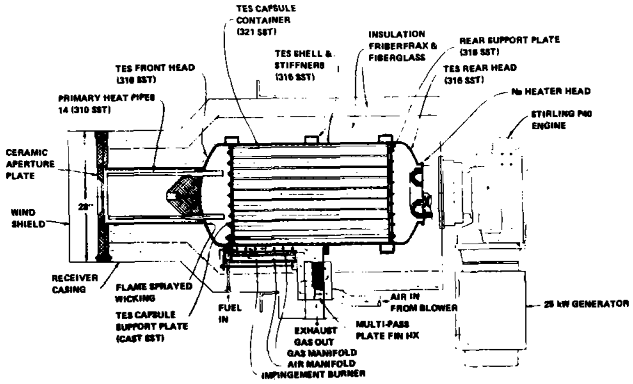

Figure 2. Heat Pipe Solar Receiver with Thermal Storage and Fossil Fuel Combustor

The key design factors for the HPSR are shown in Table 2.

Table 2. Receiver Performance and Operational Data for HPSR Baseline Design

RECEIVER		
Concentrator Dia.		10.3 m
Active Concentrator Area		82.8 m^2
Concentrator Efficiency		0.9259
Focal Plane Power		76.6 kW_t
Aperture Dia.		16.5 cm
Intercept Factor		0.98
Solar Power Input, Rated		75.1 kW_t
Receiver Losses		
Reflection	0.85 kW_t	
Reradiation	3.99 kW_t	
Convection	1.30 kW_t	
Conduction	0.47 kW_t	
Total Receiver Losses		6.61 kW_t
Receiver Efficiency		0.908
Maximum Heat Pipe Temperature		1625°F
Heat Pipe Total ΔT		80-90°F
Power Output		68.5 kW_t
TES (SECONDARY HEAT PIPE)		
Power Input, Rates		68.5 kW_t
Storage Time (Latent & Sensible @ 66.2 kW_t)		0.8 Hour
Thermal Losses		2.3 kW_t

TES Operating Temperature	
Maximum	1535°F
Minimum	1480°F
Range	55°F
Power Output	66.2 kW_t
COMBUSTOR	
Required Combustor Power to TES	68.5 kW_t
Combustor Efficiency	0.65 est'd
Operating Mode	On-Off
STIRLING ENGINE/GENERATOR	
Engine Thermal Power Input	66.2 kW_t
Engine Efficiency*	0.396
- 150 ATM He	
- 1800 RPM	
- 1529°F	
- Sodium Condenser	
Engine Power at Above Conditions	26.2 kW_s
Generator Efficiency	0.93
Generator Output	24.4 kW_e

*Conservative estimate; with sodium heater head efficiency will be about 0.43 for approximately 8.6% greater electric output for the above design.

For both of the above systems the power output is about 25 kW_e. Operating with the same engine-generator set at the identical specified engine-generator efficiencies and engine operating conditions the tabular data provides a close comparison of the characteristics of the two solar receiver systems. This design data was based on the use of the JPL test bed concentrator (TBC); those concentrator characteristics were used to guide the design of these receivers (under separate contracts) and to define the required area and diameter of the concentrator for the purposes of the one year solar insolation performance and economic analyses of this study.

Since the above baseline designs have been based on a significant amount of design study and experimentation supported under separate contracts, they provide a basis around which to perform parametric analysis of variations in TES storage time and use of fossil fuel combustors.

A qualitative visualization of the extent to which the TES and combustor can interact in providing flexibility to the system is shown in Figure 3.

For equivalent power levels the TES, alone, (in the HPSR) provides design level power without the use of fuel provided the solar insolation is uninterrupted. The duration of the power block can be extended, but the power level must be reduced to provide the solar energy for use over the extended period. Likewise, the power level can be lowered to accommodate periods of interrupted solar insolation, otherwise the power output must be terminated briefly during various periods of the day to allow for recharging. In any event the thermal cycling under varying solar conditions will be very much less than a direct receiver without TES or combustor.

The DSSR, with combustor only, provides reliable power over a potentially larger block time at the expense of less solar utilization and greater utilization of fuel. The combustor must be run continually at 10% or more of total power.

The HPSR with TES and combustor provides a high ratio of solar to fossil power and utilizes fossil

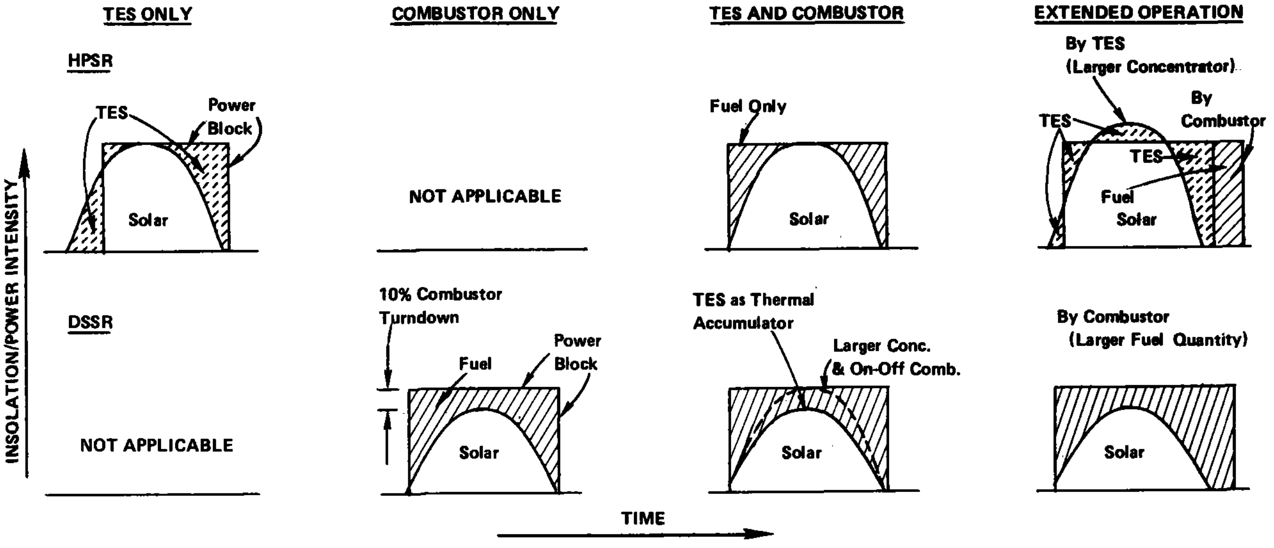

Figure 3. Qualitative Visualization of Various Uses of TES and Fuel Combustors with Daily Solar Insolation

power in a limited way only to make up for deficiencies in solar insolation. The TES provides the system thermal storage to permit efficient on-off combustor power and minimum use of fuel. As presently conceived, the DSSR with a continuous minimum 10% of power by combustor can utilize TES only as a thermal accumulator. With an on-off combustor however, a larger concentrator could be used and fuel consumption could be reduced.

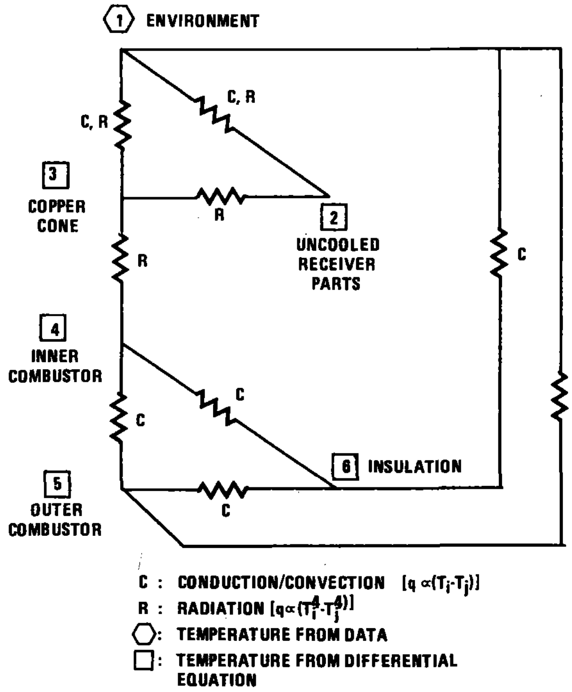

Figure 4. Advanco DSSR Nodal Network

Finally, extended operation of both systems of current design concept can be accomplished by the use of supplemented combustor power. The system with the capability for added TES, however, can introduce a large concentrator and provide some extended period of performance on solar power alone, whereas this added power must be provided by combustor power for the DSSR.

The above generalizations are intended to indicate the general characteristics of these systems. The merits of adding varying amounts of TES to both types of systems will be assessed through the performance and economic analysis.

III. Thermodynamic and Economic Performance Analysis

Based upon the above system descriptions and engineering data for the two systems, the heat flow and energy conversion in each is to be treated by means of a finite element analysis using lumped sum blocks of energy inputed to the system. Solar energy insolation and other data from Edwards AFB on a one minute interval basis is integrated through the finite element computer model. For the DSSR, a six node network is used; a thirteen node network is used for the HPSR. The nodal networks for the two receivers are shown, in electrical network form, in Figures 4 and 5. The combustor and solar heat inputs, as dictated by control logic are introduced into the system. Conduction or convection heat flow between the various nodes is calculated, for example, by:

$$q_{ij} = C_{ij} (T_i - T_j) \qquad (1)$$

and for radiation by:

$$q_{ij} = K_{ij} (T_i^4 - T_j^4) \qquad (2)$$

where q is the heat flow rate in watts, T is the absolute temperature and the subscripts represent node numbers.

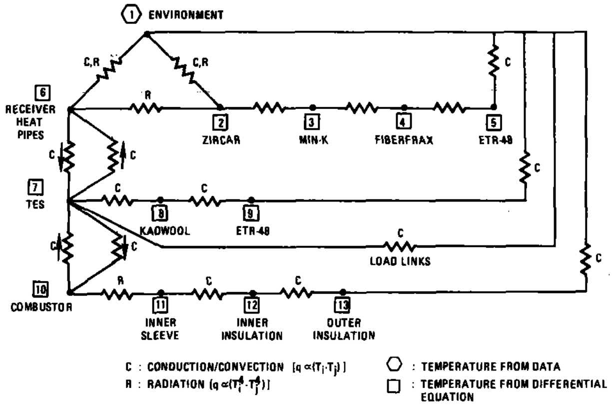

Figure 5. HPSR Model Nodal Network

To solve for the various C's (and R's in radiant heat transfer) it is necessary to know both the tempeature distribution throughout the system and the energy flow at various points. These have been determined from more detailed design studies conducted in the separate receiver development programs. It is assumed that these C's and R's are constant with temperature.

After supplying nodal mass and specific heat data the simultaneous differential equations of transient heat transfer are then written for each node and integrated numerically on the computer. A control subroutine monitors temperatures and makes the appropriate control decisions, such as to start the Stirling engine or to turn down the burner.

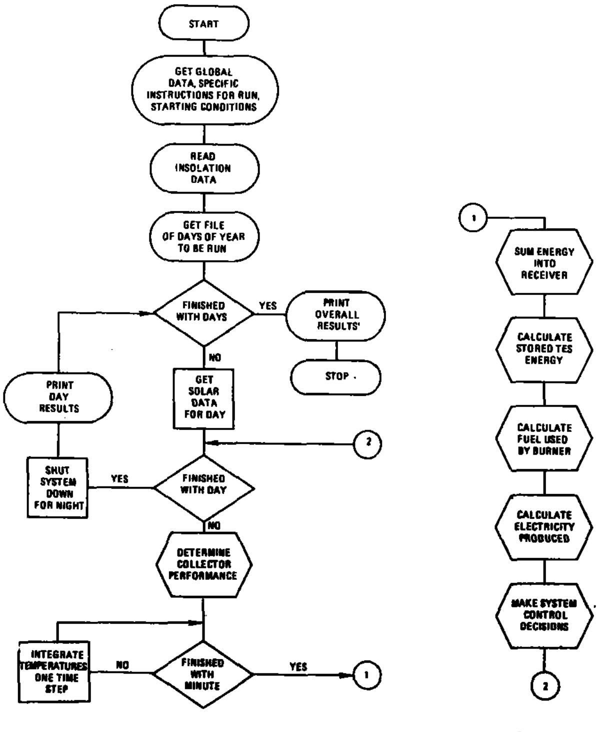

Figure 6. Flow Chart for Solar Insolation Computer Code

Figure 6 shows the flow chart for the solar insolation computer code as the program integrates, minute by minute, the fuel required and the energy produced.

The various cases which had initially been intended for calculation included, for the DSSR, the baseline case with combustor only and 15 minutes or more of TES; they included for the HPSR with TES only, TES durations of 1/4, 1/2, 1, 2 and 5 hours and separate cases for the HPSR, with TES and combustor, at identical TES durations.

The economic analysis of the DSSR and HPSR will be based upon the above cases and will be measured by the cost of electricity developed by accepted utility industry standards. The methodology to be used will be based on JPL 5040-29, "The Cost of Energy From Utility Owned Solar Electric Systems" by J.W. Doane, et al. Input data for the economic analysis include the Utility Description Data and the General Economic Conditions shown in Table 3.

The annual system output and fuel expense will be determined from the performance analyses of the various systems.

Table 3. Table of Nominal Values

Name

Symbol	Nominal Inputs	Nominal Value
	Utility Description Data	
N	System Operating Lifetime	30 years
β_1	Annual "Other Taxes" as a fraction of CI^*_{pv}	0.02
β_2	Annual Insurance Premiums as a fraction of CI^*_{pv}	0.0025
τ	Effective Income Tax Rate	0.40
D/V	Debt to Total Capitalization	0.50
C/V	Common Stock to Total Capitalization	0.40
P/V	Preferred Stock to Total Capitalization	0.10
k_d	Annual Rate of Return on Debt	0.08
k_c	Annual Rate of Return on Common Stock	0.12
k_p	Annual Rate of Return on Preferred Stock	0.08
	General Economic Conditions	
g	Rate of General Inflation	0.08
g_c	Escalation Rate for Capital Costs	0.08
g_o	Escalation Rate for Operating Costs	0.10
g_m	Escalation Rate for Maintenance Costs	0.10
y_b	Base Year for Constant Dolalrs	1978
	Nominal Intermediate Outputs	
k	Cost of Capital to (and internal rate of return in) a "Typical" Utility	0.08
$CRF_{k,N}$	Capital Recovery Factor (8%, 30 years)	0.0888
$\overline{FCR}$	"Typical" Annualized Fixed Charge Rate	0.1483

*Present Value of Capital Investment.

Table 4. Estimated Capital Costs and Operating and Maintenance Costs of Solar Stirling System Components

Component	Capital Investment Cost	Annual O&M Cost (As Percent of Capital Cost
Land	\$1000/acre	N.A.
Concentrator	\$ 100/m²	2%
Receiver	\$ 6/kWt	5%
Thermal Energy Storage	\$ 15/kWt + \$10/kWt hr	5%
Combustor	\$ 4/kWt	10%
Generator	\$ 33/kWe	2%
Stirling Engine	\$2500	10%
Controls	To be Determined (TBD)	10%
Balance of Plant	To be Determined (TBD)	TBD

Tentative capital investment costs and operating and maintenance costs are tabulated in Table 4 for the various system components. These values are being reviewed and are subject to change.

The solar insolation data has been received from JPL; it has been processed to be compatible with the computer system to be used in running the program and a data file has been developed through which the computer program has access to the solar insolation and other weather data. The computer models for both systems have been developed and checked out in brief periods of solar insolation. The various cases are now ready to run for both systems.

IV. Development Requirements

An analysis of the TES development requirements for the two systems is yet to be performed. However, the general nature of these needs is known and the analysis will proceed along these lines.

For effective latent heat TES a more accurate characterization of the characteristics of latent heat materials is needed including thermal and physical properties, cost, availability, health safeguards and safety hazards.

For most effective use of the TES materials a high TES to containment and structural materials ratio is required and improved thermal transport to and from the salt and into and out of the salt are needed. Larger size, individual salt containment systems to minimize containment and structure weight and improved thermal conductivity within the salt are desirable as is the use of internal conductivity enhancement materials or design configurations on an effective basis considering cost, weight and performance. Effective thermal transport to and from the TES is needed to break the TES mass into the most effective mass-to-surface area units for economic salt containment and thermal effectiveness. Thermal transport systems such as alkali metal heat pipes or pumped loop heat transfer fluids can be improved in effectiveness as system TES requirements are changed. For the parabolic concentrator focus mounted systems, the thermal transport within a large heat pipe requires the development of improved, low cost methods of wicking or of supplying liquid sodium to the various heat sources. The investigation of complex powder metal wicks by sintering or flame spraying are possibilities as is the use of pumped loop liquid metal distribution systems.

The more promising of these opportunities will be identified and the definition, scope, cost and schedule for recommended development programs will be estimated.

V. Subscale Research Experiment Design Recommendations

For the HPSR and DSSR receiver systems recommendations are to be prepared for the conduct of TES SRE which would be designed to demonstrate the thermal performance and/or as cost effectiveness of alternative TES materials or design concepts.

One such modular experiment has already been performed under a separate contract effort for the HPSR. This experiment consisted of a single receiver heat pipe conducting heat to a secondary heat pipe containing three full sized TES containers of NaF-MgF$_2$ eutectic and a heat rejection coil simulating the Stirling engine for power extraction. At the TES power rating, this system performed well at all operating angles of inclination and in various heat transfer modes including TES charging, TES discharging, direct heat throughput and mixed mode of heat transfer. Such an experiment could be modified to evaluate alternate, lower cost wicking concepts or to extend performance demonstration to larger diameter and higher wicking distances while still retaining modular size. Pumped liquid metal supply and modifications in TES containment configuration size or conductivity enhancement are additional possibilities.

For the direct receiver with TES additions, SRE effort might involve flat plate TES storage configurations with or without the use of TES conductivity enhancers, the study of higher temperature TES systems (and their materials capability, thermal performance and cost characteristics) which could be used as a re-radiation heat source to the rear face of the present conical receiver. In addition, alternative designs have been envisioned in which Stirling engine heat exchangers have a fewer number of extended length heat exchanger tubes imbedded in a heat receiver with extended surface area for better heat transfer to and from the TES.

Such SRE will be recommended; but, in each case, the experiment must be based upon a well engineered receiver design in order that the experiments can be directed toward a confirmation, in modular form, of the performance expectations anticipated in the design.

VI. Summary

The preparation of heat transfer models and program logic has been completed for minute-by-minute solar performance analysis of the HPSR and DSSR receivers. This capability includes the incorporation of both fossil fuel combustors and TES in extending the flexibility and cost effectiveness of these systems. The cases to be run include the presence and absence of either TES or fossil fuel combustors and a variation in the TES duration. The results of these annual solar insolation studies, when completed, will be incorporated into economic analysis calculations using cost criteria acceptable for electric utility cost of electricity determinations. The relative merits of TES and, of fossil fuel combustion in these studies will be determined within the limits of the analysis. TES design concepts and subscale research experiments in addition to those already in existence will be specified and recommendations will be made at the conclusion of the work in progress to define future TES efforts designed to validate the performance and cost effectiveness of TES concepts and TES operating methods.

THERMAL ENERGY BUFFER STORAGE FOR THE SMALL COMMUNITY SOLAR THERMAL POWER EXPERIMENT

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Abstract

This paper reports the preliminary results of a DOE-funded study carried out by FACC for the application of a latent heat Thermal Energy Buffer Storage (TEBS) Subsystem to the Small Community Solar Thermal Power Experiment (SCSE). The SCSE is a 1-MWe solar thermal electric power generation system currently under development at FACC under Contract No. 955637 from JPL; it consists of multiple Point Focusing Distributed Receiver (PFDR) power modules equipped with an organic Rankine cycle power conversion unit mounted at the focus of each paraboloidal concentrator. Objective of the TEBS is to minimize plant shutdowns during intermittent cloud coverages, thereby improving life expectancy of the major subsystems with attendant reduction in capital investment and maintenance costs.

An SCSE plant performance model modified for operation with a TEBS system is used with time-varying insolation (the JPL Parabolic Dish Test Site for 1979 sampled at one minute intervals) to show that 70 to 80 percent of the potential engine shutdowns due to insolation dropout may be averted with the TEBS System. Optimum TEBS capacities and charge/discharge rate capabilities are being identified for this application.

Results of preliminary design analyses of various TEBS concepts are discussed. The TEBS concept with best potential for the SCSE application is a separately packaged phase change material storage system with active fluid controls to regulate the charge and discharge rates.

I. Introduction

This study was authorized by JPL on April 28, 1980 as an addendum to Phase II of the SCSE program. The study objective is to define the design requirements for a thermal energy buffer storage concept employing phase-change materials for application to a Solar PFDR System equipped with organic Rankine engines. The TEBS concept is intended to provide economic, non-interruptable operation of the SCSE 1-MWe plant during intermittent cloud passages. The scope of the effort encompasses the following study tasks:

(1) Establish the need and the size of latent heat thermal energy buffer storage;

(2) Identify and evaluate different types of latent heat thermal energy buffer storage, which meet JPL specified cost and weight goals;

(3) Make recommendations for specific component and subsystem development needs; and

(4) Define the subscale experiments along with costs and schedule for the successful hardware demonstration of the storage design.

Planned time phasing of these tasks is shown on the Program Master Schedule of Figure 1.

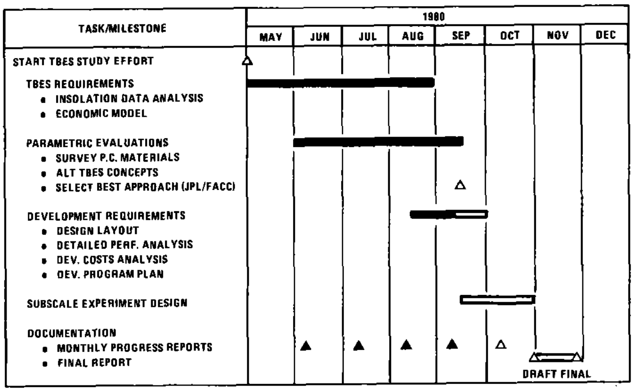

Figure 1. Thermal Energy Buffer Storage Program Master Schedule

II. Baseline System Description

A simplified SCSE system schematic is shown in Figure 2. The system is comprised of four (4) major subsystems: (1) a collector subsystem consisting of a paraboloidal concentrator and a focal plane-mounted cavity receiver; (2) a power conversion subsystem (PCS) consisting of an organic Rankine cycle (ORC) engine, a direct-coupled permanent magnet alternator, rectifier and ancillary equipment; (3) an energy transport subsystem (ETS) consisting of cables, central switchboard and dc/ac inverter and grid interface equipment; and (4) a plant control subsystem consisting of a central microprocessor and associated sensors, instrumentation and peripheral equipment.

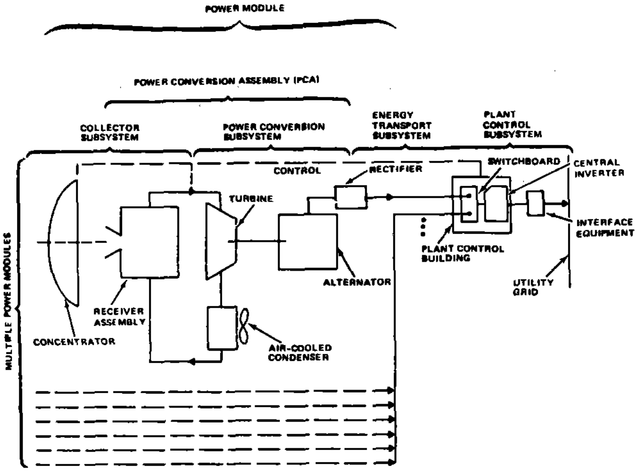

Figure 2. SCSE System Schematic

As shown in Figure 2, individual power modules incorporate the collector and power conversion subsystem and are interconnected by means of the ETS to form a power plant of virtually any size. The use of a dc electrical system permits the ORC engine to operate at variable speed - with constant turbine inlet temperature - as the solar insolation varies, with resultant high part-load efficiency.

For Phase III of the SCSE program, approximately 50 power modules will be employed to achieve a plant rated capacity of 1-MWe. The current Phase II effort involves the design, fabrication and test of a single power module and the microprocessor based plant control subsystem.

The TEBS subsystem is part of the power module and interfaces directly with the receiver and the PCS. The receiver is an FACC developed unit comprised of stainless steel tubing brazed into a copper shell; it heats the PCS working fluid (toluene) from 204°C (400°F) to 400°C (750°F). The PCS is being developed by Barber-Nichols Engineering Co. of Arvada, Colorado under subcontract to FACC. The concentrator is a 12-meter diameter parabolic dish designed by General Electric and furnished to FACC by JPL.

III. Buffer Storage Concepts

The function of the latent heat TEBS concept is to store a fixed amount of thermal energy in a phase change material (e.g., molten salt) to be used as an alternate heat source for the working fluid of the ORC engine during short periods of insolation dropout.

Two buffer storage concepts have been identified which appear compatible with the SCSE receiver and ORC engine. Concept A, shown in Figure 3, would use active flow controls to bypass the supercritical toluene through a buffer storage during charge and discharge cycles. This approach permits packaging of the buffer as a separate subsystem, but requires addition of toluene loop flow controls.

Concept B, shown schematically in Figure 4, requires the addition of storage containers of the phase change material (cells) within the receiver walls. This approach requires a new receiver design and development and could pose greater subsystem integration problems than a separately packaged buffer. Control of the charge/discharge cycle is obtained by modulating the toluene flowrate with the engine power control (throttle valve).

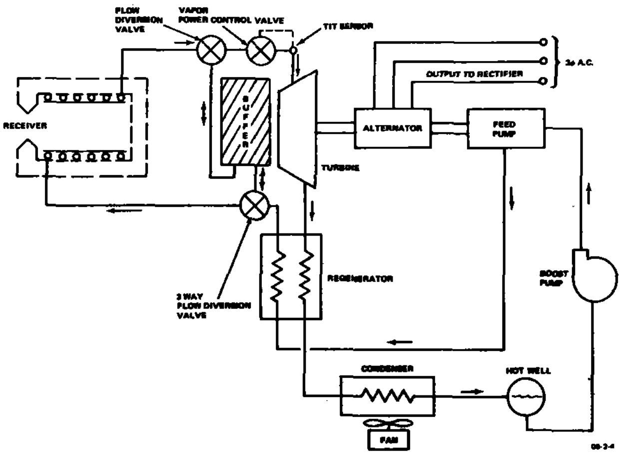

Figure 3. Buffer Storage Concept A

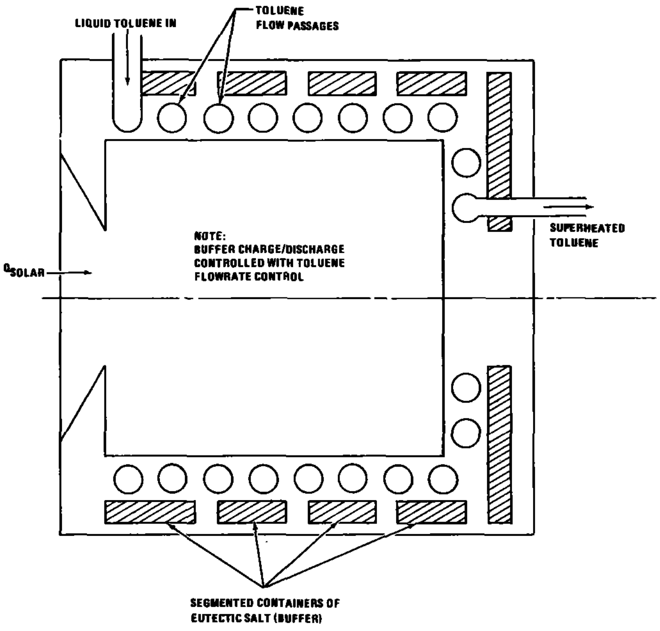

Figure 4. Buffer Storage Concept B

IV. Candidate Phase Change Materials

Important requirements for the phase change material are:

(1) The melting point must be within the operating temperature range of the engine. The constraints are that a toluene temperature greater than 412°C (775°F) (e.g., during TEBS charging) will cause degradation of the toluene. A toluene temperature of less than 343°C (650°F) during TEBS discharge will reduce ORC cycle efficiency.

(2) The material must be chemically stable and non-corrosive or have additives to eliminate corrosion.

(3) The material must be low in cost, especially for large-scale applications.

(4) The vapor pressure should be low at the maximum temperatures.

(5) The material should not be highly flammable or toxic.

A survey of candidate phase change materials shows that eutectic salts are the primary candidates, based on melting temperature and heat-of-fusion properties. Unfortunately, the eutectic salts thus far identified (metal fluorides and carbonates) with the highest heats of fusion have melting points greater than 400°C (750°F).

The best candidate thus far identified is a 43 Li_2CO_3 - 32 Na_2CO_3 - 26 $K_2CO_3$1 salt which has heat fusion of 66 cal/gm (119 Btu/lb) and a melting temperature of 397°C (747°F) which can be lowered to 383°C (721°F) with the addition of $CaCO_3$ modifier.[1] Another candidate is lithium nitrate $LiNO_3$ which has a melt temperature of 250°C (482°F) and heat of fusion of 88.5 cal/gm (159.3 Btu/lb). Information is being gathered on the $LiNO_3$ regarding cost, properties, and thermal stability. The lower melting temperature Li_2NO_3 could be used in Concept B by packaging it at receiver wall locations which are in the 250° - 300°C range during steady state operation.

V. Insolation Data

A JPL supplied magnetic tape of 1979 Edwards AFB Parabolic Dish Test Site insolation data recorded at one minute intervals was reformatted for use with FACC computer programs. A computer program is used to statistically analyze the data.

Figure 5 shows a typical computer output. The solid line is a plot of the number of annual occurrences, N, for which the time of cloud passages exceeds a specified duration, τ. The dotted line is a plot of the number of annual occurrences for which the clear period between cloud passages exceeds a specified duration, τ. Figure 5 shows that of the 2335 annual cloud passages only 630 (27 percent) were of greater than 10 minute duration. In the case of a SCSE power module a TEBS system having a 5 kW_t-hr capacity will supply sufficient thermal input to the engine to permit continued engine operation (at high efficiency) during an isolation dropout of about 10 minutes duration.

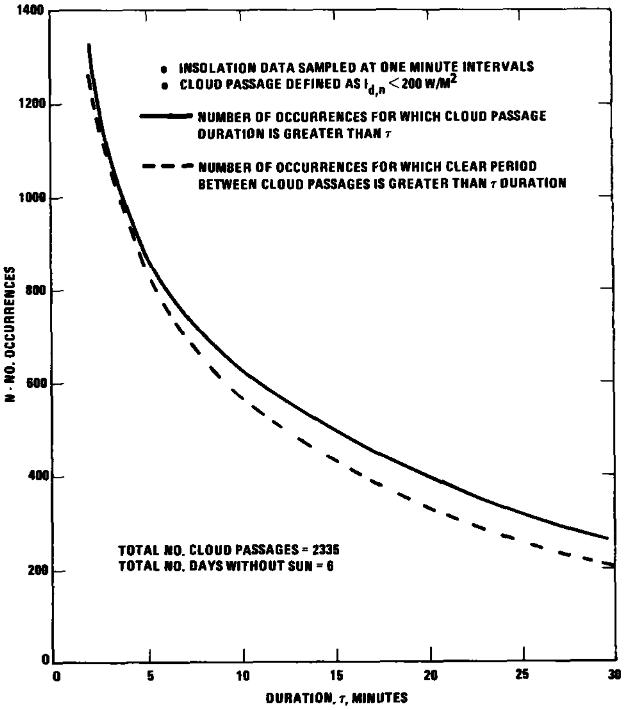

Figure 5. 1979 Edwards AFB (PDTS) Cloud Passage Histogram

VI. Plant Performance/Economic Model

Performance Model

A performance model of the SCSE-1MWe plant was developed to assist in Phase III planning. A simplified flow diagram of the computer algorithm used in the model is shown in Figure 6. A brief explanation of the model is that it accepts insolation and ambient temperature data for a particular site, sampled at regular intervals (e.g., 1 to 15 minute intervals). The electrical output is then calculated based on the computed system efficiency using the component efficiencies of the collector (concentrator plus receiver), PCS, and energy (electrical) transport system. The output of the power module is corrected for module parasitic power and integrated at the insolation sample interval for an entire year to obtain module annual energy output.

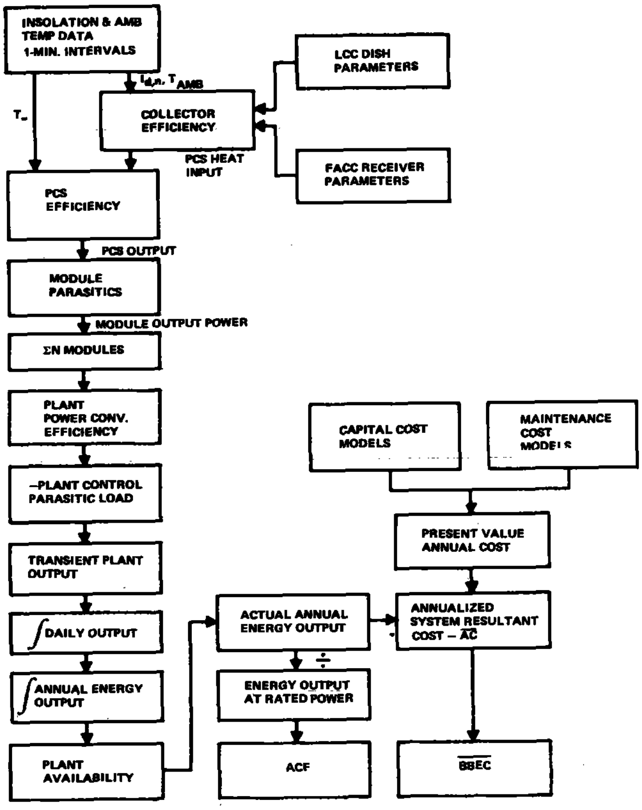

Figure 6. Simplified Flow Diagram SCSE Economic Model

The output of a nominal 1-MWe plant is then calculated using the power output per module times the number of modules less plant control parasitic power.

The integrated plant output is corrected for an assumed plant availability factor and the annualized capacity factor is calculated as

$$ACF = \frac{\text{actual energy output for a year}}{\text{rated power x hours/year}}$$

The TEBS performance inputs to the model are its latent heat capacity and maximum charge/discharge late capabilities.

Economic Model

A separate computer routine calculates the annualized system resultant cost, AC, based on present year value of capital investment costs and maintenance costs prorated over the plant life.[2]

The levelized busbar electrical cost BBEC is calculated as

$$\overline{\text{BBEC}} = \overline{\text{AC}}/\text{actual energy output per year}$$

where the denominator is the integral of plant output (corrected for plant availability due to maintenance, etc.) obtained from the insolation data.

The plant economic model was modified to include the cost of a TEBS. The preliminary TEBS system cost model relates TEBS capital investment and maintenance cost to TEBS capacity.

Objectives of the performance/economic analysis are to define TEBS design parameters (capacities, rates) and operational modes which provide (1) a minimum number of annual shutdowns, and (2) maximum electrical energy output. Reduction in number of power module shutdowns is expected to improve PCS life expectancy with a resultant cost benefit.

Preliminary Results

The TEBS operating conditions which maximize annual output with the least number of engine shutdowns were found to be as follows:

(1) Charge the TEBS (phase change heat capacity) each morning using low level insolation otherwise insufficient for efficient PCS operation.

(2) Discharge the TEBS latent heat store early enough each afternoon to expend the store at high PCS efficiency.

(3) Charge the TEBS during the day whenever the store is partially depleted and insolation is too low to operate the PCS.

(4) Also charge during the day whenever the store is partially (or completely) depleted and the prevailing insolation exceeds the thermal input required for operation of the PCS at rated power.

(5) Discharge the TEBS during the day whenever thermal input to the PCS decays (as a result of cloud coverage) to a condition causing low ORC cycle efficiency.

Using the above TEBS operating guidelines, the economic computer model was run using a range of TEBS thermal capacities and assumed charge and discharge rate capabilities. The PDTS 1979 insolation data (sampled at one minute intervals) were used as representative insolation data with intermittent cloud coverage. Results are shown in Figures 7 through 11.

Figure 7 shows the influence of the TEBS capacity on reducing shutdowns. Curves are shown for varying charge/discharge rate capabilities. Figure 8 shows the impact of the TEBS on annual electrical production. For comparison purposes the annualized capacity factor (ACF) is normalized by dividing by the annualized capacity factor $(ACF)_0$ obtained without a TEBS. (This ratio is effectively the annual system electrical output with a TEBS divided by the output without a TEBS.)

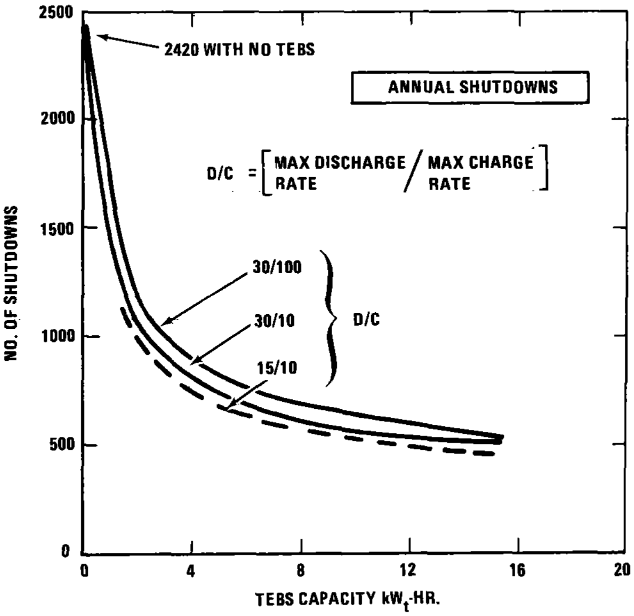

Figure 7. Annual Shutdowns vs TEBS Capacity

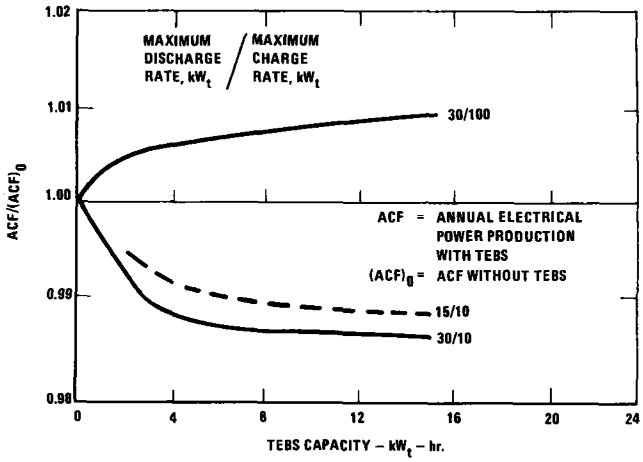

Figure 8. Variation in Annual Electrical Output vs TEBS Capacity

As shown in Figure 7, the number of annual shutdowns is very sensitive to TEBS capacity up to about 5 kW_t-hr. At a capacity of 5 kW_t-hr the total number of annual shutdowns is reduced from 2420 to 655 (73 percent reduction). The number of shutdowns is not very sensitive to the maximum charge or discharge rate. The slightly higher number of shutdowns which occur with higher charge and discharge rate capability corresponds to a higher capability to charge and discharge rapidly under conditions of a series of rapid, short duration cloud passages.

The annual electrical energy output, Figure 8, represented by the ratio $ACF/(ACF)_0$ was found to increase above unity for a TEBS with a high charge rate (e.g., 100 kW_t) capability and decrease below unity for a TEBS with a relatively low (10 kW_t) charge rate capability. A high charge rate capability allows the TEBS to obtain most of its charge energy during periods of low (<200 W/M^2) level insolation, whereas a low (10 kW_t) charge rate capability requires that much of the charge energy be obtained during periods of high insolation when the charging thermal energy could be converted to electrical production at maximum cycle efficiency.

Figure 9 shows the variation in shutdowns and ACF/ACF)$_o$ ratio with TEBS charge rate capability. Curves are shown for maximum discharge rates of 15 to 30 kW$_t$. As shown, the number of shutdowns is mildly sensitive to the charge rate capability. However, the ACF/(ACF)$_o$ ratio is fairly sensitive to charge rate capability. Figure 9 indicates that a charge rate of about 20 kW$_t$ is required to achieve ACF/(ACF)$_o$ ratio of unity. Above rates of about 40 kW$_t$ the improvement in ACF/(ACF)$_o$ rapidly decreases.

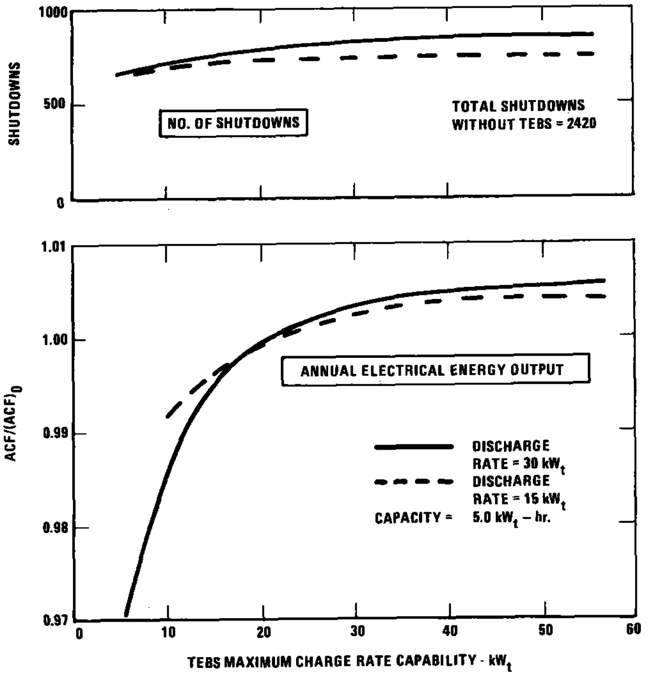

Figure 9. Variation of Annual Shutdowns and Electrical Energy Output vs Charge Rate for a 5 kW$_t$-hr Capacity TEBS

It is emphasized that these results are preliminary and may change as the buffer design concepts and costs are refined.

VI. TEBS Thermal Design

At this time, the TEBS thermal design has progressed only to the preliminary ~~investigation~~ of Concept A, a separately packaged TEBS with active flow controls. Preliminary analysis indicates that a good packaging approach is to contain the eutectic salt in an unpressurized shell with tubes containing high pressure to toluene running in bundles along the shell axis.

Charge Rate Limit

Examination of the charging heat transfer mechanism reveals that the charge rate is limited by the available Δt for heat transfer. The maximum heat transfer rate available to charge the buffer

$$Q_{charge} = wC_p(t_{vapor} - t_{melt})/860.4 \text{ kW}_t$$

where Q is the maximum charge rate possible, kW$_t$

w is the toluene vapor flowrate into the TEBS (=522 kg/hr at rated PCS power)

C_p is the specific heat of the toluene (0.65) (cal/gm-°C)

t_{melt} is the melting temperature of the phase change material, °C

t_{vapor} is the temperature of the toluene vapor entering the TEBS, °C

Because of the potential degradation of toluene, the upper vapor temperature has been limited to 412°C (775°F). The 43.5 Li_2CO_2-31.5 Na_2CO_2-25.0 K_2CO_3 eutectic salt melting temperature is 397°C (747°F). With these restrictions, the maximum possible charge rate at rated toluene flowrate is

$$q_{charge} = (522)(0.65)(413-397)/860.4$$
$$= 6.3 \text{ kW}_t$$

To obtain a higher charge rate, a lower melting temperature salt is required. It was found that the melting temperature of the Li - Na - K eutectic carbonate could be lowered to about 385°C (725°F) by addition of $CaCo_3$ modifier(1). Lowering the melting temperature to 385°C (725°F) will increase the maximum possible charge rate to 11 kW$_t$.

A series of calculations was performed for a 5.0 kW$_t$-hr TEBS using the lower 385°C (725°F) melting temperature and results are shown in Figure 10. The maximum possible charge rate defined by equation (1) is shown as an upper limit in the lower set of curves in Figure 10. The lowest charge rate curve, identified as single pass refers to a single pass of toluene vapor through 60 tubes mounted in parallel. In this case there are 60 tubes and 60 parallel flow paths which make a single pass through the eutectic salt. The low charge rates obtained with this arrangement suggest that the heat transfer is convection limited by low vapor velocity in the tubes.

To remedy this, the 60 tubes were assumed to make multiple passes through the shell with 2, 3, and 4 passes corresponding to 30, 20 and 15 tubes flowing in parallel. As shown in Figure 8, only small gains are obtained in charge rate after two passes are exceeded.

The next probable cause of the low charge rate is limiting of the heat transfer process due to conduction within the eutectic salt. This effect was offset by modifying the computer calculation to include radial fins mounted on each 12.7mm (0.50 inch) diameter tube. Six 0.90mm (0.035 inch) thick aluminum fins having 25.4mm (1.0 inch) span were assumed along the 48.3cm (19 inch) length of each tube. The results are shown as the dotted lines on the lower set of curves shown in Figure 10. As shown, a finned tube configuration with two passes extracts 80 percent of the maximum possible charge rate from the salt.

The corresponding discharge rates obtained with the various tube configurations are shown as the upper set of curves in Figure 10.

The discharge temperatures of toluene corresponding to the curves shown in Figure 10 are shown in Figure 11. The minimum acceptable 343°C (650°F) discharge temperature is indicated by a dashed line. The Concept A approach using flow controls

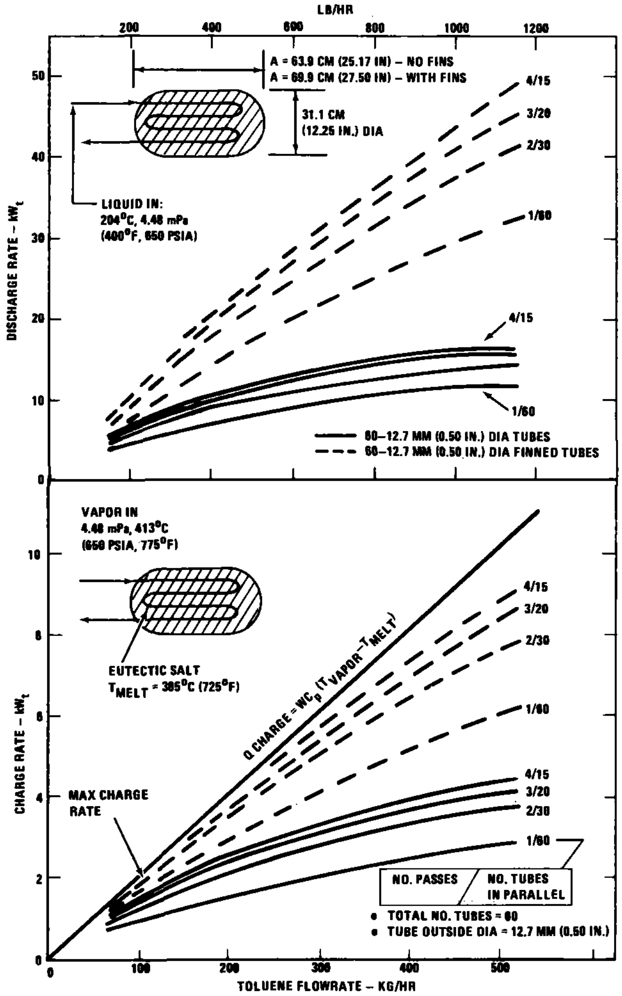

Figure 10. Calculated Charge/Discharge Rates for a Separately Packaged Buffer TEBS

would require toluene flowrates up to about 227 kg/hr (500 lb/hr) to achieve the necessary buffer thermal inputs to the PCS for the operating modes defined. As shown by the bounded curves a double pass, finned tube design is required to achieve the required toluene discharge temperature.

VII. Conclusion

The brief period of study of a TEBS for application to the SCSE 1-MWe plant has led to the following preliminary conclusions.

(1) A TEBS capacity of about 5.0 kW_t-hr will improve plant operation to the extent of elimination 70 to 80 percent of the potential shutdowns due to cloud passage.

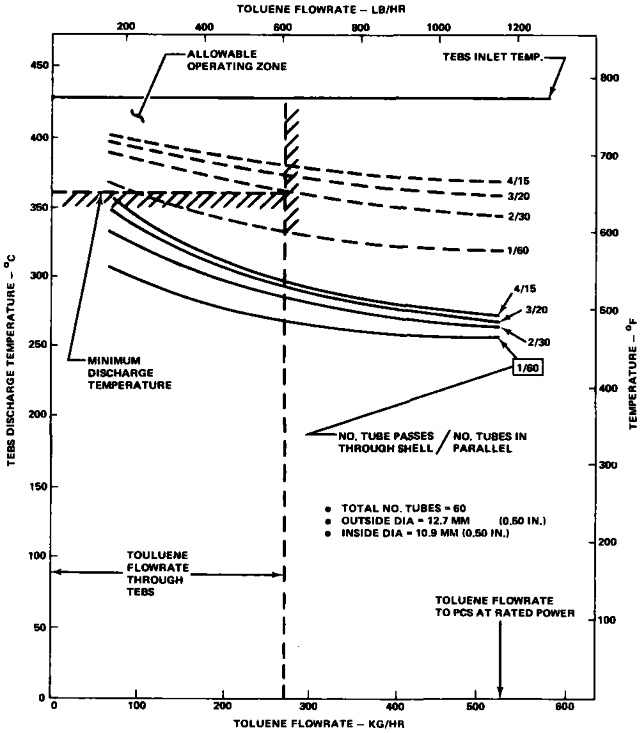

Figure 11. Toluene Discharge Temperature From Buffer TEBS

(2) A high TEBS charge rate capability and careful control of operational modes are required to improve the annual electrical energy output.

(3) In at least one TEBS design concept studied thus far, the necessary charge/discharge rates for efficient operation appear possible.

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APPLICATION OF THERMAL ENERGY STORAGE TO PROCESS HEAT RECOVERY IN THE ALUMINUM INDUSTRY

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I. Abstract

This project is directed toward determining the economic viability and institutional compatability of a district heating system that uses waste heat from an aluminum plant as the source of thermal energy. The project has been designed to show how existing energy storage techniques can enhance the utility of low temperature waste heat streams.

II. Project Status

This project is sponsored by the Office of Advanced Conservation Technologies and administered through Oak Ridge National Laboratories. Lead investigation work is being conducted by Rocket Research Company, a division of ROCKCOR, Inc. Supporting work is provided by Intalco Aluminum Corporation of Ferndale, Washington, and by the city of Bellingham, Washington. Currently, the project is in the second of four phases leading to the construction and operation of a large-scale district heating system by the city of Bellingham. This project differs from other hot water district heating systems under investigation, first in the use of industrial waste heat as an energy source and second in the plan to incorporate single-family residences as a major portion of the subscribing structures.

During the first phase, now complete, a survey of the primary aluminum industry was made to identify reject heat sources and potential users. These results lead to the selection of the low grade waste energy stream carried by the plant pollution control system as the primary energy source and district heating as the primary energy use. An energy storage system couples the basically constant energy source to the variable energy demand. Using the Intalco and Bellingham site as an example, a preliminary system was designed. The performance of this system was predicted, and economic analyses were made. The result of these Phase I analyses showed that significant fossil fuel savings can be achieved through the application of industrial waste heat to district heating systems. Furthermore, the recovered heat can be supplied to the district heat user at a cost which is competitive with existing heating systems.

A number of assumptions were necessary during this preliminary Phase I study. Specifically, these fall into four classes: those concerning the demographics of the service area, those concerning the technical equipment required, those concerning the energy source, and those concerning institutional and legal considerations. The second phase of the project was conceived to improve the accuracy of the predicted system performance by using improved modeling of these areas, thereby to establish the necessary level of confidence in the cost effectiveness of the program prior to a major commitment of funds. Each of the four major assumption areas is handled as a separate task in the present Phase II program. A fifth task ties together the information in an overall system cost analysis.

During the third phase, scheduled to begin early in 1981, a segment of the district heat network will be installed and a number of buildings converted to a hot water source. This segment represents approximately 3 percent of the full-scale system. The segment will be instrumented and monitored for performance through two heating seasons. Similarly, an experimental program at the aluminum plant will result in the installation and monitoring of one of the 12 full-scale heat exchangers and the associated portion of ductwork and pollution control equipment. The overall system design will be finalized based upon the test results from the two major system elements.

The fourth phase will continue with city arranged financing. The municipal utility will secure financing through the issuance of a mix of revenue and general obligation bonds to fund the full system construction.

III. Project Results

Overall Phase II project results have been published in several previous papers. Major findings may be summarized as follows:

1. An optimum or near-optimum service area has been defined within the potential market area. Peak demand of this area is 86 MW_t, composed of 50 percent commercial, 17 percent to Western Washington University, 10 percent to multiple residential, and 23 percent to single family residential structures.

2. All major equipment items can be supplied by domestic manufacturers at minimum technical risk and acceptable lead time. Improved technical or economic performance is possible through somewhat increased technical risk. The major topic of this paper, storage options, serves as an example of this type tradeoff.

3. Nine local industries have been evaluated as alternates to the aluminum plant as sources of waste heat for the system. Whereas none of these was found to be a suitable alternate source, two show promise either in the topping mode or as a partial backup, or as a source for future system expansion. A standby boiler remains the most cost-effective means to provide for the topping and backup functions.

4. Legislation has been drafted to eliminate any legal uncertainty regarding the authority of a municipality or a public utility district to own, finance, and operate a hot water district heating system. The energy and utility committee of the Washington state House of Representatives is currently reviewing this draft for passage during the January 1981 legislative session.

The services of two investment bankers, one local and one national, have been engaged. They will aid in the preparation of the financial data required to achieve a high rating for the Phase IV bond issue.

5. The system is economically viable.

IV. Results of Storage System Investigations

Under Task 2, the developmental status and technical risk of all major subsystems was investigated. Of particular interest is the result of investigations regarding the storage subsystem. The baseline system of surface tankage is cost effective and has minimal technical risk. Aquifer thermal storage and coal mine thermal storage show greater economic benefits but have a higher technical risk.

Surface Tankage

The baseline storage system design incorporates two insulated steel tanks each of approximately 900,000 gallons, representing energy storage of 200 MW_t hr. These tanks, as well as the topping-backup boiler, will be located on Bellingham Port authority-owned land just south and east of the Bellingham airport. Energy supplied to the consumer from storage of this size costs the system approximately half the cost of energy delivered from the topping and backup boiler, based upon full system operation in 1985. Energy saved aggregates to 2,727 MW_t hr/yr or 13 full tank cycles per year. At the cost predicted for energy in 1985, the 200 MW hr storage is a near optimum in storage cost effectiveness. Should, in the future, the value of energy exceed the predictions or the overall system size increase, additional tank modules could be added to achieve additional savings. Large storage volumes can effect additional savings, to the limit of approximately a six-fold increase for a 100-fold increase in volume.

Larger storage volumes, to be cost effective, must be characterized by lower specific storage costs. Two potential means are aquifer thermal storage and utilization of the volume of an abandoned coal mine located beneath the northern neighborhoods of the city.

Aquifer Thermal Storage

The suitability of aquifer energy storage techniques to the Bellingham application hinges upon location of a suitable permeable stratum in this region, preferably bounded above and below by impermeable strata. A search of available geological data has revealed several formations which may be suitable.

Generally, western Whatcom County is underlaid by consolidated Pleistocene deposits mildly uplifted and subsequently eroded by glacial action, as shown in Figure 1. Unconsolidated glacial deposits overlay these strata in a thickness, averaging 100 meters and varying from zero to over 200 meters. Suitable strata may be found either in the consolidated or unconsolidated materials.

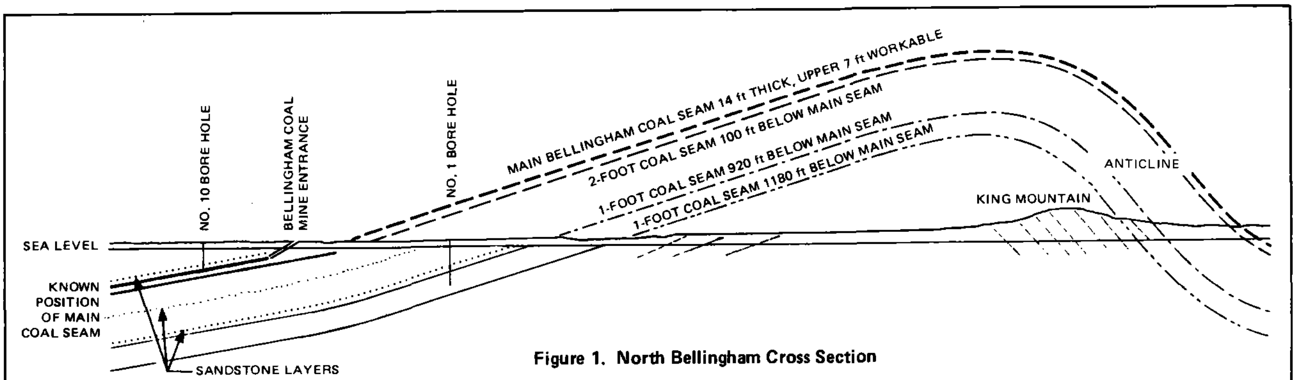

Figure 1. North Bellingham Cross Section

Water wells seldom penetrate to the consolidated strata due to the abundance of water in unconsolidated deposits. Data concerning the consolidated materials is thus available mainly from surface outcroppings and the results of bores made in search of coal. These drilling records are very accurate in description of thickness and character of the various strata encountered but do not include indications of permeability. Shale, sandstone, coal, fireclay, and claystone are the major constituents. Sandstone may show sufficient permeability to serve as a thermal storage medium, whereas shale, claystone, and fireclay are likely impermeable enough to serve as confining layers. The several coal strata serve as reference lines from which other features are measured. Three layers of sandstone of sufficient thickness were located by examination of the drilling records. The uppermost is 22 meters in thickness and bounded above by 1 meter and below by 4 meters of fireclay. Beneath the fireclay is a stratum termed "ironstone" of roughly 30 cm thickness which directly overlays the main Bellingham coal seam. The mine which penetrated this coal seam was known as an unusually dry mine. High permeability of the overlaying sandstone is questionable, as it is separated by less than 5 meters from the coal seam.

Repeated blasting during mining operations can be expected to create numerous small cracks in the overburden. Considerable seepage would be expected from a highly permeable sandstone layer.

Two additional sandstone layers lie beneath the main coal seam. The uppermost measures 15 meters in thickness, is overlaid by 11 meters, and underlaid by 12 meters of fireclay and shale. Stratagraphically, this layer is 225 meters below the main coal seam. The highest probability of suitable permeability may be assigned to this layer. Within this layer, sublayers 2 meters thick are described as coarse, and another 3 meters thick is described as very coarse.

The third layer of sandstone which lies 89 meters further down is 21 meters in thickness and is bounded by shale, fireclay, and claystone aggregating to 18 meters above and 14 meters below.

Mentions of clay streaks are made for each of these layers. Each is believed to be in communication with surface waters through upheaval and subsequent glacial erosion. Each is accessable at relatively shallow depth (less than 200 meters) within the boundary of the desired region, so that deep drilling costs can be avoided.

Unconsolidated deposits in this region are the result of glacial deposits and river flooding. Overall, the deposit thickness averages about 100 meters with increased thickness to the west and north. Limited exploration for an aquifer for thermal storage was accomplished recently without positive result. Two exploratory wells were drilled to the top of consolidated deposits. Generally, the well logs show thick bands of clay and silt with relatively slender bands of sand interspersed. A flowing brackish aquifer was found in one well; however, the thickness of the stratum at that location was less than 2 meters. It cannot be concluded from these results that a suitable formation does not exist in the region of interest. One can infer, however, that if a suitable formation exists, it is local, not regional, in extent and will require extensive exploration to locate.

Coal Mine Thermal Storage

The second alternate energy storage concept concerns using the void space of an abandoned coal mine as a hot water storage reservoir. Figure 2 is a plan view of the extent of the mine passages.

The Bellingham coal mine was active from 1919 through 1952 and yielded 5 million metric tons during that period. The mine was sealed in 1955 by backfilling with earth and gravel to a depth of 60 meters. It is believed that the mine is currently filled with fresh water through seepage from Squalicum Creek passing very near the old mine entrance.

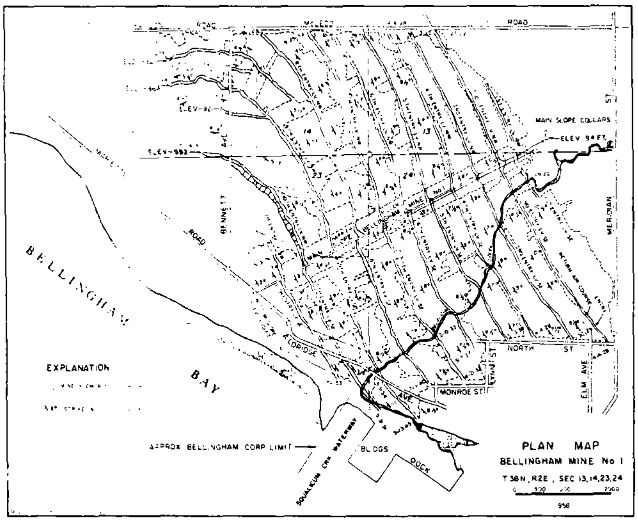

Figure 2. Plan Map, Bellingham Mine No. 1

Very detailed maps of the mine are available. The mine proceeds down a single seam 2 to 3 meters thick, inclined at 6 to 12 degrees from the horizontal. Mining began at a depth of 87 meters (58 meters below sea level) and proceeded to a maximum of 357 meters below sea level. Entry shafts were driven normal to the main shaft at 100- to 150-meter intervals. Coal was mined from "rooms" 6 meters wide, from one entry shaft to the next. Rooms were separated by 10 meters. Ventilation passages 2 meters wide were cut every 17 meters connecting the rooms. The resulting geometry is a series of 10- by 15-meter pillars supporting the "hanging wall" and the removal of approximately 53 percent of the coal in the seam. The void volume is estimated at 3 million cubic meters. This is ten times larger than that which can be utilized efficiently by the system. A period exceeding 50 years would be required to heat the surrounding rock before whole mine thermal losses would decrease to tolerable levels. Accordingly, we are investigating isolating a segment of the mine for thermal storage purposes.

A segment of the mine composed of entry levels 1 to 4 northwest will contain 12.4 percent of the mine volume and can be isolated by sealing only 42 passages. Approximately 2,500 cubic meters of concrete will be required. A special low-density aggregate may be required to avoid separation in the unusually large vertical pumping distance required. Preliminary estimates of the cost for this construction are 1.6 million dollars (1980) including the boring of access shafts, ventilation and utility shafts (subsequently used for energy storage and recovery), and surface heat exchangers. Compared to the baseline surface tankage, the cost is four times higher, the volume 100 times higher.

Performance of the partial mine volume case has been estimated based upon operation as a thermocline tank. The elevation variation of the selected segment is 65 meters, with a mean passage size 2 by 6 meters. The thermal mass of coal pillars adds an additional 60 percent to the thermal mass of the water contained.

A period of 5 years is predicted for thermal preparation of the system. During this time, all surplus energy recovered from the aluminum plant source would be stored, mostly heating the coal pillars and surrounding strata, forming a thermal barrier to heat losses in subsequent years and a reserve for future system growth.

Energy storage and recovery will be accomplished through surface heat exchangers, as shown in Figures 3 and 4, keeping district heating water and mine water separate in closed systems.

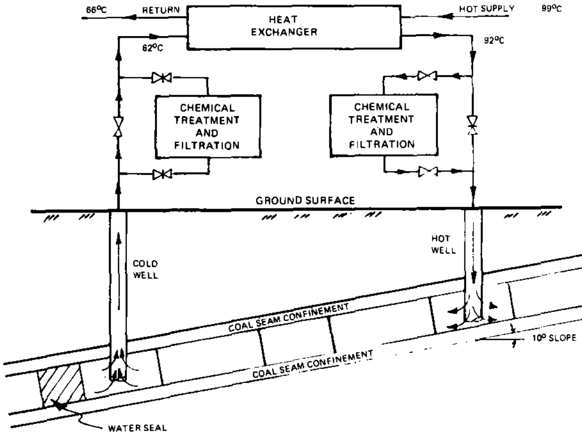

Figure 3. Coal Mine Storage Cycle

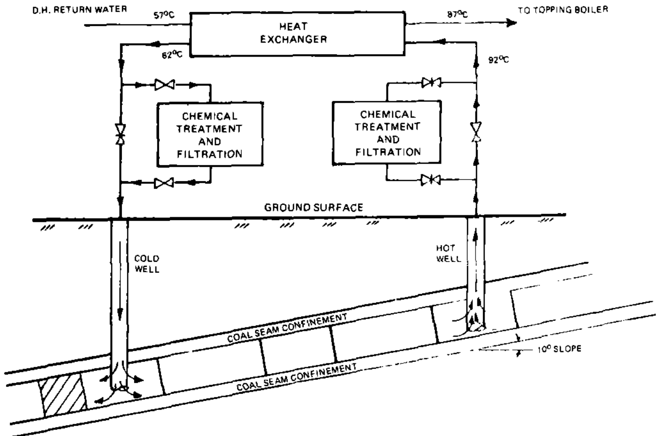

Figure 4. Coal Mine Recovery Cycle

This approach will avoid any potential interaction between district heating water treatment chemicals and the remaining coal pillars. Plate-type heat exchangers are selected for this application. The design includes 10 large commercially available units, for an average effectiveness of 0.87 and a number of transfer unit of 4.90.

In Figure 3, the storage portion of the cycle is shown. District heating supply water, which is not required to satisfy demand, is directed to the surface heat exchanger. Under nominal storage conditions, the storage water can be heated to 92 °C by the 100 °C supply water. After the heat exchanger, district heating water now cooled to 66 °C is blended with return water at 57 °C and pumped to the heat source.

In Figure 4, flows are reversed indicative of the recovery cycle. District heating return water at 57 °C is directed into the heat exchanger and heated to 87 °C. Previously stored 92 °C mine water is pumped from the mine and can be cooled to 62 °C before re-injection. Since the nominal district heating supply temperature is 99 °C, additional energy will be required before the heated water is blended into the district heating supply. This energy will be provided by the fossil fuel-fired topping and backup boiler. The coal mine storage thus acts to preheat district water before the topping boiler. The share between storage and topping for this mode is predicted at 70.7 percent storage — 29.3 percent topping.

V. Conclusions

The conclusions drawn from these studies are:

1. Surface tankage, while expensive, is cost effective at or near system startup and is conveniently expandable in capacity for future growth.

2. Aquifer storage would show good payback if an appropriate stratum can be found. There is no definite indication of a suitable stratum in the literature studied. Several possibilities were identified at relatively low probability.

3. The full coal mine volume is too great to serve as a storage reservoir under any foreseeable district heating growth pattern.

4. Isolation of part of the mine volume appears to be feasible and cost effective.

5. The decision to incorporate partial mine storage can be made after the first few years of system operation depending upon the penetration and growth rates actually achieved.

COLLECTION AND DISSEMINATION OF THERMAL ENERGY STORAGE SYSTEM INFORMATION FOR THE PULP AND PAPER INDUSTRY

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Abstract

The pulp and paper industry is a major industrial user of energy in the United States. Recent studies have indicated that substantial reductions in a mill's net energy requirements can be realized by application of thermal energy storage (TES) system technology. This concept is not as widely applied today in the U.S. pulp industry as it is in some international mills, especially within Scandinavia. This paper describes a Department of Energy study presently underway which has as it purpose the collection and dissemination of TES system technology for the pulp and paper industry with the intent of reducing fossil fuel usage. The study plan is described and a description presented of example TES systems to be studied in this technology transfer project.

Introduction

The pulp and paper industry leads all manufacturing areas in fuel oil consumption. The industry ranks fourth in purchased energy(1) with electric power providing about 12 percent of the process energy(2) Almost half (47 percent) of the industry's energy requirements are generated from its own renewable process waste. The U.S. pulp and paper industry leads the nation in self-generated and co-generated electric power, accounting for more than 40 percent of all co-generation in the United States today(3). Energy costs amount to about 11 percent of total production cost in the pulp and paper industry(3). It alone is responsible for three percent of the total U.S. energy consumption(4)

A Department of Energy study(5) has shown that the pulp and paper industry is one industry having the greatest potential for early implementation of thermal energy storage (TES) systems. This study showed that adaption of TES in 30 mills similar to the one studied in the report would save 3 x 10^6 bbl of oil per year in 1980. Conceptual designs of mechanical equipment and control systems indicated installed cost estimates of about $560,000 per installation, indicating an after tax return on investment of over 30 percent.

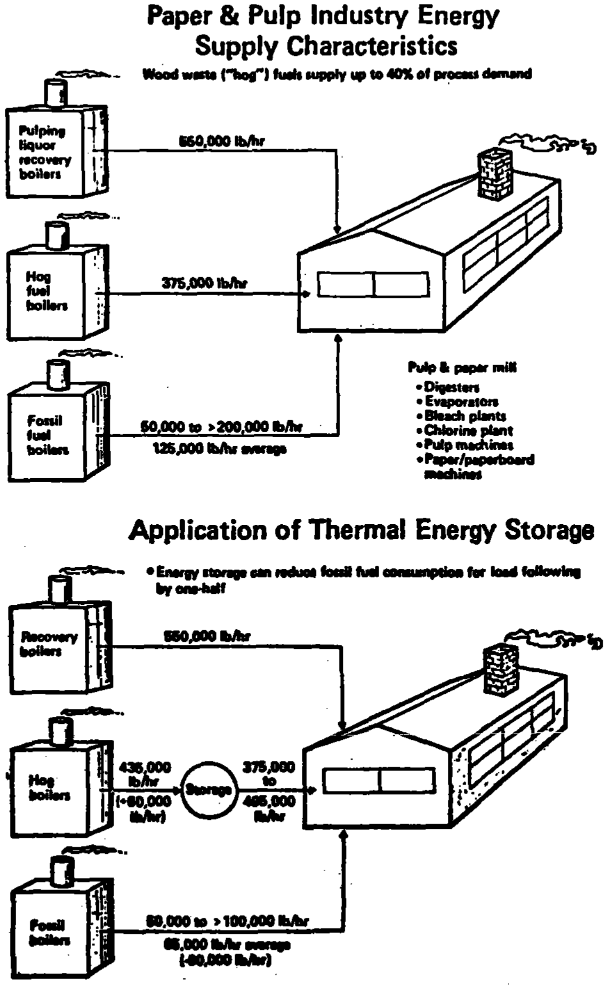
The pulp and paper industry in the United States consists of approximately 350 companies operating 750 mills.

The TES Concept in a Pulp Mill

TES is a technique whereby mill generated energy is stored to subsequently meet the rapidly varying or "swinging" process steam demands of mill operation. The storage system can accept either externally generated energy (for example, energy generated from a hog fuel boiler) or internally generated energy (for example, reusable energy released from a production operation).

In some pulp mills, the inability to follow rapidly changing steam demands with waste fuel ("hog fuel") boilers requires the reduction of hog-fuel firing in favor of increased fossil-fuel firing. This exchange of steam production between the fuel types must be large enough to permit the steam demand transients to be followed by varying the rate of fossil fuel firing. Figure 1 illustrates one example of this basic concept. In this example a significant amount of fossil energy could be conserved if some of the fossil fuel generated steam typically required to meet the rapidly varying or "swinging" process steam demand could be instead supplied by waste ("hog fuel") steam generating boilers.

Figure 1
TES Application Concept



The TES concept is also applicable to reusable energy released from a production unit operation. For example, digester blow heat can be stored in a TES system to be used later for mill production energy demands. The TES storage medium in this case might be in the form of steam or hot water, depending upon specific case situations. The "stored" energy could later be used, for example, in (a) (pre) evaporation of liquor, (b) steaming of chips, or (c) for heating water to be used elsewhere (bleach plant, pulp washers, barking, etc.) in the mill.

Hence, the TES system utilizes the "flywheel" concept to store energy which can subsequently be reused in the mill production process. This flywheel can operate either externally to the production process (Figure 1) or be integrated within the production process so long as it serves its essential function. A TES system accomplishes its objectives by temporarily "storing" energy in order to more uniformly balance the "release of energy" to match the "transient changes in energy demand rate" that occur in pulp and paper mill production. The capacity of the storage device determines the time interval of application. Generally, for practical purposes, this is limited to time intervals of less than one-half hour.

Practical Mill Concepts Affecting TES Applicability

The potential for application of TES system technology in a complex industry such as the pulp and paper industry must consider the basic industrial production processes and the fundamental cause and effect relationship of energy availability and energy demand on a rate basis. The rate and time interval of rate variation is of particular importance.

Table 1(6) illustrates different energy patterns that exist in pulp mills. The ratio between energy supplied from the outside and energy consumed from within can differ greatly from one mill type to another. In the example batch digester Kraft pulp mill, up to 87 percent of the heat demand is supplied by burning of black liquor and bark. A steam accumulator is used to reduce the peak loads on the grid (i.e., application of TES system technology). The linerboard mill has two continuous digesters to produce both base and top liner pulp grades and NSSC pulp, the latter making up 20 percent of the furnish. Seventy-two percent of the heat demand is filled by burning of black liquor and bark. The newsprint mill produces 85 percent groundwood and 15 percent sulfite pulp. Little heat is obtained by burning of waste liquor and bark. The electric energy consumption is high. Each of these mills has its own set of conditions for heat-power balances and hence different possibilities for the application of TES system technology.

As noted above, pulp is produced from wood in either a continuous or batch digestion process. Newly built mills continue to use either batch or continuous digestion, depending on a variety of project specific conditions. These digesters are some of the largest of their kind in any industry. The process requires the biggest part of the total steam demand for pulp production. A mill producing pulp using large batch digesters will experience greater short-term, interval energy demand variations. An example of steam consumption in a pulp mill is illustrated in Figure 2(7). A prescribed digester program is not feasible and for mills having a series of batch digesters, it is possible the steaming demand of multiple units may coincide with an extremely sharp rise in steam demand. In these cases, high potential exists for applying a TES system to meet the transient power demands. The batch digester "blows", which relieve pressure at the completion of a cooking cycle, represent a source of short-term energy surplus that can be stored (i.e., TES) for later use in the production process. Hence, the nature of the mill production process is a major factor in determining the possibilities of applying TES technology.

Table 1
Typical Pulp Mill Heat-Power Balances

Heat balances

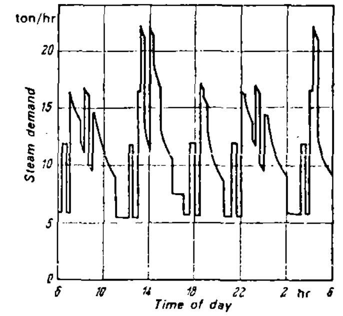
	Sulphate Pulp (a)		Linerboard (b)		Newsprint (c)	
	Million Btu/sh tn	%	Million Btu/sh tn	%	Million Btu/sh tn	%
Heat consumption						
Process	14.4	85	10.4	83	7.6	78
Steam turbine	2.5	15	2.2	17	2.1	22
Total	16.9	100	12.6	100	9.7	100
Heat generation						
Liquor	11.6	69	8.3	66	1.1	11
Bark	3.1	18	0.8	6	0.9	9
Oil*)	2.2	13	3.5	28	7.7	80
Total	16.9	100	12.6	100	9.7	100
***) Oil demand**	18 US. Gallon		29 US. Gallon		62 US. Gallon	

Power balances

	Sulphate Pulp		*Linerboard*		*Newsprint*	
	kWh/sh tn	%	kWh/sh tn	%	kWh/sh tn	%
Power consumption						
Total consumption	680	100	910	100	2 000	100
Power generation						
Turbinesteam	644	95	600	66	550	27
Purchased power)*	36	5	310	34	1 450	73
Total	680	100	910	100	2 000	100
***) Required purchased power**	36 kWh/sh tn		310 kWh/sh tn		1 450 kWh/sh tn	

(a) 990 t/d (b) 1,300 t/d (c) 1,300 t/d

Figure 2
Steam Consumption of a Paper-Pulp Factory



The paper machines in an integrated pulp and paper mill have a uniform steam demand (mainly for the heat required for drying) during normal operation. In paperworks making their own pulp, these machines therefore represent a very valuable basic load which leads to an equalization of the boiler load. With some low-strength grades of paper, especially newspaper, it is very common for the paper to tear in running through the machine. This involves stopping the machine and introducing a new strip of paper, so that the heat consumption of the drying drums is interrupted; this interruption amounting to about 5 to 15 minutes, depending on the size of the machine. During this time the steam supply is shut off and the boiler load drops very steeply. In many mills this happens so often that the safety valves blow off almost every hour, and considerable fuel losses arise, apart from the nuisance effect. Here the installation of a TES steam accumulator leads to a full solution: when the paper tears, the surplus steam is charged into the accumulator, with no abrupt change of the boiler firing rate. After work is resumed, this steam can be re-employed by discharge into the low-pressure network.

A ranking criteria can be developed to identify mills having a high potential for TES system application. The following items should be considered when developing a ranking criteria:

- Plant layout and site specific problems in transfering TES from one collection point to an important use point.
- Mill steam demand fluctuations including repetitiveness of rapidly varying or "swinging" process steam demands.
- Mill complexity, with an integrated mill having more potential use areas, assuming other factors remain constant.
- Local comparative cost both at current and projected future conditions for hog fuel, purchased electricity and oil.
- Bark boiler capacity limitations and its potential for excessive air pollution emissions at higher boiler loading conditions.
- Availability of existing equipment to serve as the energy storage vessel (such as an "old" batch digester), thereby affecting the cost effectiveness of the TES system.
- Age or degree of mill modernization which can affect the corporate decision on capital investment for a TES system.
- Possibilities of local accelerated ammortization or tax considerations which affect the decision-making process.
- Mill expansion plans which can either facilitate a timely TES installation or delay a TES decision until the expansion is completed and a new heat-power balance is determined under actual operating conditions.

Study of TES Systems

A survey of North American and international pulp and paper mills was conducted to identify the existing applications of TES systems, to obtain and analyze the operating data from a representative number of these mills and to transfer this information to the U.S. pulp and paper industry. The survey was begun only recently and is not yet completed. However, sufficient results are available to indicate that a number of typical TES case example situations exist which are believed to have a high potential for application within the U.S. industry. Table 2 presents some of these mills' conditions selected for detailed investigation. The results of the overall study will be completed by the end of 1980.

Table 2

TES System Applications Studies

Production Type	ton/year (metric)	Application
Dissolving Newsprint	140,000 245,000	Steam accumulator TES system to store steam during paper machine breaks
Sulfate (sack) Sulfite (Unbleached)	170,000 160,000	Mill owned boiler to provide district heating for adjacent community. TES system is hot water accumulator for mill transient hot water energy demands. Start-up scheduled September 1980, permitting before/after evaluation of energy demands.
Newsprint	170,000	Steam accumulator TES system to store steam during paper machine breaks and utilize steam when paper sheet is brought to full width.
Dissolving Sulfite	150,000	Boiler feedwater modulation.
Sulfate	218,000 (pulp) 286,000 (paper)	Steam accumulator for balancing steam production from recovery boiler in relation to batch digesters and board machine.

Energy Conservation and Environmental Benefits

The application of steam accumulators as TES systems is not a new technology. The concept was patented in the United States more than 100 years ago(6). The concept was first applied in Sweden's pulp industry between 1910 and 1920 using the Ruths varying-pressure accumulator to balance the boiler load via insertion of an overflow (or surplus) regulator between the boiler and accumulator. The much higher fuel oil prices that have existed in Scandinavia since World War II have been a major contriuting factor to the broader application of this technology in Scandinavia compared to the United States.

Based on available information to date, a 2,000 tons per day batch digester Kraft mill installation will permit fossil fuel savings in the order of 100, 000 bbl/yr (or about 1/7 bbl/ton of pulp). Technology presently exists to implement the TES system in U.S. mills today. A typical installation will provide an after tax R.O.I. in the order of 30 percent. It is believed the current technology transfer project will significantly benefit the pulp and paper industry energy conservation efforts.

An environmental assessment has not yet been completed relative to TES system application in the pulp and paper industry. Mill visits to TES systems in the United States and Scandinavia have not yet indicated any unacceptable adverse impacts.

Anticipated beneficial aspects include:

- Reduced total energy use per unit of pulp production.
- Conservation of resources.
- Decreased mill noise during "skying" of excess steam.

- Reduced sulfur emissions from less fuel oil consumption.

Potential adverse aspects include:

- Increased emissions of particulates.
- Increased SO_2 emissions if coal should be substituted for hog fuel.
- Increased quantities of boiler ash from hog fuel to be disposed as solid waste.
- Potential water pollution from wet ash handling techniques.
- Concern for safety factors associated with pressure-steam accumulators and with hot water lines. Impact of temperature changes during mill down-time on metal stress in accumulator systems.

These and other energy conservation and environmental factors will be considered in depth during the course of the study.

Acknowledgement

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APPLICATIONS OF THERMAL ENERGY STORAGE TO WASTE HEAT RECOVERY IN THE FOOD PROCESSING INDUSTRY

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Abstract

The canning segment of the food processing industry is a major energy user within that industry. Most of its energy demand is met by hot water and steam and those fluids, in addition to product cooling water, eventually flow from the processes as warm waste water. To minimize the possibility of product contamination, a large percentage of that waste water is sent directly to factory drains and sewer systems without being recycled and in many cases the thermal energy contained by the waste streams also goes unreclaimed and is lost from further use. A Westinghouse study* completed in October 1978 with H. J. Heinz cooperation indicated that waste heat recovery in canning facilities can be performed economically using systems that employ thermal energy storage (TES). As a result of that study, a project has been proposed by the Heinz USA Division in which a demonstration waste heat recovery system -- including a TES feature, would be designed, installed and operated at the Heinz Pittsburgh Factory.

Demonstration Project Overview

The purpose of the demonstration project proposed by Heinz USA is four-fold:

1. To design, install and place in operation a system employing thermal energy storage that will recover heat from food system waste water.

2. To monitor the operation of the waste heat recovery system in a production setting over a period of one year, to assess its performance and to evaluate the benefits that accrue environmentally and in the form of dollar and fossil fuel savings.

3. To effectively inform the food industry, particularly the canning segment, concerning the actual costs and benefits of system operation and to encourage industry acceptance and implementation of the system concept.

4. To recommend a plan for system implementation in the food processing industry.

Under the proposed management plan, Heinz USA will have overall project management responsibility and will execute the efforts of system definition review, system fabrication, installation, checkout, and operation. Other phases of the project will be subcontracted by Heinz USA. The demonstration system engineering and operational evaluation work is planned for subcontracting to the Advanced Energy Systems Division of the Westinghouse Electric Corporation. Westinghouse would then develop a detailed engineering design for the system which would include the preparation of engineering drawings, operation and maintenance procedures and manuals and predictions of system performance characteristics. In addition, Westinghouse would monitor and evaluate actual system performance, prepare performance analyses and carry out the program control and reporting functions.

It is planned that execution of the technology transfer task will be delegated to the National Food Processors Association (NFPA). As part of that effort, the NFPA would be reponsible for an assessment of the system implementation potential within the food processing industry and for an analysis of benefits that would accrue if this implementation potential materialized. Further, the NFPA would plan and conduct on-site project reviews. The reviews, attended by food industry personnel, would be used to report progress and to present project results and findings. In addition, the NFPA would coordinate the development of a plan for implementing the demonstration system concept on an industry-wide basis.

Additional details concerning the proposed demonstration project can be found in the Proceedings of the 4th Annual Thermal Energy Storage Program Review Meeting, December 1979.

Demonstration Project Status

The Heinz USA proposal was submitted to NASA-Lewis Research Center in November, 1979. It is understood the proposal may now require resubmission as a result of program transfer from NASA-Lewis to Oak Ridge National Laboratory.

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ONCE-THROUGH HEAT SUPPLY SYSTEM FOR CITY OF BELLINGHAM

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Abstract

Utilization of the waste heat from industrial facilities for district heating purposes is now under consideration in the U.S. as one of the conservation measures. A number of the U.S. studies have demonstrated that the cost of low grade heat at the industrial side, which may be utilized for district heating, is relatively low. However, to transmit the heat from the industrial plant to the heat load area and distribute the heat to the customers, substantial capital investment in the piping system is required.

Historically, centralized district heating systems in the U.S. have used steam as a heating medium for heat transport, while hot water networks have traditionally been used in Europe. For industrial waste heat utilization, hot water as a heating medium offers a number of advantages in comparison to steam and is therefore considered for the present application.

A hot water transport system is typically a two pipe system. The hot water from the heat source is delivered to the domestic and commercial customers via a supply pipe, and after being cooled in the users' system, is pumped back to the industrial plant via a return pipe. The domestic hot water (DHW) supply to the customers may be one of two types, closed or open. In a closed system, cold potable water, used for DHW supply is heated by the network water in a surface heat exchanger. In the open system the DHW is drawn off from the supply or return lines of the network and supplied directly to the customer.

A further development of the open district heating concept is the once-through heat transport system. In this system, the network water from an industrial plant is supplied through a single pipe to the customer space heating systems and after utilization is used for DHW supply. In this way all water supplied from the heat source is finally discharged overboard, i.e., it is not returned to the plant. Use of this system may result in a substantial reduction of the piping system and consumer equipment costs.

The purpose of this paper is to discuss technical aspects of the once-through system as applied to the Bellingham district heating project. The work on this project started in August 1980 and technical and economic analyses are in progress at the present time.

Introduction

A typical district heating system includes a heat source, heat exchanger equipment, storage facility, pumping station, a peaking boiler plant, a transmission and distribution network, and individual HVAC and DHW systems for domestic, commercial, and industrial use. The return water from the district network system is reheated in heat exchangers at the heat source plant and afterward is pumped into the district heating network. At times of peak heat demand, the water, in addition, passes through a water-heating boiler. The water is supplied to the domestic and commercial customers via a supply line. At the users' premises the water passes through the HVAC systems, is cooled and is returned to the heat source plant by means of the network pumps. The hot water supply to the customer may be one of two types. One system is a closed type in which the district water heats up a secondary stream of potable water in a surface heat exchanger for DHW supply. In this case the flowrate of water circulating in the network is constant and only a small amount of makeup is required to compensate for leakage. The second system is the open type where the DHW is drawn off directly from the supply and return lines to the customer. In this case, the heat source plant makeup system has to continuously provide the amount of DHW required by the customer.

For a given heat load the piping size depends on the temperature drop in the network and the type of control of heat supply. Usually the temperature drop in the district heating system is determined by an economic optimization study taking into account the annual heat load duration pattern and the power plant characteristics. The heating network investment and maintenance represents a significant part of the overall heat generation and supply system costs. Therefore, for a given heat load every effort is made to increase the temperature drop between the supply and return lines, thus reducing the flowrate of the circulating water and as a result the piping size and pumping power. This could be provided by increasing the supply temperature and/or by decreasing the return temperature.

Usually the control of heat supply is provided by keeping the temperature in the supply line directly related to the outdoor ambient temperature. This means that the heating system will automatically receive the required amount of heat but the DHW and ventilation systems must have individual controls. When the supply temperature reaches about 160°F, which is the maximum required for the DHW, supply water temperature stays at this level.

The DHW supply is a very important factor in an overall district heating system, especially of open type. The average daily heat consumption for DHW is about 20 percent of the mean overall heat load and can reach 40 percent of the maximum heat load. DHW coefficient* depends, of course, on the climatic conditions and increases for regions with warmer climates. The demand for DHW is very non-uniform and varies considerably during any 24 hour period; considerable weekly and seasonal variations are also experienced. Therefore, the installation of a storage facility to equalize the hot water consumption is required.

A district heating system with an open DHW supply was applied on a large scale by S. F. Kop'ev in 1938 in the USSR and since then has been widely accepted in practice. Many large cities with multi-million populations (Leningrad, for example) are supplied from an open district heating system. The major advantages of this system in comparison with a closed type are as follows:

1. Elimination of the heat exchanger equipment and individual storage at the users' end with an associated substantial reduction in capital and maintenance cost.

2. Utilization of large quantities of low grade heat to warm the district heating makeup water. The source of low grade heat could be power plant condensers, non-controlled vacuum extractions, exhaust of auxiliary turbines and boiler flue gases. Waste heat from industry is another source for heat supply to the makeup water. This possibility is especially important when an integrated cogeneration power plant serves both industrial customers who need high pressure process steam, and urban customers who require hot water on a district heating network. The power plant usually has to be situated close to the industrial complex in order to economically supply steam at high pressure. The location of the power plant at a substantial distance from the urban customers will not pose a problem because hot water can be pumped for extensive distances. In this case, the makeup water for the open district heating system will absorb the low grade waste heat from the industrial plant. It is estimated that about 40 percent of the DHW load could be supplied by utilizing low grade heat with temperatures of only 90 to 100°F.

3. The possibility of designing the piping network for space heating demand only without taking into account the DHW load. This results in a substantial reduction in the piping system cost.

4. Prevention of corrosion and scaling problems in the DHW systems. This is because the makeup water undergoes a softening and deaeration treatment at the power plant, while the potable water in a closed district heating system is not additionally treated.

5. Reduction in the capacity of the city cold potable water mains. This is very important because about 50 percent of the overall potable water consumption is used for DHW supply.

The disadvantages of the open system are as follows:

1. Cost increase for the preparation of large quantities of makeup water which has to meet the necessary potable water sanitary standards. For all practical purposes the water treatment should prevent deposits on the heating surfaces and corrosion of heat exchangers and network piping.

2. Difficulty in identifying the difference between DHW consumption and system leakage.

The penalties associated with these disadvantages of the open system, however, are heavily outweighed by the substantial cost reduction of the district heating system.

The utilization of the open system also offers the possibility of further reducing piping costs. This may be achieved by eliminating the return pipe in the network and using the once-through heat transport system.

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*DHW coefficient is the ratio of the DHW heat load to the overall heat demand for space heating and DHW.

Once-Through District Heating System for the Bellingham Project

In an ideal situation the water supplied from a once-through system would serve all space heating needs first, and then the heat and water requirements of the DHW part of the system. If such a perfect balance between the space heating demand and the DHW load is not provided, some of the water will have to be drained, which will result in a substantial heat and water loss. In practice the heat and water balance can very rarely be achieved, therefore, it is difficult to completely eliminate the return line of the piping network. However, the once-through system could be feasible for the transmission of the heat from the heat source to the heat load center, especially when the heat source is not situated close to the city.

In the once-through heat supply system developed by Burns and Roe for Bellingham, the hot water is prepared at the aluminum plant for utilizing the waste heat from the potline exhaust gases. At the aluminum plant the water undergoes a chemical treatment and a deaeration process. From the aluminum plant, the water is routed to the city area through a single pipe. In the city area an open two-pipe distribution system is used. From the supply line the hot water is provided first to the space heating system and the return water is then used for the DHW supply. When the temperature of the return water is below the required level, then water with a higher temperature from the supply line is added. If the water is not completely utilized in the DHW system the excess is returned to storage. When the DHW consumption is higher than that supplied from the aluminum plant, additional water flowrate is provided from the storage facility. The storage balances the heat and water supply from the aluminum plant and the district heating consumption. To keep the water temperature in this system at the acceptable level, the peaking sources are located in the heating load area. After the peaking source a typical open two pipe system is implemented. In this case the transmission and distribution systems have different temperature modes and the once-through system actually operates as a makeup system.

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OVERVIEW OF THE CHEMICAL/HYDROGEN ENERGY SYSTEMS (C/HES) PROGRAM

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Abstract

During the last year the activities within the Division of Energy Storage Systems (STOR) have been restructured under a new Office of Advanced Conservation Technologies (ACT). The goal of the ACT is to develop advanced technologies for increased efficiency and use of renewable energy resources in transportation, industry, and buildings applications. The office directs programs designed to improve the technology base underlying energy technologies and development of advanced concepts in energy storage, conversion, and utilization. The Thermal and Chemical Systems Branch in the Office of Advanced Conservation Technologies is responsible for the administration of research, development, and demonstration programs on thermal, chemical, and hydrogen storage systems. In this branch the Chemical/Hydrogen Energy Systems (C/HES) program encompasses the production, storage and transmission, and utilization of hydrogen. The current management structure and the programmatic emphasis of C/HES are summarized briefly below.

The decentralization policy initiated by DOE a year ago is progressing. Its goal is to shift an increasing amount of day-to-day management responsibility to the field, leaving headquarters with greater freedom to perform the "Washington duties", i.e., long-range planning, budget preparation, congressional responses, coordination and critical evaluations. There have been no major changes in the management structure of the C/HES program. However, for the third successive year, the program does have a different manager at headquarters. This is ameliorated by continuing access to the experience and expertise of the former program manager, Robert R. Reeves.

The C/HES program is now managed full-time at the DOE's Brookhaven Area Office (BHO) by Doug Miller. He replaces Robert Friess who previously performed the job on a part-time basis. Technical support for approximately a dozen projects under BHO's control are provided primarily by Brookhaven National Laboratory (BNL) and the Jet Propulsion Laboratory (JPL). BNL's program, which centers on hydrogen production by electrolysis and chemical heat pumps, has not undergone any major shift in direction since last year. It continues to benefit from the vigorous leadership of Al Mezzina. The JPL program, which is smaller in scope than that at BNL, continues to emphasize closed thermochemical cycles, related materials problems and economic analysis related to International Energy Agency (IEA) activities.

The heart of the C/HES program is the work in the field, which headquarters must support to the best of its ability. The largest single project in the C/HES program is the SPE Electrolyzer development. The electrolyzer is a truly modular system capable of use in conjunction with any one of a number of sources of electric current, i.e., hydroelectric, OTEC, photovoltaic, off-peak-electricity, etc. At the present time this device is being developed for use in conjunction with a small head hydro-electric project in Potsdam, NY. The longer term goals of the hydrogen project are also being pursued. These include coupling hydrogen production with solar energy sources as well as with waste heat. The emphasis on closed thermochemical cycles is of interest in these contexts.

The chemical heat pump (CHP) program, under Al Mezzina's direction, continues to focus on two systems which have several potential applications, including heating, cooling, and upgrading of low-grade thermal energy. These are the sulfuric acid and the metal hydride systems. Here again, one of the major virtues of the CHP is its modular nature, i.e., the source of waste heat can be any one of a number of sources. The use of industrial waste heat now appears to be the most likely candidate for early commercialization of these devices. The use of thermal energy from solar systems is also of considerable interest.

The prospects are good that the present level of funding for the C/HES program will remain substantially at its FY 80 level of $6.7M, with about 2/3 of this sum for hydrogen and 1/3 for chemical heat pumps. The program is varied with respect to the size of its constituent projects. This results in a variety of viewpoints and a healthy diversity of approaches to the overall program, which itself is a component of the larger problem of energy conservation. Appreciation of the merits of conservation has increased in recent years along with the understanding of its potential for decreasing the use of non-renewable fuels without the imposition of unacceptable economic and environmental penalties. That is a goal which we in the hydrogen program can support without reservation.

STATUS REPORT ON THE INTERNATIONAL ENERGY AGENCY'S (IEA) HYDROGEN PRODUCTION PROGRAM

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The IEA Agreement for the Hydrogen Production Program was signed by ten member organizations in October, 1977. At the same time, two annexes to the Agreement were approved for implementation. The initial term of the Agreement was three years, which means that extension of the Agreement is now under consideration.

During the past three years, four additional annexes to the Agreement were signed, but work on one of the original annexes was discontinued. In the following sections, a status report on each of the annexes will be given. In the initial effort, the cooperation was to be restricted to information and personnel exchange. During the past year or so, more task sharing and dovetailing of programs between member organizations has evolved. Consideration has been given to combining financial contributions for joint projects, but there are differences of opinion on whether or not these projects should be undertaken.

The only serious problem encountered during the past three years was with so-called intellectual property rights under the Agreement. The Commission of the European Communities (CEC) is a member of the IEA, but some countries within the CEC, e.g., France, are not. There was concern, particularly on the part of U.S. Department of Energy (DOE) attorneys that France could use inventions arising from the IEA Program without contributing results of its domestic program. The problem was solved by agreeing that such countries could not use any results of the program in commercial ventures unless they contributed all background information from their domestic program. This solution was particularly important because it set a precedent for later agreements under the IEA.

The DOE effort under the Agreement involves participation by the solar, energy research, and energy storage program offices. I represent DOE on the Executive Committee and also serve as Vice Chairman. J.P. Contzen of CEC is Chairman.

Annex I Thermochemical Hydrogen Production

The benefits to the U.S. of cooperation on thermochemical hydrogen production have been greater than in the other project areas, mainly because of the large effort contributed by the Ispra Laboratory of the CEC. The U.S. followed their lead in completing bench-scale facilities for demonstration of integrated processes. We are also making use of their "OPTIMO" computer code for technical and economic evaluation of thermochemical cycles. Another result of the cooperation includes identification of solid sulfate decomposition as a possible improvement over sulfuric acid decompositon in sulfur-based cycles. Also significant progress has been made in the selection of corrosion resistant materials for H_2SO_4 and HI systems. One U.S. scientist spent six months at the Ispra Laboratory and several European scientists have worked at U.S. laboratories for shorter periods of time.

Plans are now being made for a task-shared hardware test. It is likely that the U.S. will send a component for H_2SO_4 decomposition to the Ispra Laboratory for evaluation in a new test facility under construction.

Three workshops have been held for information exchange. The Commission of European Communities is the Operating Agent.

Annex II Heat Source Interface Technology

Although this annex was approved at the same time as the overall Agreement, only the U.S. and Germany agreed to participate. Also the plans included heavy emphasis on interfaces with gas-cooled nuclear reactors, an area which has been de-emphasized in the DOE program. Because of these and other problems, a decision was made approximately a year ago to discontinue effort as a separate annex. A smaller effort is now included in Annex I, with a balanced effort between nuclear and high temperature solar energy sources.

Annex III Assessment of Potential Future Markets

Work was initiated on market potential assessments in December, 1977. A common methodology and set of assumptions was established, then each of the ten participating organizations conducted an analysis for its geographic region. The results have been combined into a final report which should be published in the Fall of 1980. One of the participants, Italy, withdrew before completion of the study. An overall result is that hydrogen markets are projected to increase from 1.6×10^{18} J in 1978 to a value between 23 and 33×10^{18} J in 2025, summed for the following countries: Belgium, Canada, Germany, Japan, Netherlands, Sweden, Switzerland, and the U.S. Corresponding values for the U.S. alone are 1.0×10^{18} J in 1978 and between 20 and 28×10^{18} J in 2025. Separate projections are available for non-fuel uses, direct fuel uses as hydrogen, and indirect fuel uses, e.g., hydrogen produced for coal gasification.

Follow-on studies that have just started include a comparison between hydrogen and methane as energy carriers, and methanol which is derived from hydrogen as an energy carrier.

The Commission of European Communities is the Operating Agent.

Annex IV Advanced Alkaline and Solid Polymer Water Electrolysis

Work on both advanced alkaline and solid polymer electrolysis are aimed at reaching significant improvements in efficiency and reductions in capital cost compared to commercially available alkaline electrolyzers. The emphasis in Europe and Canada is on alkaline systems, while the emphasis in the U.S. is on a solid polymer system. Thus a quid pro quo was established at the time the annex was signed. To avoid major difficulties with proprietary information, cooperative work on alkaline systems does not include equipment design. Instead, the effort focuses on development of high temperature separators and better electrocatalysts. For example, data are being generated on the following new separator materials: polyantimonic acid in polysulfone matrix (Belgium), metal gauze-oxide composites (CEC), polytetrafluorethylene impregnated with potassium titanate (Japan), and $NiCO_2S_4$ (U.K.).

The principal contribution of the U.S. is the engineering development of electrolyzer components with solid polymer electrolytes, but we also contribute results of applied research on alkaline systems.

The U.S. is Operating Agent for Annex IV.

Annex V Solid Oxide Water Vapor Electrolysis

The technology for water vapor electrolysis at high temperatures is an adaptation of technology for solid electrolyte fuel cells. Applied research is still required, principally in materials and fabrication techniques, before engineering development is appropriate. There is a clear advantage to using cells that operate below 1000°C. To do this, the solid electrolytes in all likelihood must be hydrogen rather than oxygen ion conductors. Canada and Italy are contributing in this area. Germany and the U.S. are concentrating their efforts on the preparation and properties of zirconia-yttria and other solid oxide electrolytes. A major portion of the U.S. work is contributed from fuel cell development projects.

Italy is the Operating Agent.

Annex VI Photocatalytic Water Electrolysis

Work on this project started in November, 1977, with six participants and a level of effort of 15 manyears/year. During the first two years, the effort will be restricted to basic and applied research. A decision will then be made on whether or not to start a development effort. A workshop was held in Belgium in March, 1980, as a forum for discussion of past work and future plans. The existing participants are trying to convince Germany and Japan to join the project because their domestic programs are judged to be large and high quality. A progress report describing specific accomplishments will not be available until the end of the year.

Belgium is the Operating Agent for this project.

General Comments:

The levels of effort for the Program are listed in Table I by Annex and in Table II by participating organizations. The total level of effort is equivalent to $20 million in financial support. The data show that the U.S. contribution is thirty percent of the total, which means that we should and are receiving more results from abroad than we contribute. Initiation of some of the work has been slower than desired because of administrative details and a rather slow communication process, but all parts of the present program are proceeding at a productive, steady pace. All activities contributed by the U.S. are included in our ongoing domestic program, so the only cost of participation in the IEA Program are modest administrative and travel expenses.

In the future increased emphasis will be placed on task sharing as opposed to simple exchange of results. I expect that we will continue to concentrate on success of the existing projects rather than extension of the Agreement to add more projects. We hope to do better on dissemination of results, which is the main reason I offered to give this status report to our contractor community.

Table I: Participation in IEA Hydrogen Production Program by Annex

(Data in Manyears/Year of Effort)

Annex	U.S.	Others	Total
I	32	51	83
II		----Discontinued----	
III	1	10	11
IV	14	65	79
V	6	7	13
VI	6	9	15
Totals	59	142	201

Table II: Participation in IEA Hydrogen Production Program by Organization

Participant	Effort (Manyears/Year)
Belgium	9
Canada	8
CEC	60
Germany	22
Italy	19
Japan	13
Netherlands	4
Sweden	4
Switzerland	2
United Kingdom	1
United States	59
Total	201

CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS

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Abstract

The hydrogen energy R&D projects sponsored by the Division of Energy Storage (STOR) in FY 1979 were transferred to the Brookhaven Area Office (BHO) in FY 1980 in response to the Department of Energy's (DOE) program decentralization objectives. Subsequently, the Office of Advanced Conservation Technologies (AC) was created from STOR. The hydrogen energy research and development (R&D) projects previously sponsored by STOR were reorganized into two basic R&D areas (with related technologies) as part of the decentralization plan. Those two areas are:

- Hydrogen production via thermochemical cycles with related material compatability R&D, and
- Hydrogen production via electrolysis-based systems with related hydrogen storage systems R&D.

The Brookhaven National Laboratory (BNL) serves as technical monitor on all projects included in the electrolysis-based R&D subprogram and performs the management tasks associated with these projects. The Jet Propulsion Laboratory (JPL) performs a similar function for all projects included in the thermochemical cycles subprogram. Both BNL and JPL report directly to BHO. This includes technical direction on all projects, financial reporting, milestone compliance, monthly reporting, and the annual operating plan. BHO ensures that Headquarters/AC receives copies of all correspondence submitted and keeps HQ/AC appraised of all important issues. All other contractors and national laboratories will report directly to BHO. The overall program management structure is illustrated in Figure 1, including the roles of AC, BHO, BNL, JPL and The Aerospace Corporation.

C/HES Program Overview (1980 - 1981)

Hydrogen Production Systems and Chemical Heat Pumps have maintained their lead budget and programmatic priority. Modest activities, deriving from technology spinoff, are planned to examine near-term resource recovery options. The C/HES major program elements are: (1) Electrochemical Production Systems; (2) Thermochemical Production Systems; (3) Chemical Heat Pumps. Minor elements are: (4) Chemical Storage Systems and Materials; (5) End-Use Applications and Systems Studies.

(1) Electrochemical Systems The engineering development of General Electric's Solid Polymer Electrolyte Water Electrolysis System has progressed to the fabrication, assembly and continuous test of a 200 kW unit. Findings have shown no inherent design or electrochemical limitations to meeting system cost and performance projections; thus scale-up of electrodes from 2.5 ft to 10 ft^2, consistent with proceeding to multi-megawatt designs, was approved. In FY 81 actual fabrication of scaled-up systems will await clear demonstration of electrolysis module cost reduction as well as improved performance efficiency of 2.5 ft^2 electrode systems. Fabrication improvements look to quality control as well as elimination of electric resistance problems.

Advanced alkaline water electrolysis system components and materials testing results have been equated to cost. Preliminary evaluations suggest that these advanced systems may produce hydrogen at costs similar to those projected for SPE systems. Also, efforts have been initiated looking to scaled-up vapor lift or static feed alkaline electrolyzers. Successful implementation of the static feed concept may offer capital cost reduction advantages as well as permit the direct electrolysis of impure water feeds.

(2) Thermochemical Systems Given a high temperature heat source, worldwide investigations have pointed toward indentification of closed cycle reactions which would provide for the dissociation of water into hydrogen and oxygen while preserving the intermediate reagents for recycling. While early U.S. efforts were directed toward ties with nuclear heat sources, the prospects of using solar energy high temperature sources and storage schemes will be emphasized in the future.

Process development actions have concentrated in two areas (1) sulfur/iodine thermochemical water splitting cycle at General Atomic Company; and (2) the hybrid sulfur cycle at Westinghouse. The processes each offer a common sulfuric acid decomposition step to interface with high temperature sources. Additional efforts into identification of other thermochemical cycles and related electrocatalysis are ongoing at LASL and the Institute of Gas Technology.

The thrust of activities in FY 81 will aim for selection of the optimum process with ties to high temperature solar heat and the upgrade of technology state-of-the-art which will permit such selection. Support systems engineering studies will be conducted for competing processes which will identify cost of hydrogen production for the several options under investigation.

(3) Chemical Heat Pumps Requirements analyses addressing technical, cost and marketing factors for sulfuric acid/water chemical heat pumps were completed. Findings have pointed to system designs which will find application as industrial chemical heat pumps capable of upgrading 200°F to heat to "marketable" 300°-350°F process steam. The subcontractor indicates return-on-investment potential of 1.5 to 2 years.

Engineering development tests of calcium chloride/methanol chemical heat pumps show that targeted performance goals are attainable. Capital/operating cost trends indicate that market penetration of this solid/vapor, low-pressure system will be seriously inhibited. The desirable materials properties of relatively innocuous calcium chloride and methanol compared to corrosive acid systems or toxic NH_3 are offset by cost penalties to override heat transfer and mass flow limitations, therefore, while market acceptance for residential/commercial applications may be more promising, cost/economics considerations will probably prevail.

A competitive procurement for development of metal hydrides chemical heat pumps was initiated. Target date for award of contract has been set for late FY 80. Industrial response to the competitive RFP was most encouraging in terms of the expressions of interest demonstrated on a national and international level.

Consistent with goals and objectives for Chemical Heat Pump development and commercialization, a contract has been let which will permit continuing technical, cost and marketing analyses of promising systems. Evaluations will consider market penetration potential in light of current and emerging competitive technologies. These evaluations will be applied to developing criteria and rationale for the current as well as future programmatic action regarding CES/CHP development.

(4) End-Use Applications and Systems Studies Merchant hydrogen production and marketing from small hydropower sites continues as the nearest-term renewable resource conversion opportunity. A contract has been executed with New York State Energy Research and Development Authority (NYSERDA). This is a cost-shared effort equally divided among DOE, NYSERDA, and the City of Potsdam. NYSERDA will complete analytical and design efforts associated with small hydropower application to hydrogen production. Cost analysis will define whether dedicated excess power can be used to produce and market merchant hydrogen to the local industrial community.

"Over the fence" hydrogen marketing from small hydroelectric sites was examined. It has been concluded that site availability in close proximity to a single user would seriously limit the replication potential of the concept. Further, cost impacts arising from conventional financing compounded by commercial return-on-investment requirements would drive costs out of the competitive range.

Consideration is being given to a reevaluation of the natural gas supplementation option, although no programmatic commitments have been made. Driving the systems reevaluation rationale is the conclusion that intermittent renewables such as solar and wind energy conversion systems virtually mandate storage. An alternative to costly bulk storage systems is to gain "energy credits" by direct injection of hydrogen into available distribution networks. Successful development of hydrogen separation schemes may be more cost effective than the bulk storage option.

(5) Storage Systems and Materials In the last quarter of FY 80, development efforts were initiated to examine the prospects of using metal hydrides in an industrial process off-gas resource recovery mode. Pretreated refinery gases passed through metal hydrides chemical separations systems offer up to 0.1 Q per year of recoverable hydrogen as a valuable commodity. Cost projects for the separation process indicate several-fold savings over the current price of hydrogen obtained from hydrocarbon steam reforming or partial oxidation processes.

Bench-scale metal hydrides chemical compressors have been fabricated and tested in FY 80. Design and performance data obtained from the development test units will be applied to development and fabrication of field test prototypes.

Bulk storage of hydrogen in glass microcavities was investigated through the conduct of characterization tests of commercially available microspheres normally used as plastic fillers. Cost and performance trends based upon evaluation of test results indicate a need for materials optimization in order for microcavity storage (MCS) to be a viable mobile or bulk storage option. Microsphere production appears to require an optimum sodium/silicate materials content so as to effect a compromise of hydrogen permeation, retention and delivery rates consistent with storage application scenarios.

FY 81 Programmatic Guidelines

Pressures are being imposed on the technological community to respond to near-term commercialization goals. Also, it is becoming increasingly apparent that conventional fuel prices as projected for this time frame are still less than current hydrogen production costs. These two factors provide the major criteria for program formulation in FY 81 and beyond.

While projects in chemical heat pumps development fall within the criteria for near-term technology transfer, hydrogen energy storage systems are relegated to a base technology development role seeking out targets-of-opportunity which may offer near-term impact. Budgetary constraints will force programs to compete for funding allocations which in turn will be made in accordance with guidelines for near-term impact. Yet, the ultimate benefits accruable from hydrogen as an environmentally benign energy form, as an energy carrier, and as a versatile commodity remain valid. These considerations alone justify modest research and development support to hydrogen energy storage systems. A premium must be paid to ensure against the uncertainties of our present-day vulnerability to international whim and future considerations of an environmental nature. In FY 81, DOE should give due consideration to beginning technology transfer via an evolutionary process. In most instances, engineering development can be viewed as individual or separable hardware projects; but when these projects are integrated into an overall concept carrying through from, say, renewable resource conversion to hydrogen production to storage and/or distribution and end-use, a series of technical, legal and institutional complexities can arise. These issues may be treated more comprehensively with input derived from industry hands-on testing and evaluation. Implementation of such system engineering studies will require "across-the-board" interaction among DOE divisions and branches as well as industry participants. Project activities for FY 81 are summarized as line item listings by program element. The listings are presented in order of programmatic priority which in turn will be reflected in budgetary allocations by priority ranking.

1981 Budgetary Overview

Each of the program elements indicate a planned growth over FY 1980 funding. The required BA for FY 1981 ($7400K) is approximately the same as FY 1980, and BO requirements for FY 1981 are 22% greater than the FY 1980 funded BO of $6306K. Each of these elements indicate a pattern of growth over the FY 80 funding. The following summary reflects an overview of the financial trend for fiscal years 1980-82:

Electrochemical Production Systems SPE Water Electrolysis Systems development will receive top technical oversight priority. Emphasis will be placed on demonstrating cost reductions at GE in electrocatalysts as well as on demonstrating improved electrochemical efficiency (85%).

Advanced Alkaline Water Electrolysis development activities will concentrate on completion of electrocatalyst, electrode, and materials testing. New efforts to validate the potential of static feed systems will be completed. DOE policy will determine possible future consideration of the design and fabrication of a several-hundred kilowatt advanced alkaline water electrolysis system incorporating all design and material advances in state-of-the-art.

Support activities to advanced water electrolysis will take the form of efforts into advanced electrocatalysis and materials. New starts will deal with high temperature electrolysis and anode depolarizer systems.

Thermochemical Production Systems The two thermochemical production systems currently under development will be continued at about equal funding levels. Emphasis will be shifted toward process modifications leading to coupling to solar high temperature sources. Investigations of competitive process economics will be performed to provide data for 1981 selection of the process for a solar demonstration pilot plant.

Modest support activities in the areas of alternate process chemistry and materials compatability will be funded. JPL in-house efforts will focus on understanding of the mechanical chemical and economic comparison between the two major processes in preparation for the decision on the solar pilot plant process selection.

Chemical Energy Storage (CES) and Chemical Heat Pump (CHP) budgets reflect a modest increase of 10% over FY 1980 BO funds. This is affected, in part, by the initiation of BNL in-house R&D to support CES activities and the intensification of CHP contract activities initiated in FY 1980. The

	1980		1981		1982	
	BA	BO	BA	BO	BA	BO
Electrochemical Production, H_2	2.1	2.0	2.3	2.4	2.4	2.3
Thermochemical Production, H_2	1.3	1.4	1.7	1.6	2.8	2.0
Chemical Heat Pump	2.7	1.1	1.3	1.6	1.4	2.0
Chemical Storage Systems	.8	.6	.8	1.0	1.0	.8
End Use Applications	.3	.2	1.3	1.1	.7	1.0
Total $\$10^6$	7.2	5.3	7.4	7.7	8.3	8.1

CHP activity was transferred to BNL during FY 1980 and funding projections through 1982 reflect the program focus and direction outlined in the BNL CHP Five-Year Plan (BNL 27955).

Rocket Research will proceed with fabrication and assembly of a 1,000,000 BTU/150,000 BTU/hr sulfuric acid/water CHP following DOE/BNL approval of system design. The unit will undergo performance verification testing and plans will be initiated for unit field testing.

Metal hydrides chemical heat pump development activity will begin at the awarded contractor facilities. Concept development will have been completed to set the stage for engineering development test unit design and fabrication.

Cooperative DOE/BNL/Exxon development of a $ZnBr_2/LiBr_2$/Methanol industrial CHP will begin and design/performance parameters identified based upon criteria as apply to the most promising industrial application. Based upon analytical/experimental component and materials evaluations, residential/commercial prospects for a $ZnBr_2/LiBr_2$/Freon CHP will re reviewed as a potential project task.

TRW will proceed with cost-value analyses for systems currently under development or in project formulation phases. These analyses will deal with the cost competitive and performance competitive comparisons with current and emerging technology.

Storage Systems and Materials Chemical separation/purification systems development will assume lead priority within this program element. Initial phase activity evaluation will set the stage for future process development. Support efforts complementing this activity will deal with hydrogen separation from natural gas mixtures.

Chemical compressor design and fabrication will proceed to field test prototype systems which will tie to make electrolysis systems hydrogen output considered as feed in a natural gas supplementation application.

Microcavity hydrogen storage efforts may be redirected from bulk characterization of commercially available materials to optimization of materials consistent with application design and use parameters.

BNL in-house technical support will be directed toward validation as well as extension of advanced MCS development and application. Investigations will be initiated for considering "hydrogen storage and transport" in NH_3 and CH_3OH. Cost, energy balance and environmental considerations will be weighed against conventional and advanced storage schemes.

End-Use Applications & Systems Studies End-use applications funding will more than double as the NYSERDA effort at Potsdam NY gets underway. A modest effort will be funded jointly with the State of Alaska to perform a preliminary evaluation of the production of hydrogen from renewable sources available within Alaska. This study will emphasize wind and water power energy sources coupled with Alaska's unique energy requirements.

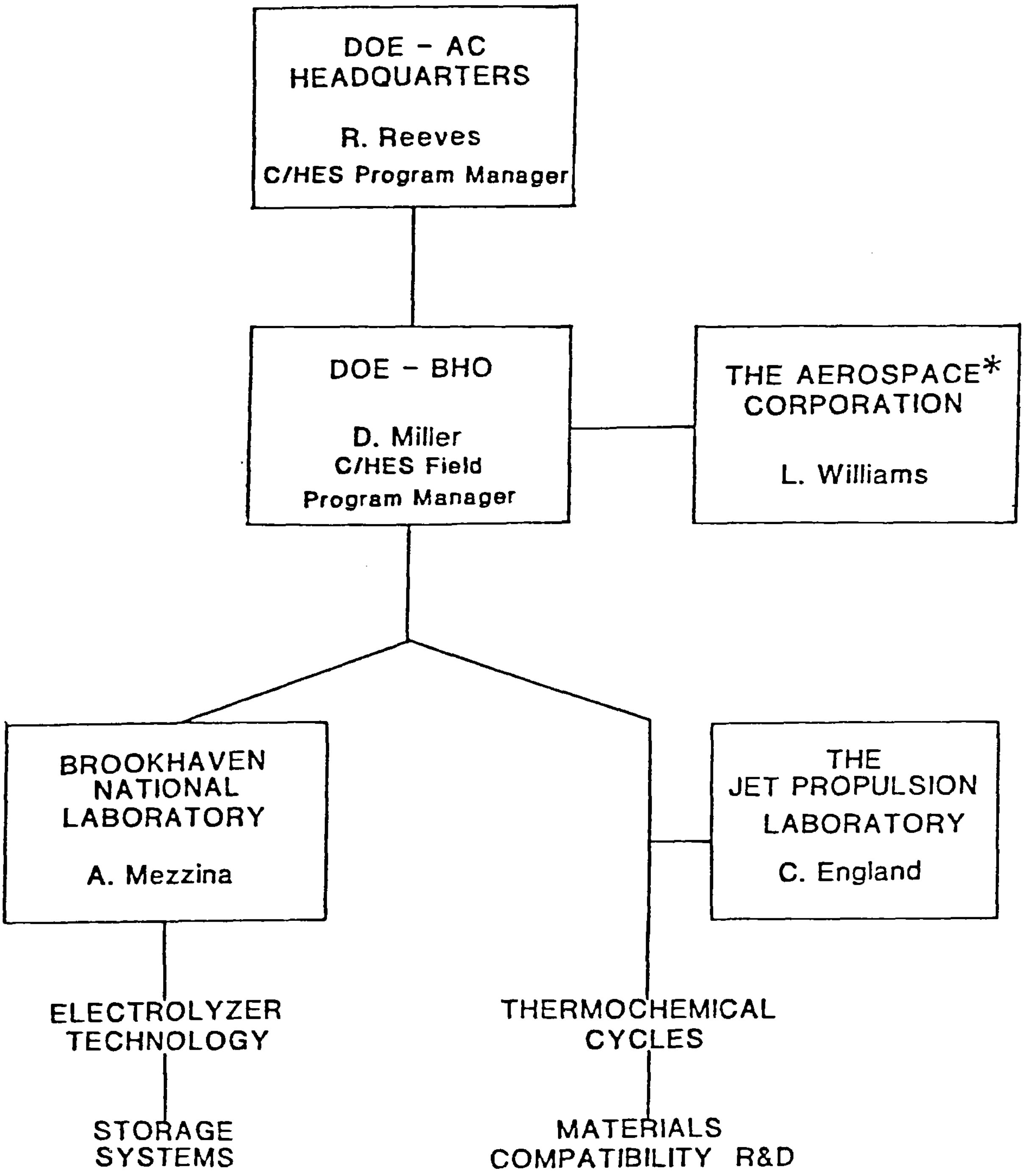

FIGURE 1. DOE C/HES PROGRAM ORGANIZATION CHART

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*Technical Support Contractor

THE SULFURIC ACID/WATER CHEMICAL
HEAT PUMP/ENERGY STORAGE PROGRAM

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Abstract

Temperature enhancement of industrial waste heat streams (industrial heat pumping), and heating and cooling of buildings with energy storage appear to be promising applications of the sulfuric acid water chemical heat pump system presently under development. The current project is structured to verify these capabiities and to enhance near-term commercialization. To this end, a large-scale verification test unit (VTU) has been designed which incorporates many commercial mass producible design features and materials. The nominal storage capacity is 10^6 Btu, with a power rating equal to 150,000 Btu/hr. The unit is scheduled to be constructed and tested closed loop during 1981.

An engineering model CHP/CES system has been designed, fabricated, and tested closed loop with a nominal 25,000 Btu/hr charge and discharge rate and 150K to 300K Btu storage capacity, depending on the number of tanks. Preliminary testing of commercial grade acid plumbing and valves is complete with no equipment failures. Testing is continuing to study component life and system configuration.

Introduction

The Energy Storage Division of DOE is currently funding development of chemical heat pumps at Brookhaven National Laboratory. Among the potential applications are building heating and cooling, off peak electrical energy storage, and industrial waste heat recovery. At present the DOE programs are centered on liquid and solid phase reactions such as metal hydrides, ammoniated salts, methanol-based salts and the sulfuric acid and water system described in this paper. Development of the sulfuric acid system has been contracted to Rocket Research Company since the program began in 1976.[1, 2, 3]

Currently, Rocket Research is under contract to Brookhaven National Laboratory to conduct a four-phase program. Phases 1 and 2 are completed and consisted of a requirements analysis and detailed design of the VTU. Generic applications have been identified which include industrial waste heat pumping, space conditioning, air or gas moisture removal, steam accumulation, cogeneration and energy storage. The VTU design incorporates two of the above applications: waste heat pumping and space conditioning. The design incorporates combined generator/condenser and absorber/evaporator reaction components made of steel shells coated with acid-resistant porcelain. Teflon-lined acid plumbing and valves will be used, and the acid storage tank will be fabricated from steel lined with porcelain and will be capable of vacuum operation.

The remaining Phases 3 and 4, consisting of VTU fabrication and testing, respectively, will be conducted in FY 81.

Design Requirements

As discussed previously[4], the major components of the sulfuric acid system consist of: acid storage, water storage, generator (acid/water separation), condenser (water only), evaporator (water only), absorber (acid dilution), heat source (and collection system) required to drive the cycle, low-temperature source (and collection system) required for heat pumping, and parasitic power sources such as liquid pumps.

Operational Boundaries: The limitations imposed by the properties of sulfuric acid and water on the operation of the CHP/CES are summarized in Table 1. The limits of 720°F for the generator and absorber represent operation at a concentration of 98 weight percent, and system pressure of 30 psia. Higher system pressures can be designed by operating at lower acid concentrations since the vapor pressure of water increases. However, in practice minimizing system pressure through selection of acid concentration will provide lower capital costs and safer system operation. Temperatures higher than 720°F are possible, but material problems along with a more complex chemical separation process will tend to limit the applications. The minimum operational temperatures and concentrations in the acid system are controlled by the application. For example, the minimum temperature in the absorber of 105°F has been established as the practical limit for building heating systems. Depending on the evaporation temperature, the minimum acid concentration could be as low as 55 weight percent. Other applications could dictate lower temperatures and concentrations.

Table 1 Sulfuric acid CHP operational boundaries

Component	Limit
Generator	Max temp: 720°F Max concentration: 98 Wt% Min concentration: Application controlled
Absorber	Max temp: 720°F Max concentration: 98 Wt% Min concentration: 55 Wt% (for heating mode: others are application controlled) Min temp: 105°F (for heating)
Condenser	Max temp: Application controlled Min temp: 35°F
Evaporator	Max temp: Application controlled Min temp: 35°F (no acid); -55°F (acid added)

The limits on the condenser and evaporator are controlled by the freezing point of water. An exception is possible by recirculating acid in the evaporators.[3] This extends the freezing point to -55°F, and allows heat extraction from ambient air during subfreezing weather.

External Heat Sources: Previous development work was directed towards the solar application.[2, 3] During the current program, the requirements for the high-temperature source have been expanded to consider alternate energy inputs such as fossil fuels, industrial waste heat and electricity. The CHP has the potential of conserving energy using these sources because of its ability to pump heat and operate with a coefficient of performance (COP) greater than unity.

When considering fossil fuels as direct energy drivers for the CHP, energy storage will not be required in most cases since there generally is no diurnal peaking problem as with electricity or long-term intermittence as in the solar case. However, to be cost effective, burning efficiencies of at least 75 percent should be obtained in order to achieve a total system COP greater than unity. The CHP will conserve fuel with lower burning efficiencies, but at a cost that would be higher than direct conservation through improved combustion.

Using electrical energy as a driver is nearly 100 percent efficient, and is attractive because the system storage capability can significantly reduce utility peaking problems. If the CHP/CES system charging cycle were controlled by the utility, further optimization of generating equipment could be realized in both building heating and cooling applications. Note that the system discharge cycle would be controlled by the user, and at the point of storage depletion, the utility control would be overridden so that the system would operate in the absorption cycle mode.

Utilization of industrial waste heat also requires little or no storage capacity if the CHP is designed to upgrade waste process heat to a higher temperature which is then used in the process. Rapid payback of the system is anticipated through fuel conservation. For these applications, the CHP reaction components, primarily the absorber and evaporator will be designed for higher pressure operations than the generator and condenser. This is the opposite of the design requirements for heating and cooling applications where the CHP is abstracting energy from the surrounding environment. However, the component configurations are expected to be similar to previous designs tested in the prototype unit.

An equally important CHP design requirement is the specification of the type of low-temperature source to be used as the evaporator energy driver.[6] Several options are being considered: ground coupling, ambient air and water. Two applications which do not require a significant capital investment for a low-temperature collection system are building cooling and industrial heat pumping. The use of water sources such as lakes, aquifers, ponds, ocean, etc. yield excellent CHP storage densities and high COP performance throughout the heating seasons. Extraction of energy from the air requires the least expensive capital investment at the cost of lower energy storage densities and reduced COP. Ground coupling systems use PVC pipe buried below ground levels to extract stored energy in the ground. High system performance, as with water systems, are achieved at the cost of high capital equipment and installation.

A performance comparison of the three methods for driving the evaporator is summarized in Table 2. The heat exchanger area requirements are much lower for the air-driven evaporator (air over the tubes) than for either of the other two systems; but because it operates at such a low evaporator temperature and pressure, the operating performance is very low. The lower capital investment costs would rapidly be negated by the higher parasitic blower operational costs. Ground-driven evaporator heating requires nearly twice the heat exchanger area (air through the tubes), but again the higher operational performance could outweigh differences in capital investment costs. Furthermore, the ground-driven system would not require circulation of acid in the heat exchanger loop to depress the freezing point, an added control complexity in the air-driven system.

Table 2 Evaporator low temperature source

	Heat exchange area (ft^2)	Min acid concentration (wt %)	Energy density (Btu/lbm)	Combined heating COP (ideal)
Air-driven evaporator:				
Air over tubes	124	89	270	1.30
Air through tubes	2,800	82	320	1.40
Ground-driven evaporator:				
(assumes h = 4.0 Btu/ ft^2-hr-°F)	4,800	69	480	1.55

Assumptions:

Minimum heat rate from absorber: 150,000 Btu/hr (at 130°F)
Energy storage requirements: 10^6 Btu
Condenser temperature: 105°F
Maximum acid concentration: 98%

The above low temperature source systems will provide the basis for further analysis to determine the most cost-effective system for heating purposes. The capital cost of these systems will also be compared to the cost of aquifer thermal sink systems or surface water (i.e. ponds, lakes, etc.) systems.

Industrial Heat Pump

The industrial heat pump, used for temperature enhancement of waste heat streams, is an important application of the sulfuric acid system studied during this program.

Conservation of energy in the industrial sector by reclaiming waste heat is a national goal and appears economical at today's energy prices. Waste heat can either be used directly for building heating or industrial processes if the temperature is high enough. However, waste heat is typically found at temperatures lower than desired. Heat pumping systems can be used to reclaim this waste heat at the desired process temperature. Typically compressor-driven Rankine cycles are used. The chemical heat pump, or absorption cycle, can also be utilized and does not require the compressor work input.

The sulfuric acid system can be operated in a continuous cycle to upgrade low-temperature waste heat. Four reaction components are required: a generator, condenser, evaporator, and absorber. In this process the waste heat source is input into the evaporator while the condenser is driven by a low-temperature source. This means that the operational pressure of the evaporator and absorber is higher than the generator and condenser. Therefore, the heat retrieved in the absorber will be much higher than that required to regenerate (concentrate the acid).

There are several promising waste heat sources for the industrial chemical heat pump, ICHP. One of the most promising, because of its simplicity, directly utilizes industrial waste water such as condensate, cooking water, cooling water, etc. Figure 1 presents a schematic of this configuration. The warm source water (waste heat) is input into the system in two places. First it is throttled into the evaporator, which is operated slightly below the saturation pressure. Water vapor is flashed and transferred to the absorber by means of the chemical potential of the incoming concentrated acid in the absorber. The water vapor condenses and dilutes the concentrated acid at a temperature higher than the waste heat source. Heat is removed from the dilute acid and supplied to the process at temperatures of 150°F to 380°F, with waste heat input temperatures of 130°F and 250°F, respectively. The dilute acid is then throttled as it enters the generator, giving off an equal amount of water vapor (per unit of time) as transfered in the absorber. The water vapor is condensed in the condenser at a temperature in the range of 40°F to 60°F, using cooling water. The concentrated sulfuric acid leaves the generator, at which time it is heated by the second input of waste heat to recuperate the energy lost in the generator throttling process before entering the absorber.

The performance of the industrial heat pump is typically defined as an electrical coefficient of performance (COP_e) rather than the total energy version. Essentially the heat extracted from the waste energy source is considered as "free" heat since it would normally be rejected. The use of the term "free" in this analysis is qualified by the fact that often times, waste heat loss has an inherent value to the industrial user. This must be considered on an individual basis, and may affect the economic payback time. However, for purposes of performance comparisons, the waste heat input will not be included. The parasitic work required to drive the equipment is converted directly to thermal units without the three to one electric power conversion efficiency. Therefore, COP_e is defined as:

$$COP_e = \frac{Q_{out}}{W_{parasitic}}$$

where:

Q_{out} = heat rate (Btu/hr) to the hot process

$W_{parasitic}$ = electrical power (Btu/hr) required to pump water and acid through the CHP and heat exchangers

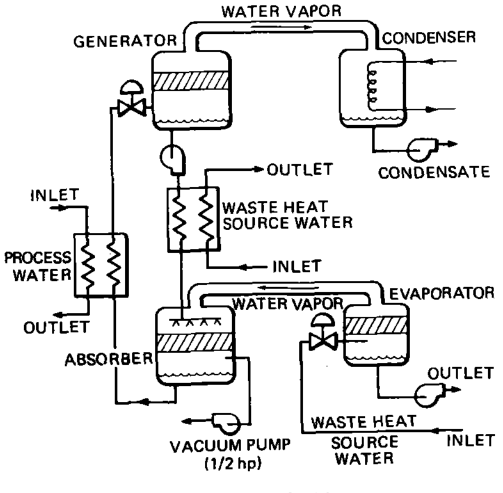

Fig 1 Industrial chemical heat pump

ICHP's can be optimized for particular applications. Calculated COP_e as a function of the waste heat source temperature is presented in Figure 2 for various ratios of process heat extracted, divided by the heat input from the waste heat source. A condenser inlet temperature of 50°F, parasitic power for the pumps shown in Figure 1, and a process water temperature rise of 20°F were assumed for these calculations. Also shown crossplotted is the maximum temperature delivered to the process. As the waste heat source temperature is increased, the COP_e increases. Typical values for the ratio of process heat delivered to the waste heat supplied vary from 0.5 to 0.1. Thus, the waste heat supply must be from 2 to 10 times larger than the process needs. Note

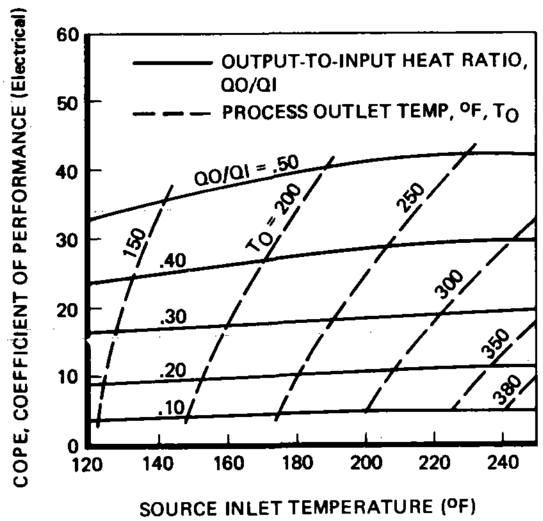

Fig 2 Industrial chemical heat pump performance

that temperatures as high as 380 °F can be produced but at substantially reduced COP_e and heat ratio. The performance of a sulfuric acid ICHP at a given waste heat source inlet temperature of 210 °F is presented in Figure 3. In this case, temperatures as high as 320 °F can be achieved. Values of COP_e range from 46 to 5, with corresponding heat ratios of 0.5 to 0.1.

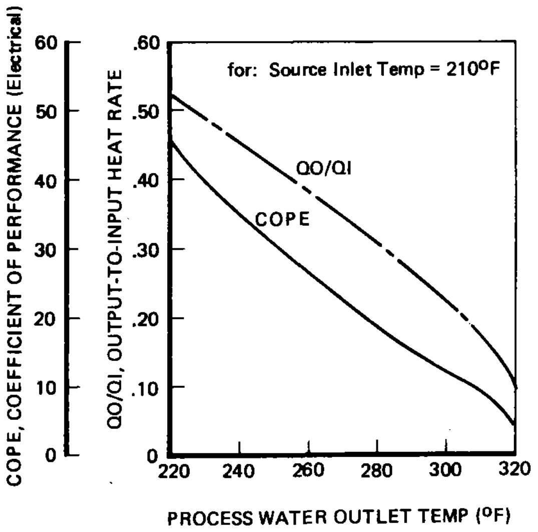

Fig 3 Performance of the industrial chemical heat pump

The above performance of the ICHP was limited to utilization of the same waste heat source to drive the evaporator and heat the concentrated acid. However, if higher temperature waste heat is available to heat the concentrated acid (e.g. exhaust heat stream) in addition to the warm water waste heat source, significantly higher temperatures could be produced for process heat. Also, the addition of evaporator and condenser heat exchangers will allow the system to extract waste heat from sources other than water. The capital cost will be higher in this case, but performance will be improved through lowered parasitic power. These will be studied in future analyses.

ICHP Economics: A sample calculation will demonstrate the cost effectiveness of reclaiming heat from warm waste sources for secondary processes using the sulfuric acid industrial chemical heat pump. For example, if rejected condensing water at 210 °F is available to heat water for a secondary process requiring a temperature of 260 °F, the COP_e from Figure 3 is equal to 27. The corresponding process heat-to-source heat input ratio would be approximately 0.38. For a system designed to provide 1×10^6 Btu/hr (MM Btu/hr) process heat (with 2.63 MM Btu/hr waste heat), the hourly cost to burn No. 6 fuel oil at an efficiency of 83 percent and a cost of \$4.6/MM Btu[5] is:

$$\begin{array}{l}\text{Fuel cost} \\ \text{(No. 6)}\end{array} = \frac{\$4.60/\text{MM Btu (MM Btu/hr)}}{0.83} = 5.54\ \$/\text{hr}$$

With the national average for electricity[5] at 0.05 \$/kW-hr, the hourly cost to operate the sulfuric acid ICHP is:

$$\begin{array}{l}\text{ICHP operational} \\ \text{cost}\end{array} = \frac{(\text{MM Btu/hr})(0.05\ \$/\text{kW-hr})}{(3{,}412\ \text{Btu/kW-hr})\ (27)} = 0.54\ \$/\text{hr}$$

The hourly operational savings for the ICHP is therefore \$5.00/hr or 90 percent of the cost of burning oil. A preliminary capital cost of a turnkey 1 MM Btu/hr ICHP has been estimated based on a production quantity of 100 units. Assuming 24-hour operation, at the above hourly fuel savings, it will take less than 2 years to pay back the investment. This represents a simple rate of return on investment greater than 50 percent. Furthermore 1,760 barrels of fuel oil will be conserved annually per system (per MM Btu/hr delivered). If the electricity used to operate the ICHP is derived from fossil fuel fired facilities, the savings is reduced by 160 barrels to 1,600 barrels per year, taking into account the three to one thermal to electric conversion efficiency.

The outlet temperature for the waste water released from the ICHP evaporator will be 190 °F in the above design. If the heat released from 210 °F to 190 °F has an inherent value to the industry, the above economics would be adversely affected. However, considerably longer payoff time such as 4 to 8 years is acceptable to many industrial firms.

Engineering Model Testing

The principal components of the engineering model test system, as it has been tested in the present contract, consist of a glass acid tank including a packed column of Raschig rings, a 316 stainless steel water tank, two glass shell and tube heat exchangers, a Duriron (high silicon iron) acid pump, and commercial grade Teflon-lined steel piping and valves. The system is loaded with approximately 150 lbs of 93 percent H_2SO_4, and is nominally capable of producing 25,000 Btu/hr and storing 150,000 Btu with the single acid tank. All components are supported by a tubular framework. A control panel mounted on the structure and duplicated remotely governs the acid and vacuum pumps, and charge and discharge valves. Inputs from 19 thermocouples, 1 turbine flowmeter, and 1 pressure transducer are recorded on a computerized digital data logger and strip-chart recorders. System rotometers are provided to monitor water flow rates. A more complete description of the system and its operation is given in References 2 and 3.

To date, the engineering model test system has been in operation 576 hours, accumulating 111 tests of which 89 were closed-loop charge/discharge cycles, including 33 cycles having peak acid temperatures of 400 °F, producing concentrations of 96 to 98 percent. An approximate total of 17.5 million Btu's have been charged and discharged. Closed-loop operation has been demonstrated with Raschig ring packed column heights ranging from 2 to 8 inches.

Recently, the engineering model CHP/CES unit has been modified to incorporate a horizontally mounted combined generator/absorber porcelain-lined reaction canister termed the VTU-M. Figure 4 shows the modified system, including the glass ambient or vacuum storage tank, the test vessel and the modified plumbing. Dilute acid is pumped out of the glass tank, through the heat exchangers, through a throttle valve, and into the VTU-M. The water flashes off and condenses in a PVC tray contained within the upper portion of the VTU-M. Cooling water is supplied through a coiled copper condenser. Acid carryover is limited by Raschig rings covering the distribution manifold in the bottom of the vessel. The concentrated acid drains into an approximately 1-gallon hold-up volume equipped with a sight port and then either flows directly into the pump by means of a recirculation loop or returns to storage. The VTU-M canister has been mounted above the acid level in the glass tank to allow the acid to return to storage without pumping.

The condenser loop is a closed loop, pumped system with a heat exchanger plumbed to city water. Condensing temperatures > 100 °F may be attained in this configuration.

The construction and test of the VTU-M has provided the opportunity to test the horizontally mounted combined generator/condenser or absorber/evaporator geometry, as well as

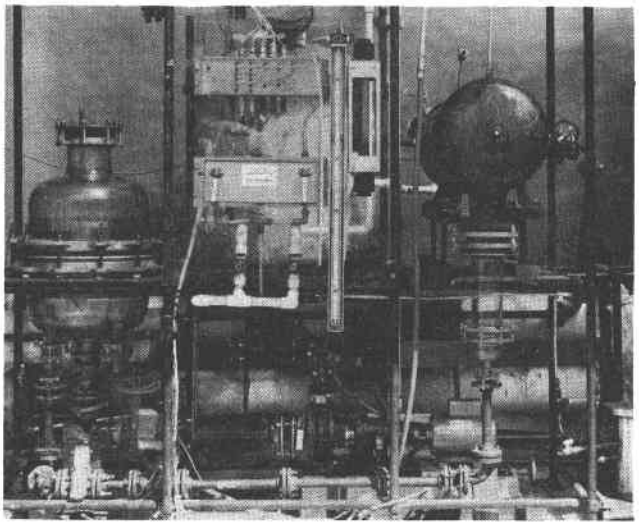

Fig 4 VTU-M engineering model test system

obtain materials information and explore new vacuum sealing techniques. The porcelain-coating is an economically attractive material which will be inspected during and after testing for durability.

Verification Test Unit Design

The verification test unit (VTU) design was completed in September of this year. The VTU will be operated in two modes: industrial heat pumping and heating and cooling (HVAC) with storage. As mentioned earlier, the nominal power rating will be 150,000 Btu/hr, with 10^6 Btu storage capacity for the HVAC system. Figure 5 presents an artist's conception of the VTU in the HVAC configuration. In the foreground are the acid and water tanks which will be constructed of steel. For protection against corrosion, the acid tank will be coated with porcelain and the water tank will be painted. The four reaction components are located in the background, and have been combined into two horizontal units: the generator/condenser, and evaporator/absorber. The shell structures for the reaction components will also be steel coated with porcelain and are mounted on a common steel bracket.

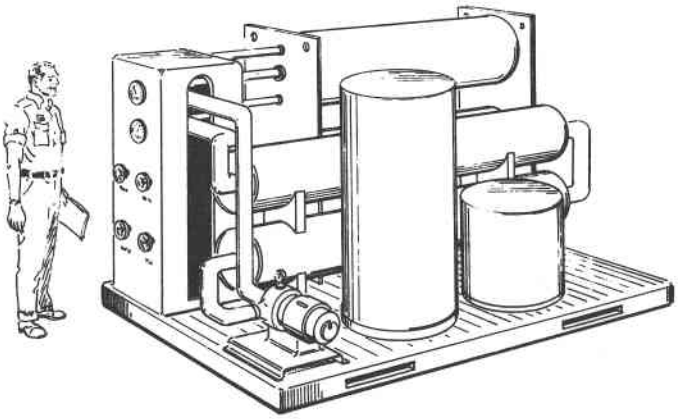

Fig 5 Artist's conception of the VTU

The two acid heat exchangers are located between the reaction components and the acid tanks. Commercial glass shell and tube heat exchangers, 60 square feet each, manufactured by Corning, will be used because of their cost effectiveness and corrosion resistance. The acid plumbing circuit will be manufactured from Teflon-lined steel pipe which has proven satisfactory for all acid concentration, temperatures, and pressures during previous engineering model testing. Two fluid-circuit designs will be used because of the requirements for the two operational modes. However, the reaction components and heat exchangers will remain unchanged. Acid storage will not be used for the industrial waste heat pump mode. The test program will be divided into two parts: testing of the industrial heat pump, followed by the HVAC storage system. Construction of the VTU is now underway and is expected to be completed by the end of March 1981. The testing of the VTU will begin in April and be completed by September 1981.

Acknowledgements

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A CHEMICAL HEAT PUMP BASED ON THE REACTION OF CALCIUM CHLORIDE AND METHANOL FOR SOLAR HEATING, COOLING AND STORAGE

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Abstract

Tests have been completed on an engineering development test prototype of the $CaCl_2$-CH_3OH chemical heat pump. The unit, which has a storage capacity in excess of 100,000 BTU, has successfully completed over 100 full charge-discharge cycles. Cycling data show that the rate of heat pumping depends strongly on the absorber-evaporator temperature difference ΔT, ranging from 1.15 moles CH_3OH per mole $CaCl_2$ per hour at $\Delta T = 40°C$ to 0.094 M/M/hr at $\Delta T = 55°C$. These rates are more than adequate for solar heating or for solar cooling using dry ambient air heat rejection. Performance degradation after 100 cycles, expressed as a contact resistance, was less than 2°C, and it appears that the resistance will not be increased by further cycling. The heat exchangers showed some warpage due to plastic flow of the salt, producing the contact resistance, but additional stiffening should prove adequate to guarantee a cycle life >20 years. The experimental COP for cooling was 0.52, close to the theoretically predicted value. (In an optimized system, the cooling COP should be >0.55.) An economic analysis for Washington, D.C. shows that, by the three standard economic decision criteria (payback period, years to recovery of down payment, and years to net positive cash flow), the $CaCl_2$-CH_3OH heat pump should be cost competitive with conventional heating (gas) and cooling (electric) alternatives. Furthermore, because the system is solar driven, absolute fuel savings will exceed other (non-conventional) alternatives.

Background

The $CaCl_2$-CH_3OH chemical heat pump has been developed to provide solar heating (including domestic hot water), air conditioning, and thermal energy storage in a single unit. The system design and predicted performance has been described in a number of recent publications.[1-6] Work carried out to date has included the reaction thermodynamics and kinetics, heat transfer, storage energy density, heat exchanger design, experimental cycling rates, overall system design, and projected annual performance. In this paper, we briefly review these earlier studies, and then discuss the results of a recent 100-cycle performance evaluation on the 100,000 BTU engineering development test prototype. Projected system economics are also discussed in some detail.

System Design

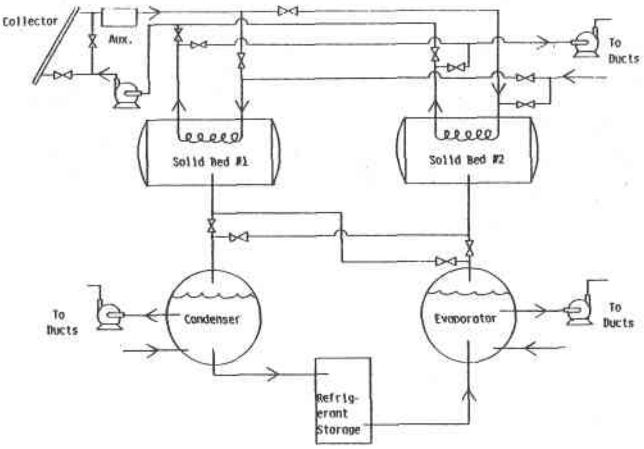

Fig. 1. Schematic design of the $CaCl_2$-CH_3OH chemical heat pump

The schematic design of the overall system is shown in Fig. 1; for clarity, the domestic hot water (DHW) preheat components have been omitted. The solar collector heat exchange fluid is valved to either of the two storage beds; alternatively, backup heat may be used. The heat produced by CH_3OH condensation is used for space heating or DHW as required, or is rejected to outdoor ambient air. Typically, the collector temperature will be 130°C (well within the range of evacuated tube collectors), while the condensation temperature will be around 45°C, permitting indoor air to be warmed to conventional duct temperatures, or heat rejection outdoors without excessive fan power. The evaporator is valved to the second storage bed, allowing simultaneous solar collection and heat pumping, which is particularly important for solar cooling. The heating and cooling coefficients of performance, including potential storage losses, have been carefully estimated theoretically, and are expected to be in the range 1.5-1.6 for heating and 0.5-0.6 for cooling. As noted below, these values have been confirmed experimentally. Steady-state performance coefficients, which are often used in system evaluations, are considerably higher, but are not particularly meaningful.

Reaction Thermodynamics

Equilibrium measurements[1] of the methanol vapor pressure above a mixture of $CaCl_2$ and solid-phase $CaCl_2 \cdot 2CH_3OH$ have shown that the reaction proceeds in a simple step. The vapor pressure data are described by the equation

$$\ln P(\text{atm}) = -6255/T + 15.2$$

from which the enthalpy and entropy of reaction are found to be

$$\Delta H = 51.7 \text{ kJ (mole } CH_3OH)^{-1}$$

$$\Delta S = 126 \text{ J (deg}\cdot\text{mole } CH_3OH)^{-1}$$

A more recent[7] direct calorimetric measurement of the reaction enthalpy gives $\Delta H = 56.0$ kJ (mole $CH_3OH)^{-1}$.

Cycling Rates

The equilibrium data imply that $CaCl_2$ at 40°C can absorb methanol vapor from an evaporator as cold as -22°C, i.e., at a 62°C temperature difference between absorber and evaporator. However, to achieve practical rates of heat delivery, a smaller temperature difference is required. Figure 2 shows the effect of this temperature difference on the rate of heat pumping. Up to 50% reaction (1:1 mole ratio), the rate of reaction is nearly constant, and can be described by the equation

$$\text{Rate (moles } CH_3OH \text{ per mole } CaCl_2 \text{ per hour)} = 0.0878 \exp((58.1-\Delta T)/11.3)^2$$

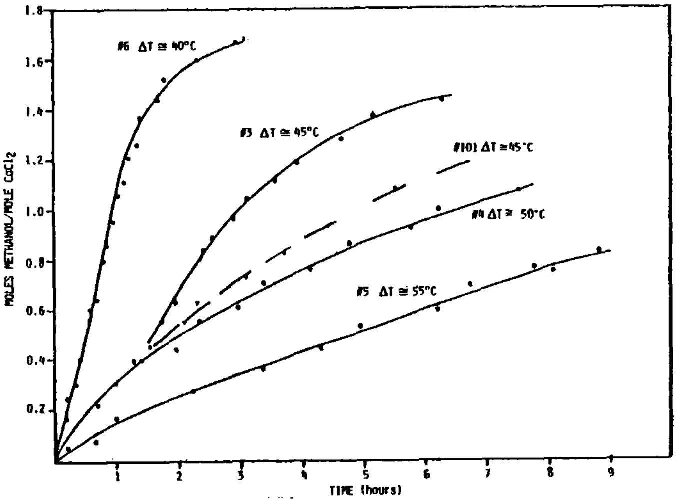

Fig. 2. Methanol absorption rates as a function of the temperature difference between the heat transfer fluid in the absorber and the evaporator. Absorber inlet maintained at 40°C.

Even at the highest ΔT examined, 55°C, the rate is more than adequate for solar heating, which requires a discharge rate of 1/12 to 1/16 of storage capacity per hour. In the cooling mode, where the evaporator is normally maintained at 5°C, the salt bed can be maintained at 50°C, allowing heat rejection to dry ambient air (35°C nominal) without excessive fan power. This also permits a high cooling rate, since the rate of reaction at a 45°C absorber-evaporator temperature difference is in excess of 1/3 M/M/hr.

The experimental results shown in Fig. 2 were obtained from our engineering development test unit, which has a storage capacity in excess of 100,000 BTU. The primary role of this unit is to test the $CaCl_2$ reactor/heat exchanger at a scale approaching that which would be used in a typical application (e.g., single family residence or small commercial building). Details of the heat exchanger design have already been given elsewhere[1,5]; it is based on the use of $CaCl_2$ pellets contained in aluminum finned copper tubes of the type normally used for baseboard heating. Our experimental results confirm that the heat transfer performance of this heat exchanger is well-suited to solar storage and heat pumping.

Projected Annual Performance

Computer simulations of the performance of the $CaCl_2$-CH_3OH system have been carried out using the TRNSYS solar simulation program together with a number of specially written subroutines.[2,3] TMY solar and meteorological data were used to assure compatibility with other simulations. Figure 3 shows the calculated variations in heating and cooling solar load fractions with collector area for Washington, D.C. The cooling load in Washington is highly sensitive to window placement and shading; as shown, proper use of passive solar design techniques can reduce the cooling load considerably.

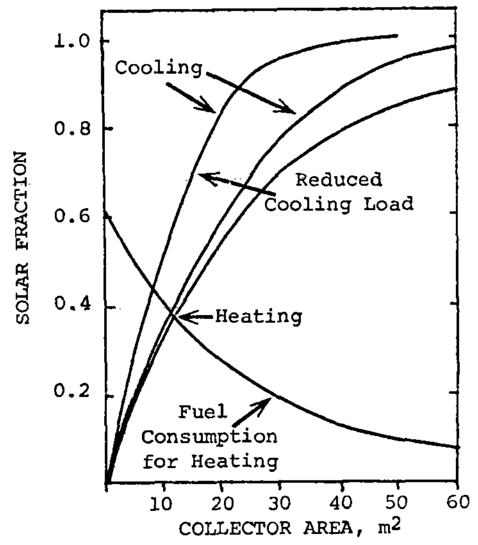

Fig. 3. Calculated annual residential performance of the $CaCl_2$-CH_3OH chemical heat pump in Washington, D.C. The two cooling curves reflect the effect of extra window shading.

With a collector area in the vicinity of 25 m^2, the $CaCl_2$-CH_3OH heat pump should be capable of meeting over 90% of the cooling load with solar energy. Fuel consumption for heating is reduced by about 80%. Part of this fuel reduction is due to solar collection, and part due to the high COP of the heat pump operating in the backup mode. Even without a solar collector, the heat pump COP reduces heating fuel consumption by about 40%.

Recent Performance Results

Energy Balance Experiments

During the cycling evaluation of the engineering development test unit, measurements were made of the energy flows into the salt bed heat exchanger and the methanol evaporator/condenser. The results are shown in Table 1. The calculated results are based on the known heats of methanol vaporization, condensation, and reaction with $CaCl_2$, and on the heat capacities of the chemicals, container materials, etc. The agreement between calculated and experimental results is within 5% for both process steps, and the heat "missing" on round-trip closure is less than 1,000 BTU in each loop. These results show that the analytical methods used for performance analysis are entirely satisfactory.

The experimental coefficients of performance may be calculated using the data in Table 1. For example, the coefficient of performance for cooling is simply the heat absorbed during methanolation (73,700 BTU) divided by the heat input during demethanolation (142,800 BTU), which equals 0.516. This is lower than is expected for an optimally designed system (>0.55), due to the high thermal masses of the components used at the present stage of development. Nevertheless, the current COP exceeds our original

Table 1. Comparison of Experimental Results with Calculated Heat Flows. Energy into System is Positive.

Stage	Process	Time (min)	Salt Bed Loop (BTU)			Methanol Tank Loop (BTU)		
			Calc.	Exptl.	Calc-Exptl.	Calc.	Exptl.	Calc-Exptl.
I	Cool Salt Vessel	53	-24,073	-23,515	-558	460	-430	890
II	Methanolation 71.1 liters	317	-104,690	-109,435	4,745	77,690	73,700	3,990
III	Heat Salt Vessel Cool Methanol Tank Demethanolation 71.1 liters	437	139,363	142,800	-3,437	-88,750	-84,160	-4,590
I & II		370	-128,763	-132,950	4,187	78,150	73,270	4,880
(I&II) + III			10,600	9,850	750	10,600	10,890	290

projections, and represents a more than satisfactory level of performance.

Long Term Cycling

In order to project the long-term performance of the heat pump system, the engineering development test unit was taken through a series of methanolation-demethanolation cycles. Several different salt bed tray designs were tested. Two of the designs proved to be inadequate: due to plastic flow of the salt, the heat exchangers warped to the point where they were no longer useful. Two other designs performed satisfactorily throughout the 100-cycle test. No degradation of the salt cake was observed; however, expansion and creep of the salt increased the contact resistance. This in turn decreases the reaction rate at a given absorber-evaporator temperature difference, as shown in Fig. 2. However, the increase in contact resistance after 100 cycles is less than 2°C, and it appears that the resistance does not increase further with additional cycling. The estimated lifetime of the current salt bed design appears to be of the order of 5 years.

The expansion forces due to the chemical reaction have been estimated; surprisingly, they are quite modest. Thus, it appears that additional stiffening of the heat exchanger could eliminate the contact resistance entirely. Tests are currently underway to determine whether this can be accomplished. Alternatively, one can choose to accept a lower salt density and a 2° contact resistance, thereby eliminating the problem of plastic flow. One method or the other should allow the design of a heat exchanger with a lifetime >20 years.

Economic Analysis

As with any projection into the future, economic analysis is fraught with difficulties. Inflation rates, fuel escalation rates, mortgage rates, tax rates and tax credits all are important yet uncertain. The actual cost of the heat pump itself is uncertain, since price is strongly dependent upon the level of production and sales. Future solar collector prices are uncertain, particularly for evacuated tubes, which represent a relatively new technology. Our approach to these difficulties is to state our assumptions as clearly as possible, so that the analysis can be repeated by others, and compared to the analyses of other systems, under assumptions that differ from our own. By and large, the assumptions used here are conservative or at best, realistic; we have not assumed a future in which fuel prices require solar energy.

Heat Pump Pricing

The estimated cost of the heat pump components, exclusive of assembly labor, is estimated to be approximately $5,000. This includes backup and a DHW preheat system. This cost is based largely on OEM prices, at a level of production circa 100-1000 units per year. Clearly, the cost in true mass production would be lower, and standard cost-reduction formulas could be applied. Our costing is hence like the cost of building an automobile from replacement parts.

The cost of assembly and installation is estimated to be $2,000. This is based on 150 hours of shop labor and 50 hours of field labor. Once again, the shop labor estimate is based on manual assembly, rather than on more automated methods that would be appropriate for larger scale manufacture.

To these basic costs we have added 30% for overhead, plus $5,000 for the cost of 25 m^2 of installed evacuated tube collector. Thus, the total installed system cost is expected to be about $14,000. This is a cost, not a selling price, but we will use it as a basis of the payback analysis so that benefits and costs may be directly compared. Manufacturer's profit would be taken from the production learning curve.

Fuel savings are based on the following current estimates for Washington, D.C. The cost of fuel for heating is estimated at $500, for domestic hot water, $180, and for electric air conditioning, $80. These estimates may seem low, but they are consistent with current consumption for a modern, well shaded and well insulated house. The projected savings factors for the $CaCl_2$-CH_3OH chemical heat pump are 0.8, 0.7, and 0.95 respectively, for a fuel savings of $600 out of the $760 total.

Payback Analysis

To compare the projected economics of the $CaCl_2$-CH_3OH heat pump with a conventional heating and cooling system, it is first necessary to put them both on an equal footing. If the system is to be installed in a new building, a credit must be taken for replacement of the conventional heating and cooling system. (Note that the cost of the $CaCl_2$-CH_3OH system includes gas-fired backup.) We estimate the replacement credit at $4,500, including gas furnace and electric central air conditioner. Second, it is necessary to take into account the federal tax credit of $2,200.* In the payback analysis, this is used to cover the down payment.

Five or six separate rates must be estimated in order to determine the projected economics: general inflation, mortgage, fuel escalation (more than one rate may be involved), future cash discount, maintenance, and tax rate. For consistency, we have used the rates suggested by Bezdek, Hirshberg and Babcock (BHH)[8]; these rates have been recommended by the Solar Energy Research Institute[9] for comparative economic analyses. Although they are only a year or two out of date, the suggested rates seem low by present standards (e.g., 5% inflation and 8.5% mortgage). We have therefore presented an alternative analysis (BHB+5) in which the inflation, mortgage, discount and fuel escalation rates are all increased by 5%. Results of the two analyses are shown in Tables 2 and 3.

Three criteria are generally used to estimate customer acceptance. First is the number of years required to achieve positive cash flow; BHB assume a three year criterion "because most homeowners expect rapid savings for an 'energy conserving' investment." Under the BHB set of economic assumptions (Table 2), this criterion is met; with a higher inflation rate (Table 3), positive cash flow begins in the fourth year. The second criterion is "the number of years required for accumulated savings to offset initial cash payments and early cash flow losses," assumed to be five years, "based on today's average housing turnover rate." Table 2 shows that the $CaCl_2$-CH_3OH should meet this criterion easily -- the system pays back from the beginning. At a higher inflation rate, however, six years are required. The third criterion ("payback period") is the number of years for accumulated savings to equal the remaining loan principal, assumed to be ten years. Calculated values are 12.3 years (BHB) and 11.4 years (BHB+5). Thus, under the BHB set of economic assumptions, the $CaCl_2$-CH_3OH heat pump easily exceeds two of the three economic criteria, and nearly meets the third; under much more pessimistic economic assumptions, the system lies on the edge of presumed customer acceptability. This analysis therefore shows that the $CaCl_2$-CH_3OH solar driven heat pump should be highly cost effective under all but the most pessimistic scenarios.

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*Current law (PL 96223) provides a $4,000 credit.

Table 2. Payback analysis of the $CaCl_2$-CH_3OH solar driven chemical heat pump for Washington, D.C. using the BHB set of economic assumptions.

Year	End of Year Principal	Income Tax Saved	Insurance and Maintenance	Fuel Savings	Net Savings	Present Worth of Net Savings	Sum of Present Worth
1	7443	194	150	660	201	183	183
2	7272	190	157	723	-47	-39	144
3	7088	185	165	793	11	8	152
4	6887	181	173	870	74	51	202
5	6669	176	182	954	144	90	292
10	5269	143	232	1514	621	240	1217
15	3165	93	296	2407	1401	335	2719
20	0	19	378	3833	2670	397	4591

Table 3. Payback analysis of the $CaCl_2$-CH_3OH solar driven chemical heat pump for Washington, D.C. using the BHB+5 set of economic assumptions.

Year	End of Year Principal	Income Tax Saved	Insurance and Maintenance	Fuel Savings	Net Savings	Present Worth of Net Savings	Sum of Present Worth
1	7511	308	157	690	27	23	23
2	7411	304	172	791	-192	-145	-122
3	7297	300	190	907	-97	-64	-186
4	7167	296	209	1040	12	7	-179
5	7020	290	230	1192	138	69	-110
10	5929	251	370	2364	1131	280	921
15	3873	178	595	4697	3164	389	2676
20	0	40	959	9342	7308	447	4808

Acknowledgments

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A COST-EFFECTIVENESS EVALUATION OF CHEMICAL HEAT PUMPS

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ABSTRACT

The DOE Office of Advanced Conservation Technologies is developing several concepts for chemical heat pumps, including those based on sulfuric acid, methanolated salts, metal hydrides, and ammoniated salts. In this project, the chemical heat pump technologies are compared with a baseline of existing HVAC technologies and a set of emerging competitive technologies. The basis for comparison is system cost effectiveness in one or more specific applications, with levelized annual cost taken as the measure of cost-effectiveness. The specific applications are a residential building and a commercial building, each requiring HVAC services, and each evaluated in Boston and Alburquerque. An industrial process-heat upgrading application is also included. For each system, the net consumption of fossil fuel resources is evaluated, and environmental/safety aspects identified.

I. Introduction

A chemical heat pump is a device that extracts thermal energy from a low-temperature source and rejects it to a higher-temperature sink. Unlike vapor-compression heat pumps which use the vapor-liquid phase characteristics of a single working fluid, chemical heat pumps make use of reversible physiochemical reactions between a working fluid (vapor) and one or more stationary phases (solid or liquid). Chemical heat pumps are being developed by DOE because they offer the promise of lower overall cost and greater efficiency than separate units for heating, cooling, and (in solar operations) storage. They are also being considered for industrial process heat upgrading applications.

Chemical heat pumps must compete with existing HVAC and industrial process-heat technologies; including gas and oil-fired furnaces, vapor-compression heat pumps, and vapor-compression air conditioners. In addition, they will compete with emerging technologies such as solar-thermal heating, solar-driven absorption air conditioning, and ground or aquifer-coupled vapor-compression heat pumps. An applications-specific comparison between the chemcial heat pump systems, the baseline systems, and the emerging technologies will enable the promised benefits of the CHP's to be weighed against the cost of ownership and operation.

II. Methodology

The methodology for this evaluation includes definition of the HVAC and industrial process-heat loads, characterization of HVAC systems to be used in meeting these loads, evaluation of the cost-effectiveness and energy-effectiveness of each system, and an assessment of the environmental and safety aspects of each system.

Load Characterization

Two buildings were chosen to represent residential and commercial HVAC loads. The residential structure is a well-insulated, single-story, frame dwelling with 1500 square feet of living space. It meets the energy conservation standards of ASHRAE 90-75 and is maintained at 70°F during the winter and 75°F during the summer. The internal heat loads (sources) include three occupants and a normal complement of kitchen and household appliances. The building envelope is assumed to be subject to the ventilation and infiltration effects normally associated with residential structures. The instantaneous heating or cooling load for the residential structure is approximated by equation (1),

$$Q(\text{Btuh}) = (FV)\ (QT)\ (TA-TI) + QI \qquad (1)$$

where the parameters are detailed below:

QT = 427 Btu/hr-°F (UA value for transmission load of residential structure)

QI = internal load
= 3075 Btuh during heating season
= 4000 Btuh during cooling season

TA = outdoor temperature

TI = interior design temperature
= 70°F for heating
= 75°F for cooling

FV = factor to include ventilation-related sensible and latent heat load with transmission loss
= 1.37, heating, Boston and Albuquerque
= 1.73, cooling, Boston
= 1.64, cooling, Albuquerque

The use of this instantaneous load in the calculation of annual energy cost is described.

The commercial structure is a well-insulated, three-story structure with 40,320 square feet of useable floor space. It meets the energy conservation standards of ASHRAE 90-75. Internal heat loads (sources) include 403 people, as well as a lighting and equipment load. Ventilation is maintained according to ASHRAE standards. The HVAC system for the commercial building is assumed to be energy-efficient, incorporating regenerative heat exchange to recover energy from ventilation exhaust air and making full use of internal load management to satisfy HVAC needs. The commercial building is maintained at the summer (75°F) and winter (70°F) temperatures only during a 10-hour period each day, 250 days each year. The building is described as the sum of two zones, (1) an interior zone which is subject to internal loads and ventilation and (2) a perimeter zone which is subject to transmission and solar loads as well as internal loads and ventilation losses. As an example, the calculated temperature dependence of the heating/cooling load for the occupied perimeter zone of the commercial building is shown in Figure 1.

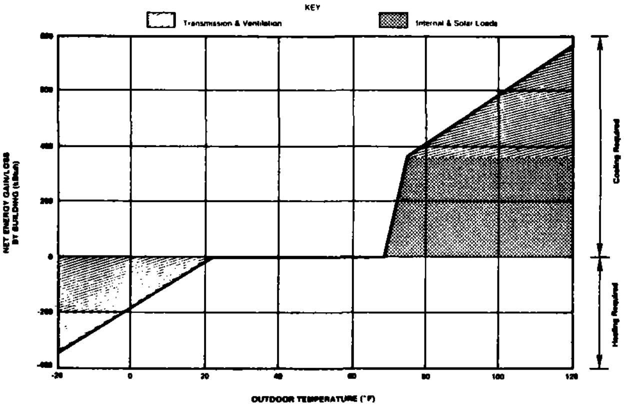

Figure 1. Heating and Cooling Loads for the Perimeter Zone in an Occupied Commercial Building (Albuquerque)

The structures are representative of those capable of being built in the near future, and represent the coming market for HVAC systems. Retrofit of the less-efficient buildings which dominate the existing population is not considered. The impact of this approach on the evaluation is to reduce the importance of energy cost relative to capital-related costs and maintenance.

Location Characterization

The residential and commercial buildings are characterized in each of two locations, Boston (MA) and Albuquerque (NM). These locations present a contrast between heating and cooling requirements, and a comparison of areas with different levels of annual insolation. The climate in each city is well characterized by 10-year average temperature records, assembled as a population distribution with total hours each year that the ambient temperature falls within a sequence of 5°F temperature ranges, or "bins." The availability of a detailed temperature demography enables integration of HVAC system performance over the full temperature range, including the temperature dependence of structure heat load just described, as well as the temperature coefficient of the HVAC system (i.e., COP).

Baseline System Characterization

The baseline systems include the following commercially-available components:

Residential

- Electrically-driven, vapor-compression heat pump with electric resistance backup.
- Conventional furances (gas and oil fired) with electrically-driven, vapor-compression air conditioning

Commercial

- Large-scale central HVAC, with electric furnace and chiller.
- Large-scale central HVAC, with gas-fired furnace and electric chiller.

Each system is characterized with respect to performance, capital cost, maintenance cost, and energy consumption. The data were culled from manufacturer's literature as well as technical journals, and represent typical commercially-available components and systems in real installations.

Residential. First-cost data were assembled for several levels of equipment "quality". Figure 2 is one example for gas-fired furnaces. Usually, "quality" is directly related to equipment lifetime and energy efficiency. Maintenance cost was estimated as the cost of an annual service contract. Installation cost was estimated as the sum of a labor charge plus equipment-specific materials such as the flue for an oil or gas-fired furnace. Energy requirements for each component were characterized by the performance relative to primary energy source (COP, EER, thermal efficiency, et al.) plus the magnitude of the secondary energy required for pumps, blowers, controls, etc.

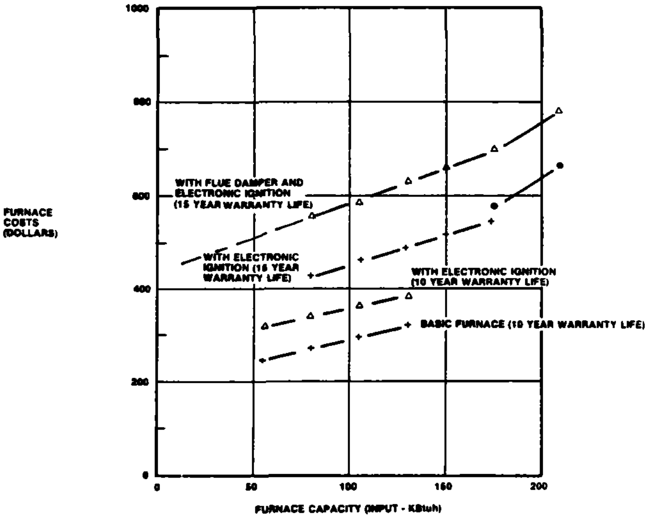

Figure 2. Gas Furnace Costs

Commercial. The HVAC system for the commercial building is based on heated or chilled water which is run through the heat exchanger in an air handler to provide building heating or cooling. The perimeter and interior zones are controlled independently. The system is assumed to be designed for energy conservation, in that ventilation control and interior load management are used to the fullest extent to maintain each zone at the design point. Ventilation air exchanges heat and humidity with exhaust air, using a commercially-available economizer. Building temperature is allowed to fall to 50°F during winter, non-business hours. Ventilation and cooling are not provided during summer nonbusiness hours.

As in the case of the definition of the building loads, the HVAC systems are characterized as modern, relatively efficient systems which might be found in new construction. This will tend to reduce the influence of fuel price in the cost-effectiveness comparisons.

Energing System Characterization

The emerging HVAC systems are those technologies which are in the later stages of development or which are commercially-available but are not yet widely used. They are presumably the "new" technologies which will compete with chemical heat pumps, including:

- Active solar-thermal heating (hydronic) with gas-fired backup and electric vapor-compression air conditioning.
- Solar-coupled absorption air conditioning as a variation on the above system.
- Solar-coupled vapor-compression heat pumps.
- Ground or aquifer-coupled vapor-compression heat pumps.

The basic principles of HVAC system operation and building load management which were established for the baseline systems are maintained for the emerging systems. All that changed was the "prime mover" or energy source for the system; the delivery, economizer, and control systems remain the same. The emerging systems are not backed up by a large commercial data base, and their cost/performance characterization is not as "clean" as for the baseline systems.

Active Solar (hydronic). The location-specific performance of an active solar-thermal system is simulated with the familiar F-Chart methodology, a set of generalized performance charts based on application of the TRANSYS model. F-Chart is a simplified algorithm for determining the fraction of the heating load which will be met by the solar system; it involves correlation of long-term performance to solar system design, building construction, and the weather. Given the long-term cost-effectiveness goals of this study, the F-Chart method is felt to be suitable. Equipment performance is based on manufacturer's data, such as that summarized in Figures 3 and 4. Moderate-performance solar collectors were assumed because they satisfy the temperature requirements of the HVAC system. Building and climatic data were developed for the baseline characterization. The gas-fired backup (heating) and vapor-compression air conditioning (cooling) systems are taken from the baseline characterization.

Solar-Coupled Absorption A/C. Again, the F-Chart methodology is used to characterize the performance of the solar collector/storage system. The F-Chart calculations were modified to use only the "hot-water" algorithms, with the hot-water demand determined from building cooling load and the COP of the A/C unit. High-performance collectors were assumed because of the temperature requirements of commercial absorption air conditioners. The system is not evaluated as a stand-alone A/C unit, but, rather, as a variation on the previous solar-hydronic case. The vapor-compression A/C was replaced by an absorption unit, with cooling backup energy provided by the existing gas-fired heating backup unit (for the commercial building only.)

Solar-Assisted Heat Pumps. Low-performance collectors and a specially-designed vapor-compression heat pump will provide heating-only service. The modified F-Chart algorithms and technical data from a major equipment manufacturer will serve to characterize performance for this concept. Electric resistance heating as backup is assumed, and air conditioning is supplied by baseline vapor-compression systems.

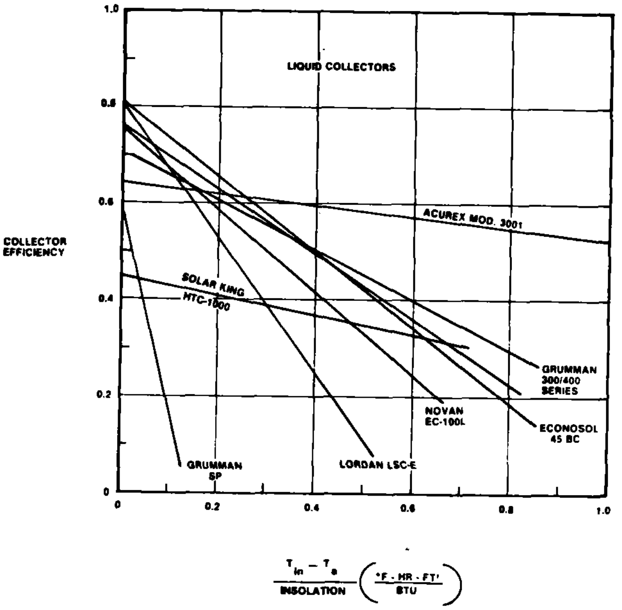

Figure 3. Performance Characteristics of Existing Liquid Solar Collectors

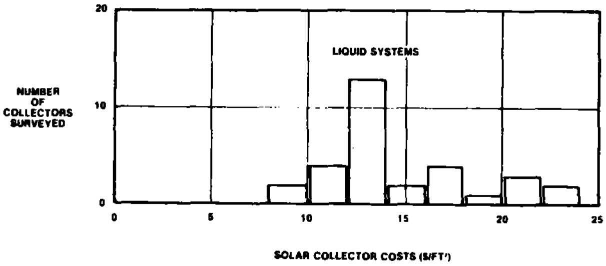

Figure 4. Distribution of Flat-Plate Solar Collector Costs

Ground-Coupled Heat Pumps. The sytem under consideratiion includes a conventional heat pump which has been thermally coupled to a large volume of earth through a long section of buried pipe and a circulating-fluid loop. The heat extracted from the earth during the heating season and rejected to the earth during the cooling season is equalized through exchange of heat with the surrounding earth and with the ambient air. The specifically-designed heat pump used for the solar-assisted application will also be used here, modified to handle cooling services as well. The characterization of conventional heat pumps will be combined with performance modeling of the earth storage system to describe the system. Backup heating is assumed to be via electric-resistance furnace.

Chemical Heat Pump Characterization

The objective of the CHP characterization is to develop an independent estimate of system cost and performance for candidate CHP concepts; including those based on sulfuric acid/water, methanolated salts, metal hydrides, and ammoniated salts with, possibly, one more advanced system. The characterizations will be derived from engineering modelling of the individual systems, based on system descriptions provided by the developers. The modelling effort will focus only on the specific system configuration being advocated by the developer. It will follow the general algorithms established during development of a detailed system model for the HYCSOS metal hydride system, with modification as necessary to describe the characteristics of individual sytems. The level of detail will be such that critical thermophysical effects such as temperature drops and pressure drops will be evaluated. The intent is not to create a detailed design model for each system, but to verify the engineering validity of the key determinants of system performance. At the time of preparation of this paper, the CHP characterization is just getting underway.

Cost-Effectiveness Evaluation

The general methodology for combining the climatic, building structural, and HVAC system component characterizations into an overall cost-effectiveness comparison is shown in Figure 5.

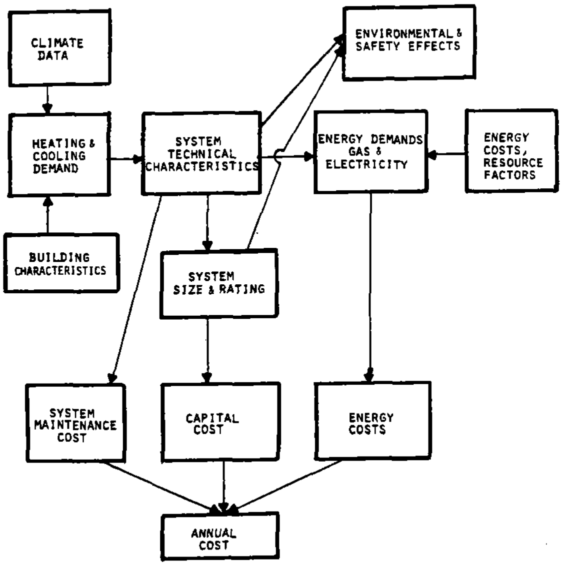

Figure 5. Methodology for HVAC System Cost-Effectiveness

The economic analysis is based on levelized annual cost calculated in "constant" dollars through the use of inflation-free interest and escalation rates. The total annual cost for a given system is the sum of the capital cost, the maintenance cost, and the energy (fuel) cost. The capital cost component is taken as the annual payment required to amortize the system cost over the system lifetime at the inflation-free interest rate (i) i.e.:

Annual Capital
Component =

(System Cost) x (Amortization Factor)

$$\text{where: Amortization Factor} = \frac{i}{1 - (1+i)^{-n}}$$

Expressed in "constant" dollars, the annual maintenance cost is contant because it is assumed to escalate at the general inflation rate. The energy cost increases by an inflation-free escalation rate (e). In order to levelize the escalation, the annual energy cost is discounted to the present value (mid-1980) at the inflation-free interest rate (i), and the present value of the sum of all energy costs over the 20-year evaluation period is then expressed in terms of a constant-payment "mortgage" at the inflation-free interest rate. Expressed mathematically in terms of the first year energy cost:

Annual Energy
Component = (First-Year Energy Cost)
x (NPV Factor)
x (Amortization Factor)

where the amortization factor is indentical to the definition for capital cost for a 20-year lifetime (n=20) and

$$\text{NPV factor} = \frac{\left[\frac{1+e}{1+i}\right]^{20} - 1}{\left[\frac{1+e}{1+i}\right] - 1}$$

The inflation-free interest and fuel-escalation rates are given below:

Residential interest (i)	=	2%
Commercial interest (i)	=	6%
Electricity escalation (e)	=	0.6%
Gas escalation (e)	=	3.2%
Oil escalation (e)	=	2.6%

III. Results

The CHP cost-effectivenss evaluation is a relatively new project and, as of the writing of this summary paper, no comprehensive results have been generated. The baseline has been defined but, rather than present these results out of context, they will be combined with a discussion of all results at the Annual Contractor's Review.

DESIGN AND PERFORMANCE OF A MULTITUBE METAL-HYDRIDE HEAT PUMP

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ABSTRACT

For several years, Argonne National Laboratory (ANL) has been developing a metal-hydride heat pump based on the principle that certain metal alloys produce heat when they combine with hydrogen to form hydrides. Past work at ANL has concentrated on demonstrating the feasibility of the concept and on development of metal alloys suitable for this application. In this paper, the design of a unique multitube metal-hydride heat pump that can be cycled rapidly is described, and its performance is analyzed. Each tube contains a high-temperature hydride at one end and a low-temperature hydride at the other end. The design features a large number (above 200) of individual tubes and includes external thermal-regeneration loops to reduce the performance losses inherent in thermal cycling. The analysis models the entire heat-pump cycle and includes one typical result of a complete simulation of the regenerative heat-exchange process. A calculation is performed to predict the coefficient of performance (COP)in the heating mode for a given tubular design.

I. INTRODUCTION

A major R & D objective associated with the engineering of a metal-hydride heat pump is development of a design of predictable performance. One such design that has been under development at Argonne National Laboratory (ANL) for several years[1,4] is the multitube hydride heat pump (MTHP). The design features a large number of individual tubes; each tube contains a high-temperature hydride at one end and a low-temperature hydride at the other. The central portion of the tube is designed to allow hydrogen to flow freely between the ends but to retard heat flow between both of them. Such a design is preferable to a four-bed system.[3,4]

That system consists of two pairs of beds: while one pair is absorbing hydrogen, the other pair is being heated or cooled. A disadvantage of the four-bed system is that effective recovery of heat during regeneration is difficult to achieve. Moreover, a hydrogen leak in one hydride bed will shut down all interconnecting beds, impairing system reliability. The multitube heat pump, by contrast, has: 1) a large number of independent hydride beds; 2) no hydrogen valves; and 3) a potentially high coefficient of performance (COP) due to a novel method of heating and cooling the hydride beds. This paper describes the design and analyzes the performance of a conceptual multitube hydride heat pump, and its authors present some preliminary results of the performance of a specific design.

II. DESIGN CONSIDERATIONS

The chief component of the multitube hydride heat pump is a closed tube divided into two sections. Each section contains a different hydride, one designated A and the other B. The two sections, shown in Figure 1, are physically separated and thermally insulated; but hydrogen is permitted to flow between the hydrides.

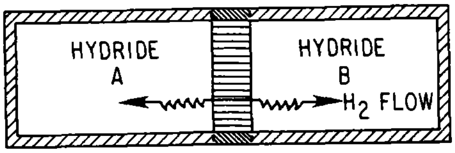

Fig. 1. Schematic of Hydride Tube

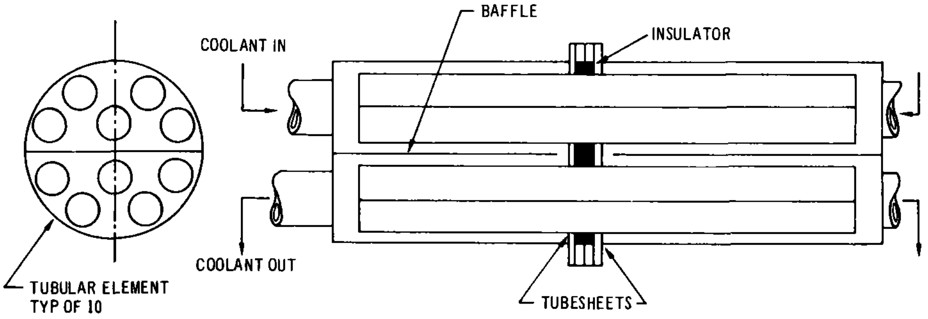

Fig. 2. Ten-Tube Bundle

A number of tubes similar to the tube shown in Figure 1 are combined to form a bundle, as shown in Figure 2. The ends of the bundle are separated by central tubesheets. The coolant, normally ethylene glycol-water, flows in one face of the unit and over the tubes; reverses direction; and then exits the same face. A baffle ensures that the coolant fluid flows completely over the tubes. A similar fluid circuit exists at the other end of the bundle. A number of bundles can be combined to form a heat pump.

In the ANL design[2], the MTHP consists of 24 bundles. The bundles are arranged side to side in a cylinder with a multiport rotating valve at each end, as shown in Figure 3. For the heating mode, the high-temperature, or hydride-A end, is connected to the high-temperature heat source, the house-heating plenum, and the high-temperature regeneration loop. The low-temperature, or hydride-B end, is connected to the house plenum, the outside air heat exchanger, and the low-temperature regeneration loop. The hydride-B end must also be connected to the high-temperature heat source for completion of sensible heating.

The valves are so arranged that the following actions are occurring at all times during operation: nine bundles are receiving high-temperature heat; three bundles are being cooled; nine bundles are receiving low-temperature heat; and three bundles are being heated. (See Figure 4.) As a valve rotates at constant speed, the sensible heating or cooling portion takes up 3/24 of a cycle. For convenience, the valve cycle time (one complete cycle of the valve) will be denoted by T and the time of the valve at one position will be denoted by τ. For the ANL design:

$$T = 24\ \tau$$

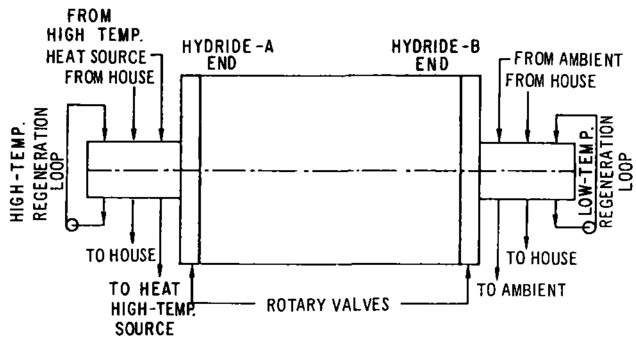

Fig. 3. Metal Hydride Heat Pump Unit

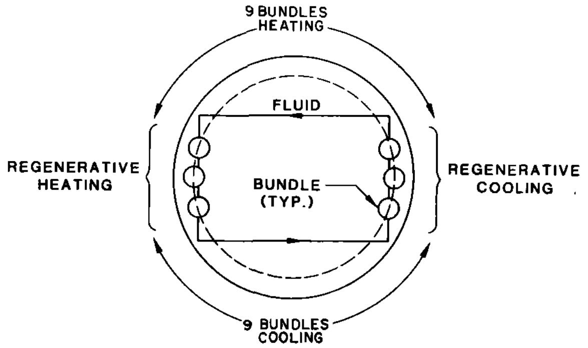

Fig. 4. Heating and Cooling of Tube Bundle

The operation of the heat pump can be described by considering one tube bundle as it undergoes a complete cycle for space heating. The bundle begins the high-temperature, heat-addition process for a period of 9 τ. During this time, heat is added by the high-temperature fluid to the hydride-A end of the bundle; at the same time, the other end of the bundle is rejecting heat. This rejected heat enters the house, and is used for space heating, by way of the heat-transfer fluid. It should be noted that the first part of the heat-addition process completes the sensible-heating portion of the process for both ends of the bundle.

At the end of the allotted time, the valve rotates and the bundle enters the sensible-cooling portion of the cycle with both ends at their highest temperature. The bundle is placed in stage I, shown in Figure 5. (For simplicity, only the high-temperature end is shown.) The regeneration loop contains a pump to circulate coolant. The coolant flows over the bundles to be heated (stages IV, V, and VI) and then over the bundles to be cooled (stages III, II, and I). After the bundle has remained in stage I for a time τ, the valve is switched, placing it in stage II; then, after another time τ , it is switched to stage III. During each time in the regeneration loop, the bundle is being heated. After a time the bundle moves from stage III into the low-temperature, heat-addition portion of the process. Before proceeding, it should be noted that the hydride-B end undergoes a similar cooling process.

The bundle enters the low-temperature, heat-addition portion of the cycle; here, bundle temperatures are above the appropriate temperature of the process. After this heat is transferred away to the coolant, the bundle accepts heat at the low-temperature (hydride-B) end, and rejects heat into the heating plenum at the high-temperature end (hydride-A). This process continues for 9 τ, at which point the valve is switched again so that the bundle enters the sensible-heating portion of the cycle.

The sensible-heating cycle is analogous to the sensible-cooling process. The bundle remains at stages IV, V, and VI for a time τ, during which it is heated by the circulating coolant. At the end of the time, the valve is switched and the cycle completed. From the above discussion, it can be reasoned that a large number of bundles was selected to allow effective regenerative heat transfer to occur between the heating and cooling bundles.

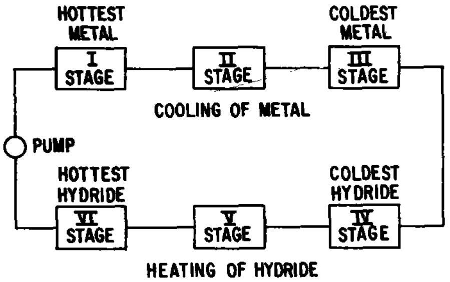

Fig. 5. Schematic of Regeneration Loop

III. THERMAL REGENERATION ANALYSIS

The analysis of the regeneration process in the MTHP is very complicated not only because the coolant temperature varies in the loop and with time, but also because the bundle temperatures are time-dependent. To understand this process, a computer model of the regenerative loops was developed.

The computer model was designed to be as simple as possible and yet retain the essential physics of the problem. The major assumptions of the model were:

- that the temperature of a bundle can be represented by a single value (i.e., that no spatial temperature gradients exist);
- that the process limiting the heat transfer to and from the bundles can be modeled as a convective resistance;
- that all bundles have identical physical and geometric properties;
- that all fluid paths have identical properties; and
- that there are negligible fluid volumes outside of the bundles.

The figure of merit of the regeneration, termed the effectiveness ε, is defined for the hydride-A end as:

$$\varepsilon = \frac{T_H - (Ti_A + \Delta T)}{T_H - Ti_A}$$

where:

T_H = heat source temperature

Ti_A = intermediate (heating plenum) temperature

ΔT = temperature loss

A similar term could be defined for the hydride-B end. The effectiveness represents the fraction of the total sensible cooling that is accomplished through regeneration. The value of the effectiveness was calculated over a range of parameters of interest. A sample result is presented in Figure 6. There, the effectiveness, ε, is plotted versus the valve time, τ, for a given geometry; for one value of the overall heat-transfer coefficient; and for three values of the fluid-transit time, θ. The fluid-transit time is defined as the length of time required for a fluid particle to flow through a bundle. The most interesting feature of this curve is the fact that effectiveness values greater than 50% (i.e., corresponding to simple mixing) are obtainable. This result is due to the three-stage heating (or cooling) of the bundles.

IV. ESTIMATE OF THE COP OF A MULTITUBE HEAT PUMP

With the calculation of regeneration effectiveness performed separately, an estimate of the coefficient of performance (COP) of an MTHP can be made. This is done by calculating, for a complete cycle, the amount of heat added by the high-temperature source and the amount of heat rejected to the building for space heating. Following the analysis outlined in Ref. 1, the COP can be expressed in terms of a system design, thermodynamic hydride properties, and operating temperatures. To estimate the COP, a knowledge of the heat of dissociation of the hydrides, the thermal capacity of the materials in the bundle, and the coefficients of regeneration effectiveness are required. Using the design parameters for the specific case shown in Table 1, selecting a regeneration effectiveness of 0.8, and assuming that all the heat of dissociation of the hydrides is active, it can be shown by calculation that the COP for heating is 1.55. However, for lower regeneration effectiveness, the COP rapidly decreases to a limit of 1.0 (no regeneration). However, the upper limit on the heating COP for an ideal reversible (Carnot) heat pump operating between the temperature limits shown in Table 1 is 1.86.

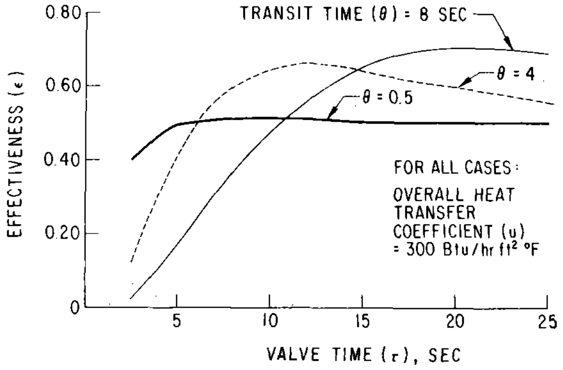

Fig. 6. Typical Result of Regeneration Analysis

Table 1. Heat-Pump Design Parameters

Number of bundles	24
Number of tubes per bundle	10
Outside diameter of tube (in.)	0.625
Overall length of tube (ft)	4
Hydride-A	$LaNi_{4.575}Al_{0.425}$
Mass of Hydride-A (lb)	100
Hydride-B	$LaNi_5$
Mass of Hydride-B (lb)	80
Coolant	Ethylene Glycol-Water
Coolant velocity (ft/sec)	4
Cycle time (min)	8
Heat load (Btu/hr)	50,000
Operating temperatures (°F):	
Heat source (T_H)	220
Heating plenum (Ti_A, Ti_B)	110
Low-temperature Hydride (T_L)	20

V. FURTHER WORK

The work reported in this paper should serve as a preliminary step for the design of a metal hydride heat pump. Further efforts will require the development of a computer program to optimize, on the basis of cost performance, the design of a realistic heat-pump system. In addition to the analytical work, experimental data on heat transfer to and from hydride beds must be obtained.

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HYDRIDE CHEMICAL COMPRESSOR
PHASE I

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R.A. Nye, Denver Research Institute, Denver, CO

Abstract

A proof-of-concept bench-size hydride compressor has been successfully built and tested. In continuous operation this unit delivered 20.3 liters/min (43SCFH) at a pressure of 42.2 atmospheres (650Psia). The efficiency however was lower than anticipated. The operation of this small unit revealed several important factors which influence the overall efficiency of such a hydride hydrogen compressor. The reduced efficiency of the bench scale unit was caused by mechanical design details (such as excessive amount of copper due to the electrical heating system) as well as problems with the hydriding alloy (reduced capacity at elevated temperatures and decrease in plateau pressure after 700 cycles of operation). A pilot-scale unit to be built in Phase 2 of this program will eliminate the undesirable features uncovered during the tests of the proof of concept unit.

I. Introduction

The ability of metal hydrides to absorb hydrogen at low pressure and desorb it at higher pressure is the basis of the hydride chemical compressor (HCC). The features which distinguish the HCC from conventional mechanical compressors are its ability to consume waste heat at low temperature and to compress hydrogen to virtually any pressure with a relatively simple apparatus.

Hydrogen compression is a vital step in most industrial uses for hydrogen. Noteworthy examples are hydrogenation of organic substances in the chemical and food industries, hydrocracking and hydrotreating of petroleum products, and most importantly, ammonia industry uses. The most conservative growth projections for these conventional pressurized hydrogen markets indicate several fold increases by the end of this century. If large scale synthetic fuel production is begun, be it gasoline, methanol, methane, or hydrogen itself, potential growth in demand for hydrogen compression is staggering.

Metal hydride compressors offer the possibility of being manufactured, operated and maintained more economically than their mechanical equivalents, in processes where their special properties can be used effectively.

This program was initiated to demonstrate the feasibility of manufacturing a hydrogen compressor based on metal hydride technology and to investigate the important variables governing the operation of such a compressor.

II. Objectives

The objectives of Phase I of this program were to test the concept of a hydride hydrogen compressor, and to establish what technological refinements are necessary for scale up to an industrial size unit.

In a follow up Phase II, the performance of a hydride compressor will be compared to that of a conventional compressor.

The following preliminary specifications had been set for the proof of concept, bench scale unit to be tested during Phase I:

Input Pressure	1 Atm.Abs. (15 Psia)
Output Pressure	120 Atm.Abs. (1780 Psia)
Capacity	0.8 Std.Liter/sec(100SCFH)
Peak Power Requirement	20 Amps @208 VAC 1 PH
Hydride Content	30kg $LaNi_{4.5}Al_{0.5}$(Annealed)
Peak Temperature	300°C

These specifications were not intended to exemplify an industrial compressor. Electric heating was selected as a matter of convenience for laboratory testing. The high temperature of operation would reveal potential cycling problems with the alloy and the container system.

The test program included cycling at least 500 cycles, and evaluating the performance of the compressor after such cycling. At the end of the test, at least one of the tube bundles was to be disassembled, to determine the condition of the hydride alloy contained in aluminum capsules.

III. Construction

The construction of the hydride compressor was described at a previous DOE contract review meeting (1). The only major problems encountered during the fabrication of the compressor was the brazing of type 316 stainless tubes to copper headers. These brazing difficulties delayed the completion of one half of the compressor. As a result, that half was cycled only 100 cycles vs 700 cycles for the other half.

The electrical heating systems was designed to match the electrical power available in most locations (208V, 30 amps, 3 phase). This size of power supply resulted in longer heating times than anticipated.

The automatic cycling timer and safety unit described previously performed satisfactorily.

IV. Test Results

For test purposes the compressor was connected to a conventional hydrogen storage cyclinder as shown on Figure 1.

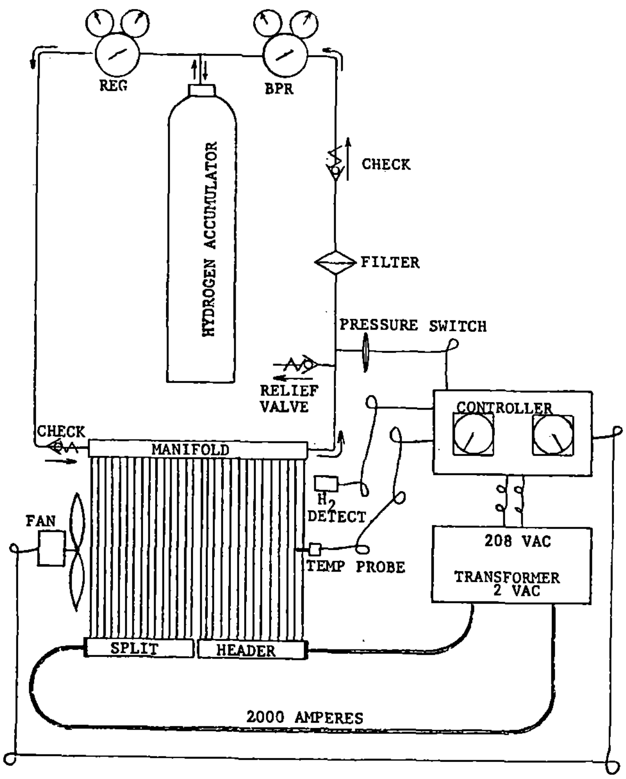

Figure 1. Test Set-up

The input pressure regulator was adjusted to supply hydrogen to the compressor at a low pressure P_1 (P_1 = 23 Psia). This pressure was selected slightly above ambient pressure, for safety reasons, to prevent potential in-leakage of air into the compressor.

The output of the compressor was connected to a back-pressure regulator which could be adjusted to any desired pressure in the range 23 to 2000 psia. The quantity of hydrogen compressed was determined by the pressure increase in the storage tank.

A typical curve of temperature and pressure versus time is shown on Figure 2. Similar curves were obtained for back-pressure settings between 500 psia and 1100 psia.

After a large number of cycles, it was observed that the heating cycle required increasingly longer time to compress the desired quantity of hydrogen. Since it was suspected that this might be due to some change in the hydriding alloy, one side of the compressor was disassembled after 700 cycles, and a capsule containing the alloy was removed, under protective atmosphere. Hydriding tests of this material revealed a decrease in plateau pressure for a given temperature as shown on Figure 3.

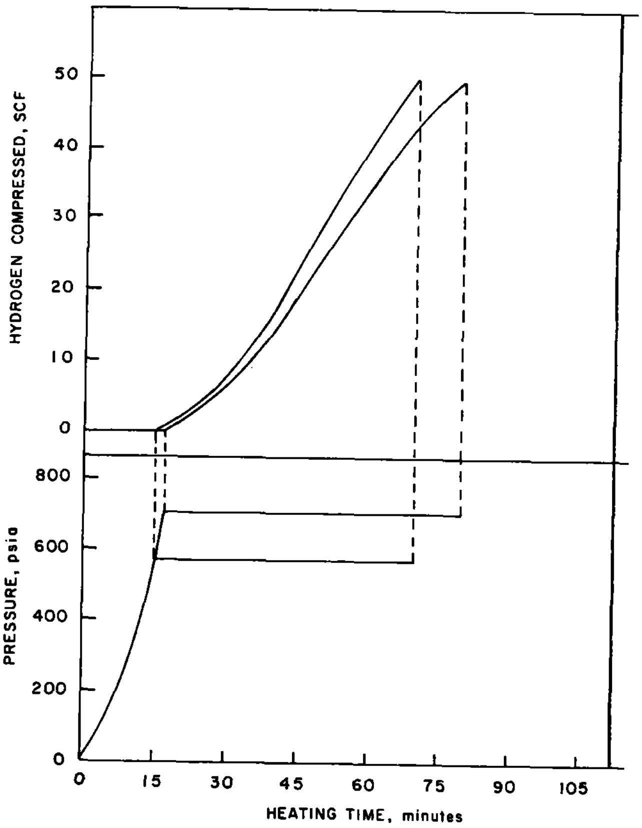

Figure 2. Compression curves for 550 Psia and 750 Psia delivery pressure.

This increase in alloy stability necessitated larger heating time to reach the desired pressure, as had been noticed during the tests. It is thought that the decrease in plateau pressure is the result of enhanced homogenization of the alloy during high temperature cycling.

Efficiency calculations were performed,from the data on power consumption and quantity of hydrogen compressed. Depending upon the compression cycle, and output delivery pressure selected, the efficiency varied between 2% and 5%. For a typical compression cycle delivering 50 SCF of hydrogen at 650 psi in about 60 minute, the efficiency was 4.5%, compared to a calculated theroretical efficiency of 22% or a predicted practical efficiency of 12%.

A step by step analysis of the parameters affecting overall efficiency showed that the major factors were the thermal mass of the systems, the fraction of hydride decomposed at high temperature and the residual volume of hydrogen gas in the tubes at the end of the compression cycle. In the bench scale unit, the very large thermal mass of the copper headers and buss bars was responsible in large part for the reduced efficiency. At higher temperatures, heat losses by radiation and convection became significant.

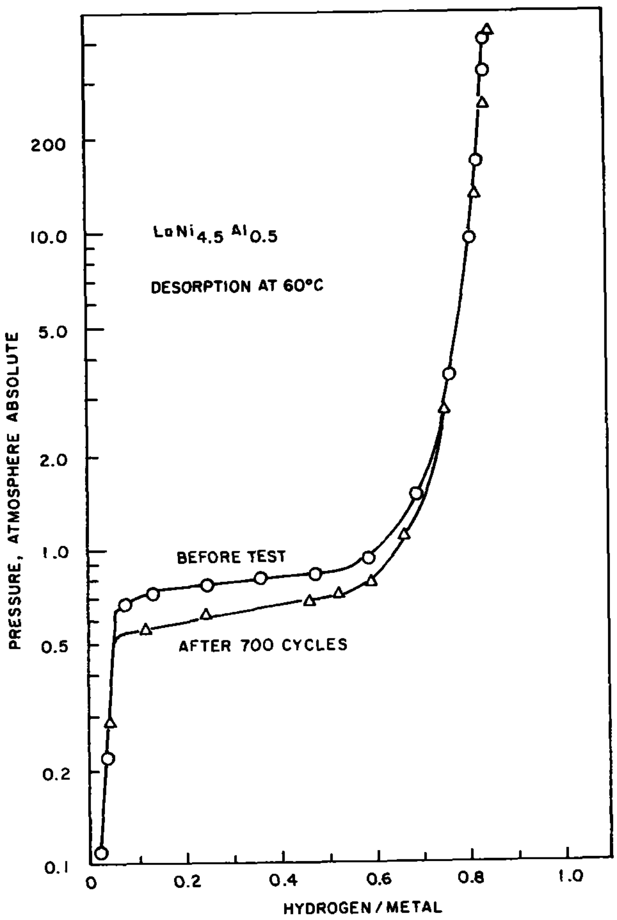

Figure 3. Effect of long term cycling on hydride plateay pressure.

V. Conclusions

1. The bench scale, proof of concept unit, has been successfully assembled and tested. A peak pressure of 75 Atm. absolute (1100 Psia) was obtained with the power supply available.
2. One half of the unit was cycled over 700 cycles. The other half, installed later because of brazing difficulties, was cycled over 100 times.
3. In continuous operation, the HCC delivered 20.3 liters/min. (43 SCFH) of hydrogen at a pressure of 42.2 Atm. (650 Psia).
4. The efficiency of energy usage in the bench-scale unit was low (4.5%) compared to a maximum theoretical efficiency of 22% and a predicted practical efficiency of 12%.
5. The reduced efficiency and low speed of compression were explained by excessive quantity of copper conductors inherent in the electrically heated compressor.
6. Analysis of hydride material from one capsule removed from the unit after 700 cycles revealed a decrease in plateau pressure. The increased stability of the hydride was reflected in longer heating time required to reach the desired pressure.
7. As a learning tool, the prototype HCC has served its purpose. It has performed a large number of cycles and provided a pilot scale experience with a new hydride alloy and a new containment technology both of which will be improved as a result.

VI. Recommendations

The low efficiency of the prototype has provoked a closer look at the aspects of design which influence efficiency. The lessons learned include:

1. Redesign the HCC containers to minimize thermal mass; (a) reduce the quantity of non-hydriding materials, (b) use material of low specific heat whenever possible.
2. Minimize the internal void-volume with improved container design.
3. Select metal hydrides with optimum characteristics for HCC performance, specifically: (a) minimize hysteresis, (b) use alloys with flat plateaus, (c) avoid phase solubility changes with temperature and pressure during discharge, (d) avoid disproportionation of some alloys (e.g. $CaNi_5$) during high temperature cycling.
4. Design for short H_2 path through the powdered hydride to minimize pressure drop.
5. Design containers to prevent container strain from expansion during hydriding (capsules proved effective).
6. Provide adequate insulation in high-temperature units.
7. Enhance heat transfer with judicious additions of high conductivity material.
8. Use heat recovery to improve overall efficiency.

VI. Plans for Phase II

For the prototype unit which will be constructed and tested during Phase II of this program, the following features are planned:

1. Replace electric heating of the hydride tube bundles by liquid heating to provide faster heat transfer and reduce heat losses.
2. Couple the hydride compressor with a water electrolyzer in order to recover the waste heat generated by that unit.
3. Select a hydriding alloy with the proper characteristics for compression, i.e. flat plateau, low hysteresis, high temperature stability.
4. Design the HCC to take full advantage of heat recovery during the cooling part of the cycle.

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DEVELOPMENT STATUS OF A METAL HYDRIDE PROCESS FOR HYDROGEN RECOVERY

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ABSTRACT

A new project seeking to develop and demonstrate a commercial metal hydride process for hydrogen recovery has been initiated by DOE through Brookhaven National Laboratory with Ergenics. The status of hydride separation technology is reviewed and the project milestones are summarized in this report.

BACKGROUND

The chemical and refinery industries currently generate over 32 MMM SCF of hydrogen daily; mostly by the steam reforming of natural gas or other premium feedstocks. Average utilization efficiency of hydrogen in these industries is only 80-90%; therefore, large volumes of hydrogen are channeled into waste or secondary streams. These streams are often low in pressure and highly contaiminated with impurities so that hydrogen recovery by conventional cryogenic or pressure swing absorption (PSA) is not economical. Development of a new process(es) to recover only 1/3 of this hydrogen would represent an annual resource recovery equivalent to 0.1 Quad of Energy.

Following several years of separate research efforts partially funded by DOE through Brookhaven, Ergenics and Air Products and Chemicals, Inc. (APCI) began a cooperative program for the commercial use of metal hydrides. This program has resulted in the formation of the Hydride Hydrogen Recovery Systesm (H^2RS) joint venture with the expressed purpose of developing systems, apparatus and equipment utilizing hydride technology for the recovery of hydrogen from mixed gas streams and the establishment of a jointly owned business venture to commercially exploit these developments.

Early in FY80, Ergenics with APCI and Inco Research and Development Center, Inc. (IRDC) as subcontractors proposed to Brookhaven a 3 year commercial development program for a metal hydride based hydrogen recovery process applicable to industrial scale (1-10MM SCF/D) waste gas streams. Phase I (15 month) addresses 1) identification of metal hydride systems, 2) assessment and demonstration of process unit operations and 3) waste stream/site selection. After review and approval by Brookhaven, Phase II and III will involve the design construction and operation of a pilot plant facility to demonstrate the commercial viability of hydrogen recovery. Phase I funding was approved August 14, 1980.

SEPARATION BY METAL HYDRIDES

The basis for the separation of hydrogen from a mixed gas stream is the reaction of hydrogen with a reversible metal hydride former (Me)

$$\mathrm{Me} + \frac{x}{2}\,\mathrm{H_2} \rightleftharpoons \mathrm{MeH_x} \qquad (1)$$

There are a number of metals, alloys and intermetallic compounds that react directly and reversible as described in Eq. 1 at practical temperatures and pressures [1-2]. Examples are FeTi, V, $LaNi_5$ and Mg_2Ni. Above a characteristic pressure termed the "plateau pressure", the hydride reaction (absorption) proceeds; reducing the pressure to below the plateau results in dehyriding (desorption). The plateau pressure, system temperature and the heat of reaction (ΔH) are thermodynamically related by the familiar van't Hoff equation.

A simple two-step separation process is thus possible. The hydrogen partial pressure in the H_2-X mixture must be kept above the plateau pressure during the absorption stage so that hydrogen is selectively absorbed into the bed. During discharge of the bed, hydrogen is desorbed from the hydride at reduced pressure. Reactor design should include gas circulation to prevent impurity gas blanketing around the hydride particles.

Advantageous features of a hydriding separation process are:

- ˙Reaction specificity - Only hydrogen reacts, process useful for dilute (30-70 mole%) hydrogen streams.
- ˙High recovery - Determined by the hydrogen partial pressure and the hydride plateau pressure.
- ˙Intrinsic high purity of the hydrogen produced.
- ˙Rapid kinetics for hydrogen absorption/desorption.
- ˙High volumetric packing density for hydrogen as a result of chemical bonding in the hydride crystal lattice.
- ˙Energy Efficient - heat of reaction typically 10-15% of the lower heating value of hydrogen and can be partially recovered.

Laboratory scale separations have been demonstrated for H_2-CH_4 mixtures using Fe_xTiNi_{1-x} alloys by Cholera[3]. Reilly[4] has reported separations from H_2-CO_2-CO mixtures with $LaNi_xCu_{5-x}$ alloys. Additional research is underway at a number of industrial laboratories although results are not publically available.

A comparative economic study of cryogenic, PSA and metal hydride processes for various streams has been made by Ergenics and APCI with private funding. The study indicates, at least for streams with tolerable poison levels, that the metal hydride process would be favored for recovering hydrogen from dilute, relatively low pressure streams. An applications map is shown in Figure 1. Metal hydrides thus offer a complimentary process for hydrogen recovery rather than direct competition with established technologies.

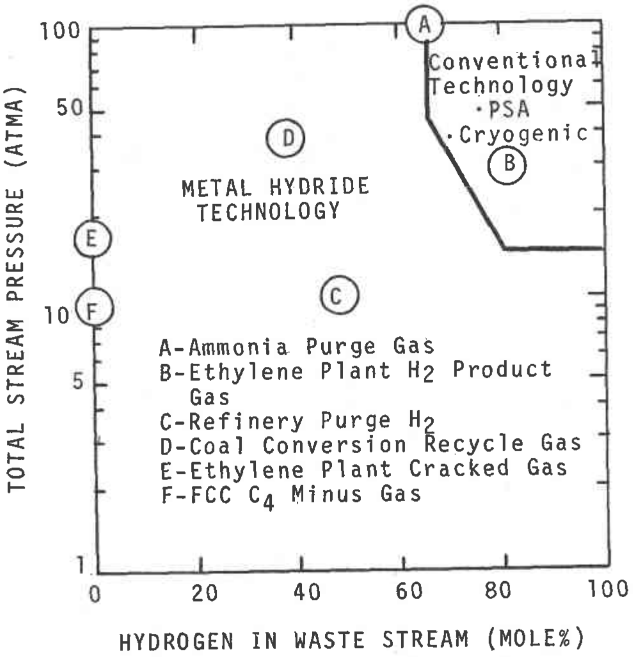

FIGURE 1 Applications Map for Hydrogen Separation Technologies

Numerous difficulties remain to be addressed, however, before this emerging technology can be considered for industrial applications. Most hydride formers are susceptible to surface poisoning by CO, O_2, H_2O and other species, commonly present in waste gas streams.[5] Poison rates and regeneration proceedures must be quantified if truly poison resistant alloys are not available. Solutions for engineering design problems associated with heat transfer, volume changes and gas pressure drops across fine particle metal hydride beds must be consistent with the large gas flows (1-10 MM SCF/D) to be encountered. And finally an economic reality, pilot plant demonstrations must clearly indicate hydrogen recovery at a cost less than that for additional hydrogen production.

PROJECT OUTLINE

Project tasks and major milestones are shown in Figure 2. As of this writing, the project is just beginning with stream surveys and hydride poisoning and regeneration testing. Following Phase I, project review and approval by Brookhaven is required before authorization for subsequent phases is granted.

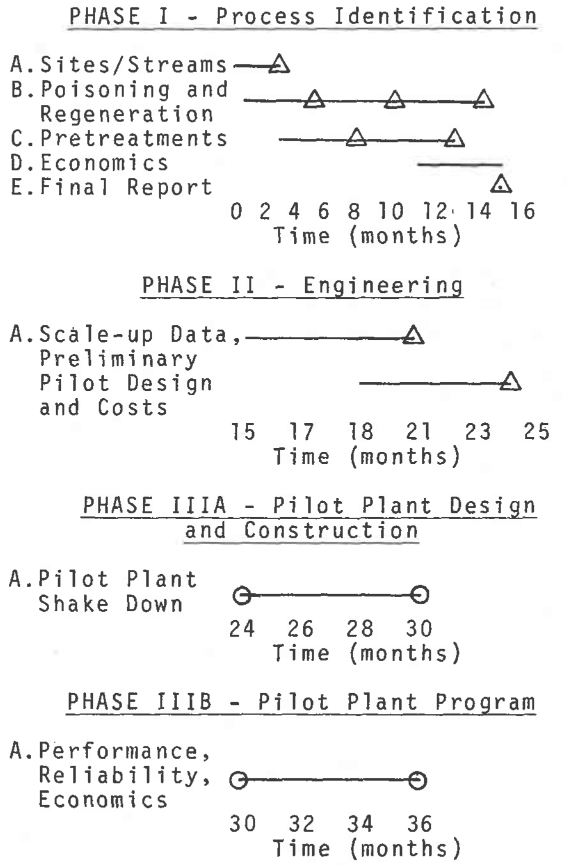

Figure 2. Program Plan and Milestones

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DEVELOPMENT STATUS OF SOLID POLYMER ELECTROLYTE WATER ELECTROLYSIS FOR LARGE SCALE HYDROGEN GENERATION

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Abstract

During 1980, progress continued on the joint Department of Energy, Electric Utility and General Electric Company - sponsored development of the Solid Polymer Water Electrolysis Technology for large-scale hydrogen generation.

Highlighting the program achievements for the year, a hydrogen generator module, capable of producing 2000 SCFH, was operated successfully for over 700 hours in the 200 kW system.

Test results and further information are presented. Technology development was continued in support of improving both capital cost and conversion efficiency. Progress made in the development of the 10 ft^2-active-area cell included completion of the initial design, the beginning of fabrication development, and installation of new facilities for cell manufacture.

Background

The solid polymer electrolyte water electrolysis technology development for large-scale hydrogen generation began in 1975 with a design study for Brookhaven National Laboratory (BNL), and has progressed since then under the sponsorship of the Department of Energy (DOE), the New York State Energy Research and Development Authority (NYSERDA), the Niagara Mohawk Power Corporation (NMPC), the Empire State Electric Energy Research Corporation (ESEERCO), the Gas Research Institute (GRI) and the General Electric Company.

The general goals of the program, established on the basis of the 1975 BNL study of a 58 MW system, are:

- Overall system efficiency: 85-90%
- System capital cost (battery limits): <$150/kW equivalent (1980 dollars)
- Life - Cells: 40,000 Hrs
- System Life: 20 Years
- Scale-Up: 2.5 ft^2, 10 ft^2
- Program Goal: Multi MW Demonstration System

Figure 1 is a milestone chart of the program showing current status.

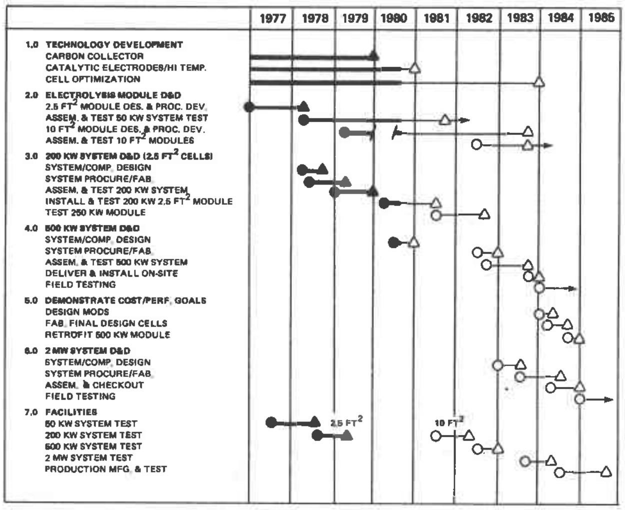

Figure 1. Major Milestones - Bulk Hydrogen Generation Program

2000 SCFH Module Buildup and Operation

Fabrication and assembly of a 60-cell module (thirty, 2.5 ft^2 cells per side) was accomplished in GFY 80. At normal operational current density of 1000 ASF, and normal working temperatures and pressures, a unit of this size will generate 2000 SCFH hydrogen. Figure 2 shows the module prior to installation in the 200 kW system.

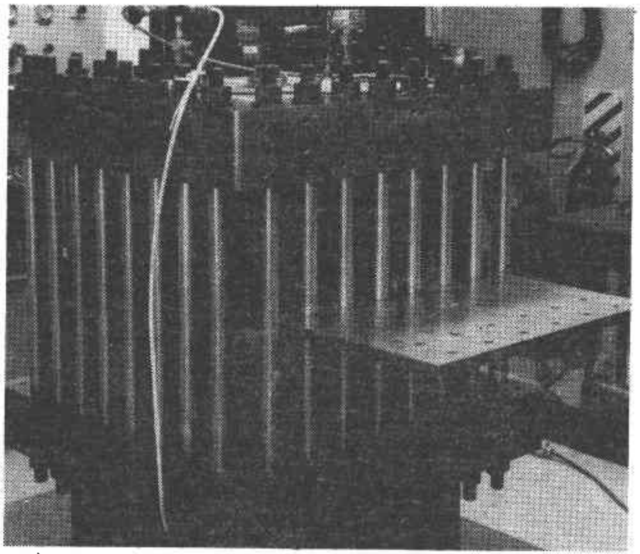

Figure 2. 2000 SCFH Hydrogen Generator Module

After assembly, the module was installed in the 200kW system test facility, shown in Figure 3.

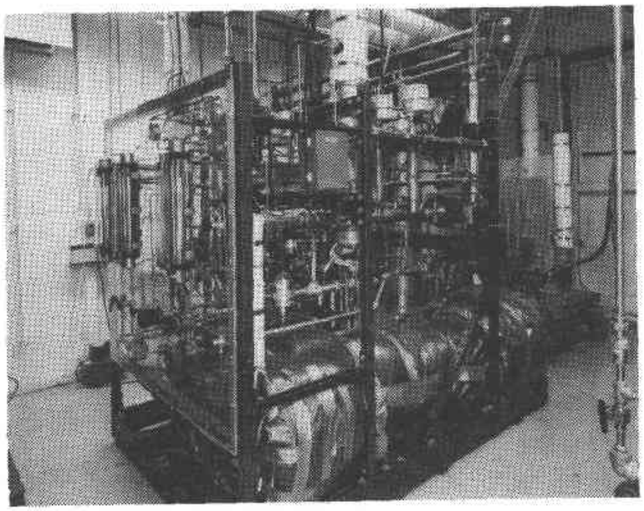

Figure 3. 2000 SCFH Hydrogen Generator in 200 KW System

The module was operated for over 700 hours in the system at an average operating temperature and pressure of 205°F and 100 psi respectively. The test was terminated after 708 hours due to an automatic shutdown caused by a spurious instrumentation signal. Subsequent leak checks revealed internal leakage in two of the sixty cells. An investigation of both cells revealed that the leakage had not resulted from a loss of seal at the sealing surfaces, but rather from damage to the membrane at the edge of the active area. The water transport through the porous anode support in this area had become marginal. Modifications to prevent such local drying are being incorporated.

2000 SCFH Module Performance

Figure 4 is a polarization curve for the average cell, and Figure 5 shows the cell voltage stability over the duration of the test. A comparison of the average cell performance of the 200kW (60 cell) module at 205°F and to that demonstrated by a 4 cell laboratory sized module at 240°F is shown in Table I.

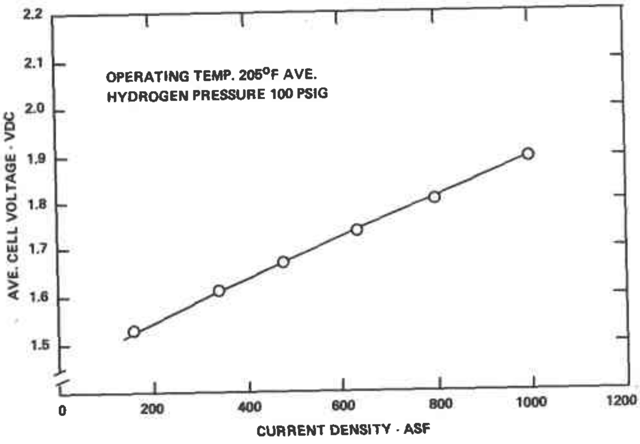

Figure 4. Cell Voltage vs. Current Density 2000 SCFH Hydrogen Generator

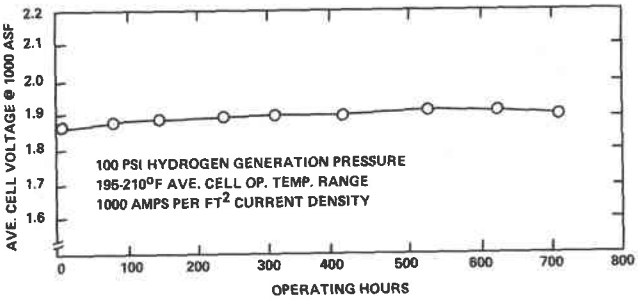

Figure 5. Cell Voltage vs. Time (1000 ASF) 2000 SCFH Hydrogen Generator

TABLE I

Comparison of Cell Performance

	Avg Cell Voltage - VDC		
	250 ASF	500 ASF	1000 ASF
Demonstrated in 200kW (60 cell) module 205°F	1.57	1.68	1.90
Demonstrated in 4 cell 3"x3" Module 240°F	1.47	1.56	1.73

Analysis of cells removed from the module indicated that a major contributor to the higher-than-anticipated voltage had been cathode contamination by an amine - most probably emanating from the anion water purification beads. A lab-sized section was subsequently cut out of one of the module's 60 cells and operated with amine-free feedwater. Performance improved markedly from an initial performance of 1.95 VDC to a final level of 1.81 VDC.

Performance Improvements

Effort is being applied to the following objectives in order to increase system performance:

- Improved control of water quality
- Reduced collector resistance
  - Foil/graphite interface
- Increased operating temperatures
- Reduced membrane thickness
- Improved anode catalysts

200kW System

The 200kW system (Figure 3) - started up in GFY '79 - has accumulated over 2500 hours of operation and is performing well in support of the 2.5 ft^2 modules. The system control has afforded the ability to operate unattended.

10 Ft^2 System Development

The design of the 10 ft^2 membrane and electrode (M and E) assembly was completed in 1979, and fabrication development of the module has now started. Facilities to produce 10 ft^2 M and E assemblies are currently being installed. It is expected that the initial 10 ft^2 membrane and electrode assemblies will be fabricated early in 1981.

500kW Prototype System

Design is underway on a prototype 500kW system. This system will feature a 5000 SCFH electrolysis module consisting of thirty-four 10 ft^2 cells.

ADVANCED ALKALINE WATER ELECTROLYSIS

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Abstract

This brief report summarizes the results of the two major investigation areas pursued during the last 12 months under the Teledyne Energy Systems (TES) contracts with the Brookhaven National Laboratory (BNL), BNL 480421-S and BNL 507416-S. A fourth generation computer program was prepared which determines the economics of manufacturing hydrogen via alkaline water electrolysis. The program was tested by identifying the relative economic merits of the TES-C-AN cathode, the electrolysis module operating temperature range, the optimal module design current density and by comparing the published goals of the advanced alkaline technology to the published SPE goals. The submitted, task final report and analytical procedures are being subjected to a critical independent review. The experimental tasks were focused on verification of the stability of the TES-C-AN cathode structure supplied to TES by the British Petroleum Research Centre, and investigating the improvements possible via new anode structures and new, thinner electrode separators. The data indicate the technology of 1.73 ± 0.02 volt/cell, 500 ma/cm^2 at 100°C (86% voltage efficiency) can be improved to 1.60 volt/cell (92.5% voltage efficiency) with small improvements to the anode and separator components. A module containing the best technology available will be assembled and tested in GFY 1981.

Introduction

This report briefly summarizes the fourth year's progress in advancing the state of the art of alkaline electrolyte water electrolysis at TES under two contracts to BNL (BNL 480421-S and BNL 507416-S). Technical supervision and guidance at BNL is provided by Mr. A. Mezzina and Dr. S. Srinivasan while Department of Energy (DOE) supervision is provided by Dr. R. Reeves. In the early phases of the program (GFY 1977 and 1978) a small, complete electrolysis system was designed, fabricated and dubbed the Applied Research Industrial Electrolysis System (ARIES). This system allowed testing of 300 cm^2 active area, improved electrolysis module components in a 5-cell test module at current densities up to 2.5 amp per cm^2, operating pressures up to approximately 6 atm, and operating temperatures up to 125°C. System input voltages had been shown by several investigators to decrease dramatically with an increase in electrolysis module operating temperature, thus increasing the process efficiency. However, as the operating temperature of the alkaline electrolyte electrolysis module was considered limited to less than 100°C by virtue of the instability of the chrysotile asbestos electrode separator, a preliminary investigation effort was also started to identify the possibility of using separators prepared from "engineering thermoplastics" such as the polysulfone family.

During 1978, a variety of reports were published describing electrocatalyst and electrode systems for improving the state of the art of alkaline water electrolysis. Therefore, the program emphasis was shifted in late GFY 1978 to identifying the operating characteristics and stability of available advanced components in the ARIES. Of the several cathode candidates tested, the best results obtained were with the TES-C-AN structure supplied to TES by the British Petroleum Research Centre. Input voltages of 1.73 volt/cell at 500 ma/cm^2, 100°C were demonstrated,[1] this representing a voltage improvement from 70 to 86% relative to the conventional uncatalyzed nickel wire screen technology. Two alternative cathodes also resulted in a respectable voltage and efficiency improvement although the relative economics of the TES-C-AN was considered slightly superior at that time.

Screening of available improved anodes was not found to be significantly advantageous. No distinctions could be determined between PTFE-bonded and thermally sintered nickel powder anodes of the same approximate surface area and both structures were technically equivalent to the less expensive, plain wire screen anode. No advantage of Co_2NiO_4, prepared via the "freeze-drying technique" as an O_2 evolution electrocatalyst, could be demonstrated at a 10 mg/cm^2 catalyst loading although a small voltage gain was observed at a 40 mg/cm^2 level.

The increase in the operating voltage efficiency of an electrolysis module allows for a decrease in the operating cost factor of hydrogen production economics. The normally more expensive electrode, however, adds to an increase in the plant capital investment. To identify the relative economic merits of the various electrodes and identify the more subtle effects of voltage improvements as well as to allow studies of these merits under a variety of economic considerations, a fourth generation computer analysis has been subsequently assembled and tested in GFY 1980.[2] The experimental testing in ARIES has been continued with the emphasis in GFY 1980 being placed on identifying improved anode structures and locating and testing improved electrode separators to allow stability testing at the 125°C regime. A brief summary of these efforts follows.

Hydrogen Economics Model

As has been noted by several investigators, given an electrolysis module design and fixed financial constraints such as operating cost rates and capital expense considerations, there is a minimum hydrogen cost when this value is calculated as a function of the module current density. The value of this hydrogen cost minimum as well as the optimum module design current density is a function of many factors. To allow verification of the extent of the improvements made by substitution of various candidate components within the electrolysis module as well as allow identification of the other critical cost components, a fourth generation hydrogen economics computer model was prepared and evaluated. At the request of BNL, the study was restricted to sizes less than 1 MW power input. For convenience during the program testing phase, most studies were carried out using an 80 KW input value.

The program functions approximately as follows. Given the input power available and having a defined electrolysis cell with respect to component costs, the temperature dependence of the energetics and life of the cell, an electrolysis module is designed. The material costs are subsequently calculated which satisfy the available electrical input for the defined plant life. With the module designed and the input power defined, the plant mass and energy balance is then determined and the corresponding required equipment sized and costed. The remaining costs associated with delivery of the subsystems to a customer's site, the construction, and startup costs, the manufacturer's profits, etc., are then summed to an overall hydrogen plant capital cost (or price) to the customer. Operating costs are subsequently calculated given the labor profiles, the materials costs, and the operating profile or percentage utilization of the plant. To establish the influence of inflation and allow a variety of approaches to the capitalization of the equipment, TES has utilized the economics subroutine established by the Electric Power Research Institute (EPRI).[3] This results in a "levelized" or time weighted average hydrogen cost. One or several of the input values of the various anticipated parameters can then be adjusted, the levelized hydrogen cost recalculated and the optimum cost of hydrogen as a function of the various input parameters can then be determined. Roughly 20 of the 262 input parameters are considered as key elements.

To date, the program has been utilized to verify the operational functionality and to demonstrate the main approaches to the advanced alkaline technology effort are aimed in an appropriate direction. Nearly all findings were quite close to the conclusions drawn in the three earlier (and considerably less complex) generations of models. The general results for 20-year plant life cases and 10% general inflation levels show the operating cost segments (electricity and operating labor) predominate (50 to 75%) the "levelized" cost of hydrogen. The electrolysis module designs optimize at current densities of 400 to 1000 ma/cm^2 depending on the economics of the electrocatalyst system, lower current densities for less efficient, low cost electrode systems. Optimum hydrogen costs occurred at the highest operating temperatures even though the accompanying predicted shortened module life increased the life cycle capital costs. The only significant surprise was the relative insensitivity of the plant utilization factor on the levelized cost of hydrogen in the 60 to 100% utilization range, again a reflection of the dominant cost factors being other than the plant capitalization.

Although the program task final report and the initially selected input assumptions are currently being critically reviewed by BNL personnel, a few specific values and quantitative trends can be presented. The plant size is one of the key features to the overall economics. In an early program verification calculation set, using a module design containing plain nickel screen electrodes operated at very mild temperatures (60°C), the 20-year levelized hydrogen cost of $6.7/Kg for an 80 KW machine was found to change by $1.3/Kg hydrogen for each decade of plant size. In the later calculation sets, comparison of the advanced C-AN cathode technology to the plain nickel screen technology showed a 12%, levelized hydrogen cost savings in the 80KW machine, using 2.5¢/KWH electricity rate and at 85% plant utilization. The C-AN cathodes have been supplied to TES by the BP (British Petroleum) Research Centre and the impact of this new technology is considered to be significant. Finally, a calculation set was made comparing the projected alkaline electrolyte technology to the published values of the goals of the SPE technology. The projected alkaline technology involves utilization of the C-AN cathode, a slightly (40 mv polarization gain) improved inexpensive anode and half the ohmic losses from the porous electrode separator. The projected technology resulted in virtually identical hydrogen costs compared to the SPE goal costs based on the limited economics published on the latter technology.

Improved Components Testing

A newly contracted technical task which was started in March, 1980 consists of locating an improved but inexpensive anode, establishing a separator with half the ohmic losses and demonstrating the stability of the improvements using the C-AN cathodes. The initial technical evaluation involved a 3-month test of the 300 cm^2 active area C-AN cathodes in the 5-cell ARIES test module (No. 13) using plain wire screen anodes and conventional asbestos separators.

The results from the approximately 1500-hour test of the C-AN cathode technology are shown in Figure 1 and included in the figure are the results from the previous test of the C-110 cathode technology (module No. 10). As may be seen in the figure, the initial results with the C-AN module improved somewhat during the first 600 hours of operation, then degraded slightly for about 400 hours and then appeared to stabilize. The advantage relative to the C-110 cathodes was still evident at the end of the test period although the cause of this apparent degradation is not well understood at this time. Life testing of research-sized (2 cm^2) pieces at the BP Research Centre has shown stability through 3000 hours continuous operation and TES in-house testing of 75 cm^2 cells tested under milder conditions also shows good voltage stability. A comparison of the volt-amp characteristics of both cathodes is shown in Figure 2.

As indicated earlier, the experimental emphasis is being directed to the "other areas" of the cell. With regard to the possible oxygen evolution anode improvement, a general letter of inquiry was submitted in December, 1979 to 29 organizations known to be working in this technology area. From the seven responses, a purchase order was placed with MPD Technology Corp. for test anodes which appear to offer a 65 mv polarization savings. A screening module (No. 14) was constructed utilizing two proprietary anodes coded as TES-A-380A, two anodes prepared by MPD and the conventional nickel screen anode. Testing was initiated at the time of preparing this report. The results show the TES-A-380A to have a slight initial superiority and, in general, the determination of the time effects remains to be established. Three other electrode concepts are being considered. Testing of polycrystalline nickel whisker electrodes, fabricated at the University of Virginia (Dr. G. E. Stoner), will be accomplished in the early fall and dialogue with two other potential vendors will be continued in an attempt to assure the best available electrode technology is assembled for long-term testing in GFY 1981.

In that further efficiency gains will be realized by operating the electrolysis module at the 125°C region, most investigators have pursued the use of alternative materials for the conventional chrysotile asbestos electrode separators. One study did however suggest that if the electrolyte is saturated with silicates, either as an initial additive or via corrosion product accumulation, then the asbestos separator would be a long-lived entity. Regardless of the material choice, the voltage loss associated with the separator must be reduced and a thin (~0.03 cm) structure appears to be required. The two alternative materials which appear attractive at this stage are polybenzimidazole (PBI) and potassium titanate. As reported previously (reference 1), PBI was shown to be both stable in KOH corrosion testing and useful as a separator in TES-sponsored single cell (75 cm^2) testing. Testing in the ARIES screening module (No. 12) was only partially successful as the PBI separators did experience a lowering of porosity during the module operation. Contact with Celanese personnel[4] has indicated PBI fibrid material may be available for further testing in early 1981. Two sources of potassium titanate separators have been recently located and samples have been obtained for testing. A porous PTFE impregnated with the titanate has been supplied by Mr. E. Torikai of the Government Industrial Research Institute (GIRI) at Osaka, Japan through the auspices of the IEA Hydrogen Annex IV program. In addition, samples of PTFE-bonded titanate fiber are being obtained from the Yardney Electric Co. (Paweatuck, CT). The material is reported to be fabricated using the new fibers manufactured and sold by the Otsuka Chemical Co. as was announced in early 1980. Studies with the new materials as well as in-house fabricated, thin asbestos separators will involve determination of the proper compression level for both gas sealing as well as minimum module voltage requirements.

The combination of stable improved electrocatalyst/electrode structures with thinner more efficient electrode separators in modern design cells operating in the temperature range of 100 to 125°C appears to satisfy the operating goals for hydrogen and oxygen production via alkaline electrolyte water electrolysis of 1.55 volts/cell at 500 ma/cm^2. The data verifying the demonstration of these applied research goals should be the subject of the 1981 summary report.

Acknowledgments

The economic analysis and task summary report was prepared mainly by M. R. Yaffe with programming assistance by M. C. Miller and M. P. Saltzman. The ARIES tests and results have been through the efforts of V. R. Lougheed. The author again thanks M. F. Gembarosky for her assistance in the preparation of the contract reports and this summary paper and F. E. Fahdt for his timely artwork.

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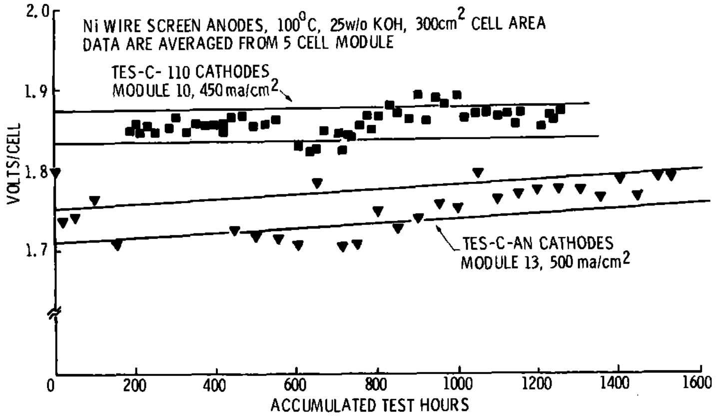

FIGURE 1: STABILITY TESTING OF IMPROVED CATHODES IN ARIES

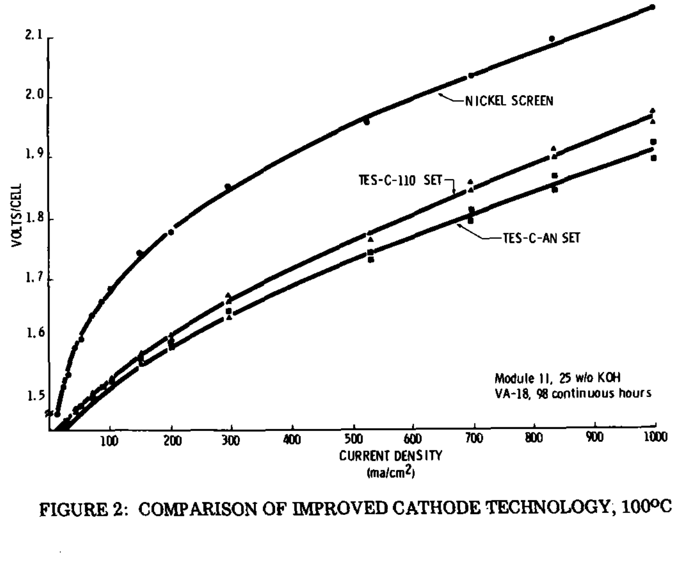

FIGURE 2: COMPARISON OF IMPROVED CATHODE TECHNOLOGY, 100°C

STATIC FEED WATER ELECTROLYSIS FOR LARGE SCALE HYDROGEN GENERATION

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Abstract

The static feed water electrolysis concept, originally developed by Life Systems, Inc., for aerospace application is being evaluated for application in large-scale hydrogen generation. The inherent potential for low cost and high performance of this alkaline electrolyte-based technique resulted in the award of a nine-month, Department of Energy funded program to Life Systems, Inc. A four-task program has been negotiated having a start date of August 15, 1980. The proposed effort will address four areas: (1) definition of upper current density levels possible with the static feed concept, (2) investigation of operation with contaminated water (e.g., seawater), (3) scale-up of cell area, and (4) definition of future scale up at the cell stack and system level.

This paper presents the static feed concept, its operation and demonstrated performance. Also, the scope of each of the four program tasks is defined. Results relating to the specific program are not presented since the program had not started at time of submittal of this paper.

Introduction

Over the past ten years, Life Systems, Inc. has developed a unique water electrolysis technology that offers the potential of significantly reducing the cost of bulk hydrogen generation through water electrolysis. Specifically, these cost reductions result from:

1. A simple, capital equipment-saving technique for feeding the water into the water electrolysis cell.
2. The development of an oxygen evolving electrode that has demonstrated superior performance (1.49 V at 150 ASF and 180 F after 18,000 hours).
3. The use of an alkaline electrolyte, which is compatible with low cost materials.

This technology, however, has been limited to smaller electrode areas (0.1 to 0.3 ft^2) and to modules of up to 15 cells. Thus, although the technology is extremely attractive, the state of its development requires scale-up in several key areas to realize the performance and cost reduction expectations.

To achieve these goals, Brookhaven National Laboratory (BNL), under sponsorship of the Department of Energy (DOE), has initiated a development program with Life Systems, Inc. to demonstrate the capability of the static feed water electrolysis system to satisfy the bulk hydrogen generation requirements of the BNL/DOE Chemical/Hydrogen Energy Systems Program. The program is a nine-month effort having a start date of August 15, 1980.

Alkaline Electrolyte, Static Feed Water Electrolysis Concept and Performance

Cell Reactions, Configuration and Operation

The half cell and overall electrochemical reactions for the static feed cell using an alkaline electrolyte are:

Cathode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

Overall: $2H_2O \rightarrow 2H_2 + O_2$

Figure 1 shows these reactions with a functional schematic of a static feed cell. The overall static water feed concept operates as follows. Initially, the water feed cavity, the water feed matrix and the cell matrix contain

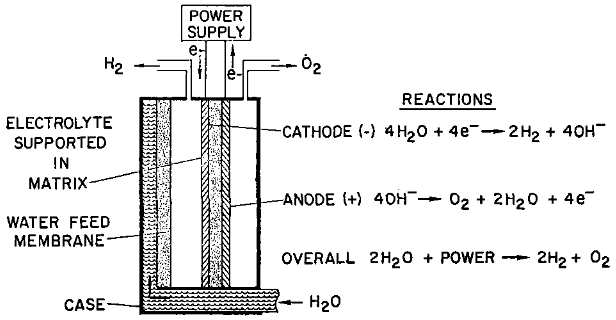

Figure 1 Static Feed Water Electrolysis Cell Schematic and Reactions

electrolyte at equal concentrations. Both the hydrogen and oxygen cavities are void of liquid. An equilibrium condition exists prior to start of electrolysis. When power is applied to the electrodes, water from the cell electrolyte is electrolyzed. As a result, the concentration of the cell electrolyte increases and, therefore, its water vapor pressure decreases to a level below that of the feed compartment electrolyte. This water vapor pressure differential is the driving force causing water vapor to diffuse from the liquid/gas interface within the water feed matrix, through the hydrogen cavity and cathode, and into the cell electrolyte. This process establishes a steady-state condition based on the water requirements for electrolysis (proportional to current density) and humidification of the product gases.

As water diffuses from the feed matrix and is removed from the water feed compartment, it is statically replenished from an external source to maintain a constant pressure, volume and electrolyte concentration within the feed compartment. Upon interruption of electrical power, water vapor will continue to diffuse across the hydrogen compartment until the electrolyte concentration in the cell matrix is equal to that in the water feed matrix. At this point, the original equilibrium condition is regained.

Figure 2 depicts two possible cell configurations; one termed "present configuration," representing present baseline, and the other termed "future configuration," incorporating a simplified cell construction with a combined coolant and water feed compartment. This configuration is ideally suited for operation with circulating contaminated or brackish water.

Static Feed System Concept

A schematic of the static feed water electrolysis system concept is shown in Figure 3. The system consists of three main parts: An electrochemical module, a water supply tank and a pressure controller. Oxygen and hydrogen are generated in the module(s) from water supplied by the water supply tank. The water supply tank is cyclically refilled as required.

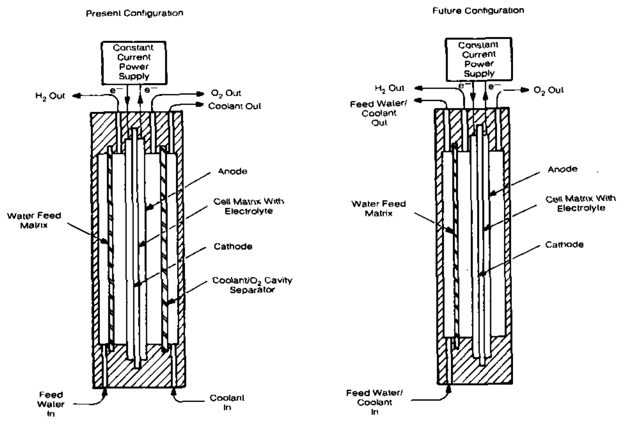

Figure 2. Static Feed Functional Cell Configurations

The pressure controller (1) maintains the absolute pressure of the system, (2) maintains the desired pressure differentials between the gas and water cavities, and (3) controls pressurization and depressurization of the system during startups and shutdowns.

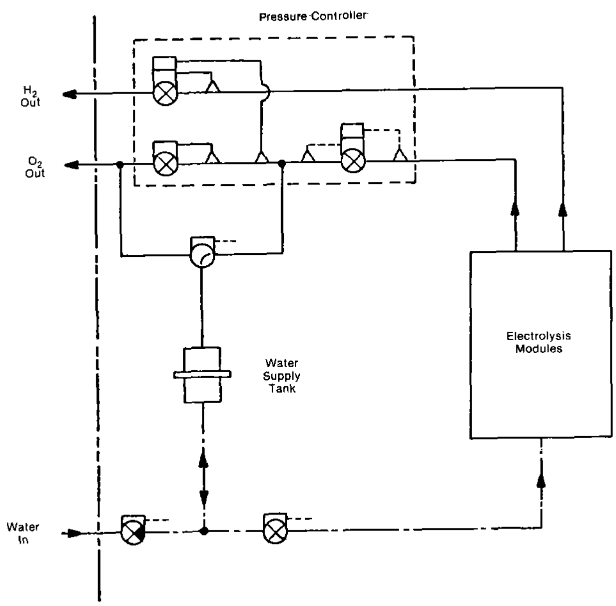

Figure 3. Static Feed Water Electrolysis System Concept

Performance

Advances in the electrochemical performance of the alkaline static feed concept, represented as single cell voltage versus current density, are depicted in Figure 4. Actual performance (cell voltage) versus current density and time (>18,000 hours) are shown in Figures 5 and 6, respectively.

Technology Development Program

A four task development program is being implemented. The scope of the proposed effort will:

1. Better define the upper current densities possible with the static feed concept.
2. Better define the ability of the static feed water electrolysis concept to operate with deionized and contaminated water.
3. Demonstrate hardware scale-up of electrode area from the present 0.1 ft^2/cell to 1.0 ft^2 or larger.
4. Establish a sequence to follow in future scale-ups (of electrode area, bi-polar plates, number of cells per module, etc.) that will result in larger gas generating capacity.

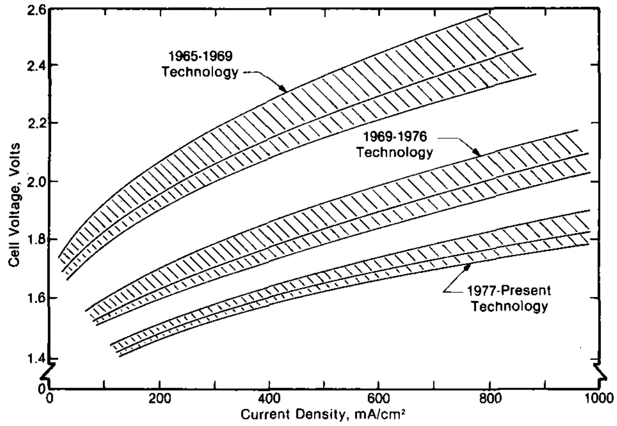

Figure 4. Major Electrode/Catalyst Performance Improvements

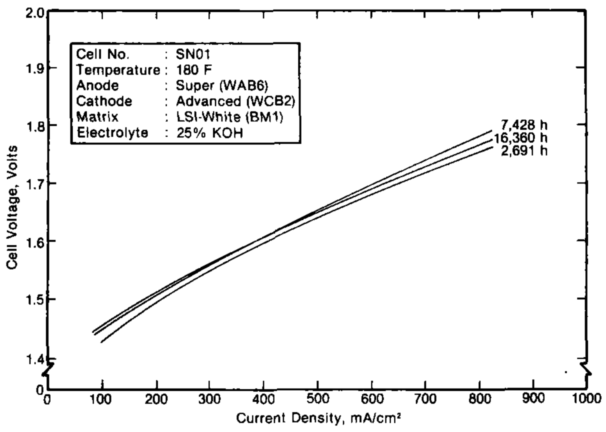

Figure 5. Cell Performance Versus Current Density

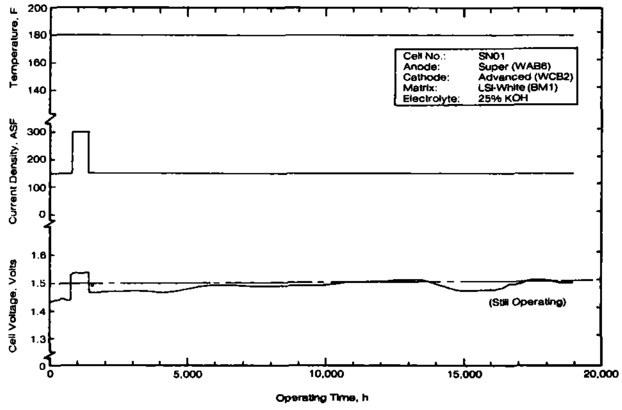

Figure 6. Cell Performance Versus Time

Elevated Current Density Investigation - Task 1

The capital cost of water electrolyzers is directly proportional to the number of electrolysis cells. Hence, capital cost is inversely proportional to operating current density. A series of experiments shall be completed, therefore, to investigate and demonstrate elevated current density operation (1,000 ASF or greater).

Contaminated Water Operation - Task 2

A significant part of the present cost of bulk hydrogen generation through water electrolysis is incurred during the purification of the water to be electrolyzed. Purification is necessary to prevent contamination of the electrode catalyst and/or cell electrolyte. In the static feed system, however, the liquid water to be electrolyzed is separated from the electrodes and cell electrolyte by a chamber containing water vapor and hydrogen.

In the baseline static feed cell configuration feed water contaminants could still affect performance by contaminating the electrolyte in the water feed compartments.

As a first step to eliminate water purification, Life Systems has already demonstrated the ability of its static feed water electrolysis system to operate using deionized water (as opposed to an aqueous solution of potassium hydroxide) in the water feed compartment. The next step, to be demonstrated under this task, is to replace the deionized water in the water feed compartment with brackish water and/or simulated seawater.

Cell Area Scale-Up - Task 3

The larger the electrolyzer cell area, the fewer number of cells that are required to generate a given volume of hydrogen. Reduction in the number of cells through increasing the active cell area reduces capital cost and keeps the number of cells within practical limits for large-scale gas production.

The capability of Life Systems' cell design to be scaled up from its present area will be demonstrated. As a minimum, a design for a 5.0 ft^2 size will be completed. Also a single cell will be fabricated to demonstrate the water feeding rate capability using a simulated water-consuming electrochemical cell.

Future Scale-Up Sequence - Task 4

Studies completed at BNL and elsewhere have indicated that end-item applications of water electrolyzers for bulk hydrogen generation require electrodes of 2 to 12 ft^2 in area.

In this task the future scale-up sequence to be followed for the static feed water electrolysis concept will be established. The goal will be low development risk and minimum development cost. Some of the factors that will be considered are:

1. The ability to fabricate electrodes of larger sizes (e.g., up to 10 ft^2).

2. The ability to prepare matrices of a size similar to that of the electrodes.
3. The ability to stack a large number of cells in series.
4. The ability to construct low resistance, low cost bi-polar current collectors.
5. The ability to scale-up the peripheral systems components.

Summary and Conclusions

The static feed electrolysis concept using an alkaline electrolyte is a viable candidate for large-scale, low cost hydrogen production. Its demonstrated performance surpasses that of other existing systems. Its inherent system level simplicity, coupled with its use of low cost materials, promises low capital and operating costs. Scale-up and other large-scale hydrogen production criteria must be evaluated to adopt the static feed concept from "space to terrestial energy applications." The four task program sponsored by the Department of Energy is the first step in that direction.

SELECTION AND EVALUATION OF MATERIALS FOR ADVANCED WATER ELECTROLYSIS

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Abstract

During the past year (7/79-7/80), the majority of research conducted on this contract concerned time dependent increases in electrolysis cell voltage. This phenomenon has been investigated at the Applied Electrochemistry Laboratory at the University of Virginia for the past four years. This report is a conclusive summary of these research activities dating from approximately March of 1976. The majority of this research was conducted during the past two fiscal years.

I. Proposed Theories for "Time Effects"

The theories to explain the variation of electrolysis cell voltage with time at constant current and temperature are:

1. Increases in the anode potential with time at constant current are due to changes in the surface oxide state.[1,2,3]

2. Increases in either or both of the electrode potentials are due to loss of catalyst material or decrease in catalyst surface area due to sintering and mechanical instability.[1,4,5]

3. Increases in the cathode potential are due to deposition of metallic impurities from the electrolyte such as corrosion products from elsewhere in the system.[1]

4. Increases in the cathode potential are due to the absorption of hydrogen by the cathode.

Before discussing these various theories it should be pointed out that any or all of the proposed mechanisms can be operative in commercial electrolysis systems and that elimination or minimization of any of them would contribute to efficiency improvement. The latter of the theories is that proposed by the investigators in May, 1978, based on the previously discussed results. The validity of the other theories is not disputed. In fact, the effects alluded to in theories 1 and 3 have been observed in this research. The time variations observed in this research were observed for the cathode potential; independent of the anode potential or its change with time, without the use of catalyzed electrodes or high surface area electrodes, with electrolytes purified by pre-electrolysis to remove metallic impurities, and with analysis of the electrodes following experiments to detect metallic impurities. It was therefore possible to investigate our theory based on hydrogen absorption, theory 4, independent of theories 1 and 2, and with precautions to minimize the contributions of theory 3.

II. The Nickel-Hydrogen System, A Literature Review

In 1952 Bockris and coworkers[6] investigated the hydrogen evolution reaction on various metals including nickel. Although parameters for the reaction on nickel were reported, it was noted that reproducibility of results was difficult to achieve. Additionally, it is difficult to find further published results for this reaction on nickel. From the results discussed in the previous section, it became of interest to search the literature for additional information on the nickel - hydrogen system. This section concerns the findings of this study.

The most significant result uncovered during this search was that nickel can form a hydride.[7,8,9] Although nickel hydride is unstable at standard temperature and pressure, it can be formed if hydrogen pressures as high as several thousand atmospheres are achieved.[8,9,10] At temperatures of or slightly above 25°C, 20,000 atmospheres of hydrogen gas pressure is required to create nickel hydride, a matter which requires further clarification. Figure 1 is a plot of hydrogen pressure vs. hydrogen absorbed by nickel expressed in atomic ratio. At pressures below the room temperature critical pressure (~20,000 atm), a small concentration, less than 0.2 a/o[18], of hydrogen is absorbed. This "phase" is called α hydride. The α hydride is essentially indistinguishable from non-hydrogen containing nickel. Theoretical calculations of the lattice expansion have been calculated and are very small; the lattice constant increases by 10^{-3} A.[18] This change is certainly not measurable by traditional techniques such as x-ray or electron diffraction. The atomic concentration can, however, be measured by gas desorption measurements.[11] Above some critical pressure, ~20,000 atm at 25°C, the H/Ni atomic ratio drastically increases and what is known as β nickel hydride occurs. This hydride is characterized by H/Ni atomic ratios greater than 0.6 depending on the pressure and by a lattice expansion of approximately 6% (3.52 A to 3.73 A). Consequently, β-NiH is readily distinguishable from

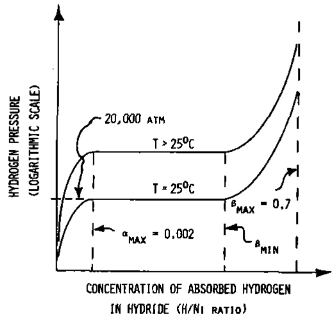

Figure 1. Hydriding Behavior of Nickel

hydrogen free nickel via x-ray diffraction techniques. X-ray diffractometry was the technique most commonly employed in the studies referenced.[9] [10] [12] Additional characteristics of β-NiH are: 1) The optical and/or metallographic appearance on a specimen surface is darker than nickel (it appears blackish);[9] 2) The absorbed hydrogen atoms occupy octahedral interstices in the face centered cubic nickel lattice[11] (the structure is therefore sodium chloride type); 3) Substantial hydride penetration can occur for depths up to 30μ; and 4) Substantial cold work is left in the nickel lattice following hydride desorption.

Before continuing with the findings of the literature search, it should be pointed out why these previous observations are so significant. First, the theory of cathodic potential-time variation in hydrogen evolution proposed by the investigators requires hydrogen absorption. Secondly, the pressures required for hydride formation in nickel are high but readily achieved electrochemically. A tenfold effective increase in hydrogen surface pressure is realized for every 30 mV increase in the cathode overpotential.[13] Typical cathodic overpotentials are 100 to 250 mV corresponding to hydrogen pressures of 10^3 to 10^8 atm. Several references verified that a hydride forms in nickel by electrolytic charging in sulfuric and other acids.[7] [9] [10] [12] Furthermore, the presence of the blackish surface is consistent with observations on nickel cathodes in KOH discussed previously. The hydride and proof of its existence via x-ray diffractometry should seemingly lend considerable merit to the proposed theory. Further experimentation will be discussed in the below.

Additional pertinent information uncovered in the literature search involve the chemistry of a nickel surface in KOH solutions and the results of anodic and cathodic polarization. The following discussion will be applicable only to 30 w/o KOH, the electrolyte of interest. If nickel comes into contact with aqueous KOH, its surface immediately transforms to a hydroxide via the following reaction,[14] [15]

$$Ni + 2H_2O \rightarrow Ni(OH)_2 + 2H^+ + 2e^- . \quad (1)$$

This anodic reaction occurs thermodynamically at -1.0 V vs. Standard Calomel Electrode (SCE) for a pH of 14.7 (30 w/o KOH). The open circuit potential of nickel when initially introduced to the KOH is about -0.8 V vs. SCE, anodic to the reversible potential for hydroxide formation. Consequently, the nickel surface transforms to a nickel hydroxide. The reaction can be followed because the open circuit potential drops from about -0.8 V vs SCE to a steady value of approximately -0.4 V vs. SCE. This open circuit potential is indicative of a stable hydroxide surface. These phenomena were experimentally verified and found to be quite useful in determining the surface state of the nickel. Other possible reactions will now be described with the aid of Figure 2. This figure illustrates the various possible reactions for the nickel - aqueous KOH system for 30 w/o KOH dependent on the Ni potential vs. SCE. The reactions as written left to right in Figure 2 are anodic and cathodic when written vice versa. Anodic reactions can only occur on the electrode for electrode potentials anodic to the reversible potential for the reaction considered. The same is true with respect to cathodic reactions for potential cathodic to their reversible potentials. Oxidation reactions produce various oxide states for nickel at potentials above (anodic to) -30 V vs. SCE. These reactions will not be discussed in detail but it is important to remember them when driving nickel electrodes anodically in order to achieve complete hydrogen desorption or surface area calculations by cyclic voltammetry. -1.107 V vs. SCE is the reversible potential for hydrogen evolution and is indicated in the figure. Hydrogen evolution occurs for potentials cathodic to or lower than this potential. In order to reduce a $Ni(OH)_2$ surface to Ni it is necessary to go to the hydrogen evolution potentials. This creates a problem for studying the kinetics of time dependent increases in cathode potential. If the surface is $Ni(OH)_2$ at time equal zero, then a certain amount of current will be utilized in the $Ni(OH)_2$ to Ni reduction reaction. Consequently, the measured potential will be due to both this reaction and hydrogen evolution. If the electrode is subjected to hydrogen evolution for a given potential - time combination which reduces the hydroxide and is brought up to -1.05 V vs. SCE, the surface will be hydroxide free. However, the nickel will not be hydrogen free! At a potential of -1.05 V vs. SCE, a substantial amount of time, perhaps several weeks, is required for complete hydrogen desorption. It is therefore necessary to find a better way of starting with a hydrogen free, hydroxide free nickel. A technique was developed and will be discussed in a future report.

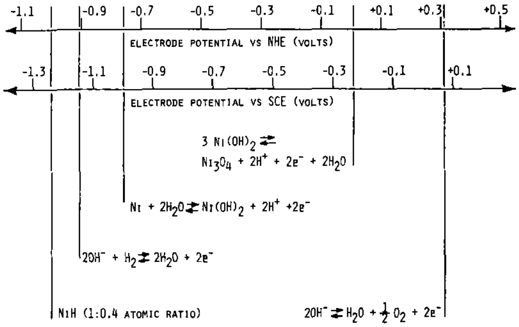

Figure 2. Possible Reactions of the Nickel - 30 w/o KOH System.

The other reversible potential shown in Figure 2 is one which is not present in the Pourbaix diagram.[16] This potential corresponds to the open circuit potential for $NiH_{0.4}$, an atomic ratio of 0.4 H/Ni. This concentration is midway between the α hydride and β hydride phases and is a mixture of the two.[11] The reversible potential was derived by monitoring the open circuit voltage behavior of hydrogen charged nickel.[11] The charging was accomplished electrolytically in sulfuric acid and the open circuit voltage and hydrogen desorption rates were measured in various electrolytes including 30 w/o KOH. The typical open circuit voltage behavior with time subsequent to hydrogen charging in H_2SO_4 is shown in Figure 3. The voltage plateau indicated in this figure corresponds to the transition from β hydride to α hydride or similarly to $NiH_{0.4}$. This potential was shown to occur at 130 mV cathodic to the reversible hydrogen potential independent of pH.

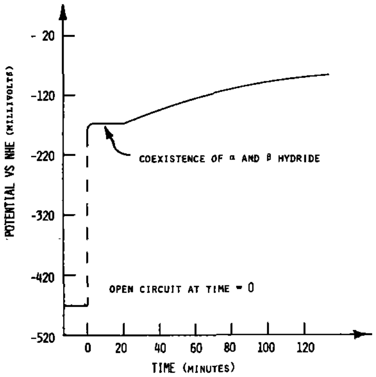

Figure 3. Open Circuit Voltage Response For Nickel Cathodes in 0.1N H_2SO_4

Therefore in 30 w/o KOH this potential occurs at $\sim$-1.24 V vs. SCE as shown in Figure 2. It is interesting to point out that 130 mV of hydrogen overpotential corresponds to very nearly 20,000 atm of hydrogen pressure, the critical pressure for β hydride formation at room temperature.

The results discussed in the previous paragraph were obtained for nickel foils about 17 μ thick thus allowing complete hydride saturation. Care should be taken in relating these observations to those for bulk electrodes where hydride saturation is only possible to about a 30 μ surface depth. However, the open circuit potential is indicative of only the surface and is a valuable technique for surface investigation.

One final important aspect of this literature search involved techniques for IR correction in electrochemical techniques. Several relevant references were found and these will be discussed along with a relatively unique technique developed by the investigators in a future report.

III. Experimental Investigation of Nickel Hydride

In light of the theory proposed by the investigators attributing cathode voltage - time increases to hydrogen absorption, the presence of nickel hydride should prove supportive. Additionally, the possibility of monitoring absorbed hydrogen concentration by x-ray diffraction data allows quantitative representation of the absorbed hydrogen concentration. This is because the extent of lattice expansion is dependent on the concentration of absorbed hydrogen.

It first seemed necessary to ascertain the ease with which x-ray diffraction could detect the hydride as reported by others.[9] [10] [12] It is also important to remember that the hydride is unstable at standard conditions and desorption occurs with the production of hydrogen gas at the surface. However, the investigators referenced indicate the hydride to be present for durations up to hours depending on charging conditions. For an initial investigation, various forms of nickel were driven cathodically with respect to platinum anodes in 30 w/o KOH electrolyte at fairly high current densities, 200 - 500 mA/cm^2, corresponding to large over-potentials and therefore high hydrogen pressures. A table of the various forms of nickel tested and the charging currents and times for each is seen in Figure 4. None of these exhibited the expected x-ray diffractometry curve indicative of the presence of β nickel hydride.

NICKEL TYPE	APPARENT CURRENT DENSITY	DURATION
200 - SCREEN	0.2 A/CM^2	3 HRS
200 - FOIL	0.5 A/CM^2	3 HRS
200 - FOIL	0.5 A/CM^2	8 HRS
200 - PLATE	1.0 A/CM^2	8 HRS
200 - PLATE	5.0 A/CM^2	8 HRS
200 - ELECTRODEPOSIT	1.0 A/CM^2	8 HRS
200 - ELECTRODEPOSIT	2.0 A/CM^2	3 HRS

Figure 4. Hydrogen Evoluation Conditions For Various Nickel Specimens.

With the inability to detect the hydride phase in nickel charged in aqueous KOH it became desirable to confirm the results of the literature articles which employed acidic electrolytes primarily, although open circuit potentials and hydrogen desorption rates of hydrides were measured in alkaline electrolytes.[11] Nickel samples were drives cathodically in 1 M H_2SO_4 at conditions similar to those listed in Figure 4. In all cases, given sufficient charging time and sufficient current densities to achieve the required over-potential as previously discussed, the β hydride phase was detected. The x-ray data and charging conditions for several of these experiments are listed in Figure 5.

NICKEL TYPE	APPARENT CURRENT DENSITY	DURATION
200 - FOIL	0.2 A/CM^2	8 HRS
200 - FOIL	0.5 A/CM^2	1 HR
200 - PLATE	0.5 A/CM^2	2 HRS
200 - PLATE	0.3 A/CM^2	1 HR
200 - ELECTRODEPOSIT	0.2 A/CM^2	2 HRS

Figure 5. Hydrogen Evolution Conditions for Nickel Exhibiting Hydride.

It now became unclear as to why the hydride would apparently not form in KOH. One complicating factor is the desorption rate of hydrogen from β-NiH at high pH as compared to low pH. Figure 6 illustrates this desorption rate as a function of pH. Notice that the desorption rate in the pH corresponding to 30 w/o KOH (14.7) is about 20 times faster than that of relatively strong acids. Additionally, it is significant that these results were obtained for hydrides generated in acid electrolytes. It would seem reasonable to suggest that the same mechanism responsible for the high desorption rates in high pH electrolytes would tend to suppress hydride formation in these electrolytes. More discussion of this mechanism will follow.

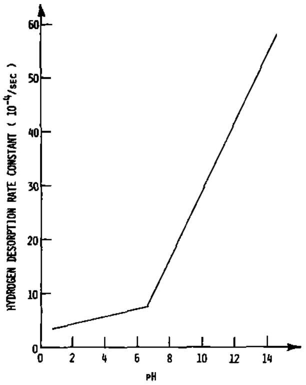

Figure 6. Hydride Desorption Rate As a Function of pH.

If this previous argument is true, then an important consideration concerns whether a hydride forms at all during electrolysis in KOH. Realizing that the formation may be suppressed and that the desorption rates are quite rapid, it became necessary to devise a different technique to investigate the cathode surface for hydride.

A technique was devised for the x-ray diffractometric analysis of nickel cathodes in-situ with hydrogen evolution in KOH electrolytes. With this set up the cathode could be driven into hydrogen evolution and simultaneously monitored by x-ray diffraction. The results of this analysis were not encouraging in that no hydride peaks could be detected even at current densities as high as 500 mA/cm^2.

A nickel foil in which hydride had been previously formed by electrolysis in acid was employed in the cell with a water electrolyte. Hydrogen evolution occurred at the surface due to hydride desorption. X-ray diffraction analysis, however, did indicate the presence of the hydride phase. This experiment verified the validity of the technique.

It is concluded from these experiments that if the hydride does form at all in KOH electrolyte, it does not do so to an extent detectable by these experiments.

Further experimentation was designed to determine whether a previously formed hydride would be stable in KOH electrolyte at vigorous hydrogen evolution conditions. X-ray diffraction was employed to confirm the presence of a hydride in a nickel foil driven cathodically in H_2SO_4. The foil was then inserted into a KOH electrolyte with immediate occurrence of hydrogen evolution for varying periods of time. In all cases, the hydride had disappeared, at least as discernable via the x-ray technique, in a period of about an hour.

The previous results lead to the conclusion that the hydride is difficult, perhaps impossible, to form by hydrogen evolution in KOH electrolyte; and that if it does, it does so in a sufficiently small surface layer as to be undetectable by x-ray diffration.

The investigation of nickel hydride does not prove or disprove the theory of cathodic voltage - time variations due to hydrogen absorption. However, it does strongly question whether hydrogen does absorb at all into the nickel lattice during hydrogen evolution in KOH electrolyte. Confirmation of this question is of prime concern in regards to the theory of the investigators.

IV. Electrochemical Investigation of the Nickel-Hydrogen System

In the previous section, it was shown that x-ray diffractometry results were inconclusive in discerning whether or not hydrogen penetrated the nickel lattice during hydrogen evolution at the nickel electrodes in an aqueous potasium hydroxide electrolyte. The theory of time variations of nickel cathode voltage as based on hydrogen absorption into the nickel was therefore of somewhat questionable validity. The key question to be answered is whether or not hydrogen is absorbed. In order to determine this, a fairly simple experiment was devised to compare the electrochemical behavior of nickel, palladium, and platinum during and subsequent to hydrogen evolution in KOH. Palladium is known to hydride readily to the extent of 0.8 H atoms per Pd atom and to be stable at room temperature.[17] On the other hand, platinum is known to absorb little or no hydrogen.[18] The two represent more or less extremes of hydrogen absorption capability and comparison of nickel to these should prove instructive. In order to implement this comparison, each of the three materials, Ni, Pd, and Pt, were driven cathodically into hydrogen evolution using a platnium anode in KOH electrolyte. The platinum anode was selected to prevent the occurrence of anode dissolution products from depositing on the cathode. The potential was controlled using a standard calomel electrode and was swept cathodically at 1 to 10 mV/sec from -0.5 volts vs. SCE potential of -2.0 volts vs. SCE. At this point, it was held for varying periods of time and then swept anodically again with potentiostatic control and at the same sweep rate to a final potential of -0.5 volts vs. SCE. The current was monitored continually during the process. The data was recorded on an HP 7045 A X-Y recorder. This technique of potentiostatically sweeping an electrode potential vs. some reference electrode potential and measuring the subsequent current between the electrode and an auxiliary electrode (counter electrode) is called voltammetry or cyclic voltammetry when the voltage cycle is repeated.

The important result of these experiments is the behavior of each electrode during the anodic sweep subsequent to the hydrogen evolution. The palladium electrode shows substantial hydrogen oxidation activity, as expected, indicated by high anodic current densities occuring just above the reversible hydrogen potential during the anodic sweep. The platinum electrode, exhibits essentially no hydrogen oxidation evidenced by small current densities coincident to the anodic sweep. These two experiments were as anticipated. The nickel electrode behavior exhibits hydrogen absorption although not as appreciably as the palladium. This is an important result because it supports the affirmative on the key question of whether hydrogen is absorbed by nickel during hydrogen evolution in KOH. This result was further confirmed by two additional electrochemical techniques. The first of these was essentially the same as the previously described voltammetric technique with the exception that the electrode was removed from the solution after hydrogen evolution for durations of one to five minutes and reinserted into another KOH cell for the anodic sweep. This was performed in order to eliminate the contribution of adsorbed hydrogen on the nickel surface and dissolved hydrogen in the electrolyte thus strengthening the evidence that absorbed hydrogen existed. The results indicated that the anodic current was indeed due to oxidation of absorbed hydrogen. A second confirming technique involved monitoring open circuit potential decay of Pt, Pd, and Ni subsequent to hydrogen evolution in KOH. The potential is monitored vs. SCE with the use of a high impedance voltage measuring instrument. The open circuit potential response for the electrodes is shown in Figure 7.

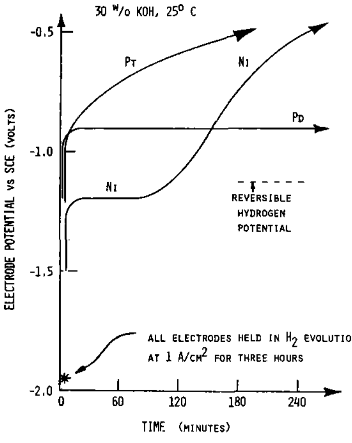

Figure 7. Open Circuit Potential Response for Pd, Pt, and Ni Following Evolution.

Note that the Pd remains at a potential of about -0.90 V vs. SCE for long times. This potential corresponds to the existence of a β hydride phase for palladium similar to that for nickel in acid, as discussed previously in this report. Additionally, palladium hydride is stable at standard conditions and this is responsible for the long time maintenance of the plateau potential. Platinum electrodes indicate little or no plateau for the same experiment, indicating little or no absorbed hydrogen. Nickel shows a definite plateau as shown in the region of 130 mV overpotential, indicative of absorbed hydrogen. The occurrence of this plateau is dependent on previous charging current density and duration. It is not maintained because the absorbed state is not stable and the hydrogen desorbs.

The previous techniques strongly suggest that hydrogen does absorb into nickel during hydrogen evolution in KOH and thereby plays an important role in time dependent voltage changes. Needless to say, further investigation of the theory is therefore warranted.

V. Electrochemical Characterization of Hydrogen Evolution on Nickel

The electrochemical parameters for the hydrogen evolution reaction on nickel were measured experimentally in 30 w/o KOH at room temperature with the following precautions:

1. The nickel electrode was inserted into the cell at -1.0 V vs. SCE with the aid of a dummy electrode to prevent hydroxide formation on the electrode as previously discussed.

2. The electrode was a nickel wire, 1.58 mm in diameter, mounted in epoxy and mechanically polished to a smooth circular cross-section. Thus the apparent surface area could be easily calculated and the true surface area of the electrode would be no more than double the apparent area. This is because the expected roughness factor of the polished electrode would not be greater than two. Therefore, the true surface area is known within a factor of two.

3. The IR correction value was achieved by a current interruption technique.

The electrode potential is initially swept from -1.0 V vs. SCE to -4.0 V vs. SCE (non-IR corrected) at 1 mV/sec. The corresponding current is recorded and the IR correction is periodically applied. The tafel slope for this initial, potential sweep rate was found to be approximately 80 mV/decade which is in reasonable agreement with the literature.[6] The i_o is found to be 3.16 x 10^{-6} A/cm^2 apparent and 1.58 x 10^{-6} A/cm^2 assuming a roughness factor of two. This result is also in good agreement with the literature.[14] At this point, the electrode was held for one hour at -4.0 V vs. SCE (non-IR corrected), which corresponded to current densities as high as 10 A/cm^2. This current density exceeds that of industrial interest, which is usually limited to a maximum of about 0.5 A/cm^2. With this procedure, the electrode will absorb appreciable hydrogen and the electrochemical parameters of the nickel - absorbed hydrogen electrode can be evaluated during a potential sweep from -4.0 to -1.0 V vs. SCE. In the lower potential region of this data the tafel slope is about 75 mV/decade while the i_o = 1.6 x 10^{-8} A/cm^2. The exchange current density (i_o) has changed appreciably while the tafel slope is nearly the same as that for pure nickel. At a potential of about -1.30 V vs. SCE the curve deviates from linearity and eventually forms another linear region with tafel slope and exchange current density nearly equal to those for the pure nickel. This deviation occurs at an overpotential of about 150 mV which corresponds to 10^6 atm of hydrogen pressure. This is nearly identical to the pressure required for the presence of β-NiH. Further, at about -1.107 V vs. SCE, reversible hydrogen potential, a distinct anodic peak is apparent. This is presumably due to the oxidation of absorbed hydrogen from the nickel.

From these experiments it has been shown that the time variations in the overpotential of nickel cathodes during hydrogen evolution involve a decrease in the exchange current density with little change in the tafel slope. This result was also found by Bockris and Potter,[6] however, it was not explained. It is suggested from the research of this thesis that the effect is due to hydrogen absorption by the nickel. In hydrogen evolution on nickel in KOH, the discharge step is believed to be the rate determining step.[6] The exchange current density can be thought of as the rate at which the discharge reaction occurs in both direction at equilibrium and at zero overpotential.

If the nickel cathode absorbs appreciable hydrogen at the surface and the valence electrons of the nickel are involved in bonding with the hydrogen, then the availability of that site for the discharge reaction would be hindered, thereby decreasing the rate of the discharge reaction and lowering the exchange current density for the reaction. This argument is suggested as a possible mechanism to explain the observed change in exchange current density.

VI. Conclusion

Previous reports[1] [4] have described a time dependent increase in the cell voltage of hydrogen producing electrolytic cells employing nickel electrodes and 30 w/o KOH electrolytes. This effect represents a continual decrease in operating efficiency and is thereby undesirable. It was demonstrated that an increase in the electrode potential of the nickel cathode, on which hydrogen evolution occurs, is a significant portion of the increase in cell voltage. This cathodic phenomenon was suggested to be related to the absorption of hydrogen by the nickel cathode. It was further evident that if the absorbed hydrogen forms a nickel hydride it does not do so to any appreciable depth beneath the surface. The theory of absorption of hydrogen by nickel was supported by comparison of the behavior of nickel to platinum and palladium via several electrochemical techniques. The kinetics of the hydrogen evolution reaction on nickel were studied. An observed change in the exchange current density, which is possibly due to absorbed hydrogen, was indicated and suggested to be a result of hindrance of the hydrogen discharge reaction,

$$H_2O + e^- \rightarrow H_{ads} + OH^-, \qquad (2)$$

due to the partial depletion of available discharge sites at the electrode surface.

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IMPROVED ALKALINE HYDROGEN/AIR FUEL CELLS FOR TRANSPORTATION APPLICATIONS*

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Abstract

Considerable progress has been made in the last few years on improvement of alkaline air electrodes for air depolarized chlor-alkali cells. Some of these electrodes from Union Carbide Corporation have been evaluated at Brookhaven National Laboratory in alkaline hydrogen/air fuel cells. In initial tests with 289 cm^2 electrodes, power densities of 100 mW/cm^2 were obtained at 0.65 V. This compares with power densities of 27 mW/cm^2 obtained by Kordesch in his vehicle fuel cell in the late sixties. Further improvements in the air electrode flow field yielded power densities of 126 mW/cm^2 at 0.65 V at an operating temperature of 70°C. At 30°C, nearly 60% of this power could be obtained at 0.65 V. The 289 cm^2 cells were units in a 16-cell 0.5 kW module. This module yielded similar power densities and its power/weight and power/volume are sufficiently attractive for it to be considered as a building block for a fuel cell power plant in a fuel cell/battery hybrid vehicle.

I. Background

It is vital that synthetic fuels from coal or renewable primary energy sources be used in an efficient and environmentally acceptable manner. The only type of chemical to mechanical energy converter in which the efficiency is not Carnot limited for transforming chemical energy to mechanical energy is the fuel cell coupled with a motor.

Fuel cell efficiency differs in two important ways from the efficiency of heat engines. Fuel cells do not exhibit the characteristic sharp decline in efficiency that occurs when the size (power) of the unit is decreased or when operation is throttled back to partial rated load. In the small power plant sizes of interest for mobile applications (10 kW to 100 kW), the fuel cell has at least twice the efficiency of an internal combustion engine and one and a half times the efficiency of a diesel engine.[1] Fuel cells have the advantage in that their efficiencies do not decrease significantly at part loads as low as 25% of rated output. This is important in applications with a variable load duty cycle, such as ground transportation.

No single factor has inhibited the development of fuel cells as much as the fact that readily available fuels such as petroleum derivatives and coal cannot be used directly in fuel cells. Much of the bulk, complexity and weight of present day fuel cells accrue from the fact that the fuels used require a high degree of processing prior to use in the fuel cell stack.[2] In mobile applications where weight and volume are a consideration, it is desirable that the fuel requires the minimum amount of preprocessing before use in a fuel cell. In the small vehicle sector of the transportation market where the energy impact is greatest, the two most attractive fuel cell options are hydrogen/air alkaline fuel cells or reformed methanol/air acid electrolyte fuel cells.[2] The respective advantages and disadvantages of the above options are outlined in Table I. The inhibiting factors for hydrogen utilization are related to distribution and storage. Advanced storage technologies such as composit tanks,[3] metal hydrides[4] and glass microspheres[5] are actively under investigation. All options show promise. With the availability of low cost hydrogen, the alkaline fuel cell is attractive in applications which require fast startup and minimum heat recovery.

Even though there is very little activity in the U.S. on alkaline fuel cells, considerable progress has been made in recent years on improvement of alkaline electrodes for air depolarized chlor-alkali cells and metal-air batteries.[6] In this study some of these electrodes from Union Carbide Corporation were evaluated in alkaline hydrogen/air fuel cells. The studies included design, fabrication and testing of single cells, multicell units and a 16-cell 0.5 kW module.

II. Cell and Module Construction

All cells and modules were built with electrodes that were obtained from Union Carbide Corporation. The overall electrode area was 361 cm^2 (19.5 cm x 18.5 cm), and the active area exposed to the electrolyte was 289 cm^2 (17.5 cm x 16.5 cm).

Anodes

The hydrogen electrodes had the Union Carbide T-2 construction. The electrodes consisted of a dual porosity nickel layer adjacent to the hydrogen plenum. The nickel layer was treated with PTFE. The catalyst layer was adjacent to the electrolyte. The overall electrode thickness was 0.040 cm.

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Table I

Advantages and Disadvantages of Fuel/Fuel Cell Option

Reformed Methanol/Phosphoric Acid

Methanol

- Advantages
  - o Storage and distribution similar to gasoline
- Disadvantages
  - o CO_2 emissions
  - o Economics uncertain

Phosphoric Acid Fuel Cell

- Advantages
  - o Not affected by CO_2 ingress
  - o Long life has been demonstrated
  - o Technically most advanced
  - o Engineering aspects such as water management are simple
- Disadvantages
  - o Requires Pt electrocatalysts
  - o Operates at ∿200°C, i.e., slow startup (∿15 min)
  - o Design of shock and vibration resistant structures is difficult

Hydrogen/Alkaline

Hydrogen

- Advantages
  - o High energy content
  - o No CO_2 emissions at end-use site
- Disadvantages
  - o Distribution and storage very different from present infrastructure
  - o Economics uncertain

Alkaline Fuel Cell

- Advantages
  - o Does not require Pt electrocatalysts
  - o Yields up to 50% of rated power ambient temperature, i.e., fast startup (∿5 min)
  - o Rugged metallic structures can be built
  - o High efficiency
- Disadvantages
  - o Not tolerant to CO_2 ingress
  - o Engineering aspects such as water management more difficult
  - o Lifetime still uncertain

Cathodes

The air electrodes had the newer Union Carbide T-3 construction which is a reverse of the T-2 construction. The dual porosity nickel layer is adjacent to the electrolyte and is not PTFE treated. The catalyst layer consists of a platinized carbon layer (0.2 mg Pt/cm^2) adjacent to the air plenum and was PTFE treated on the outer surface. The overall electrode thickness was 0.056 cm. The T-3 structure enhances back diffusion of nitrogen and improves performance.

Bicells

Figure 1 depicts a bicell which consists of two cells connected in parallel. The cells are reversed so that two anodes face one another to form a fuel plenum. The exterior surfaces of the bicells are the cathodes. Spacing was maintained in a similar fashion to that used in the single cell tests. Gases enter from the top and exit from the bottom. The electrolyte (50% KOH) enters from the bottom and exits from the top.

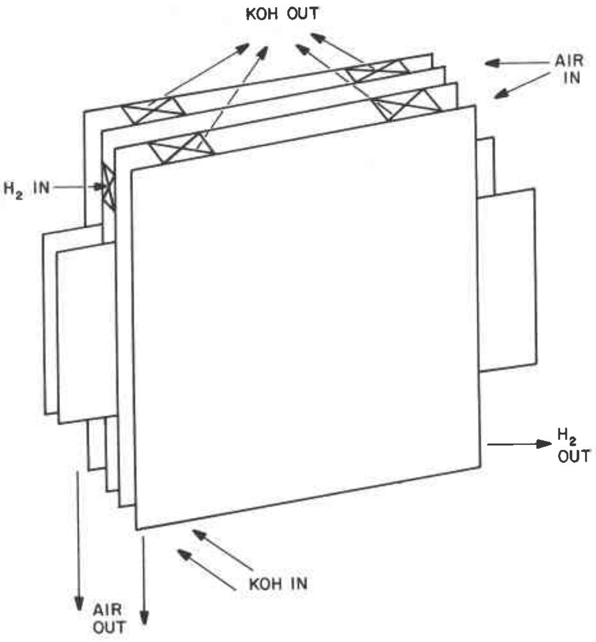

Figure 1. Alkaline hydrogen/air bicell construction showing fluid flows.

Modules

Half kilowatt module assembly was achieved by stacking eight bicells in series. Gas and electrolyte ports were introduced by inserting removable PTFE plugs prior to potting. Intercell parasitic current losses were minimized by use of tubular manifolds for the electrolyte inlet and a tubular overflow system for the electrolyte exits. The eight bicells were connected in series by welding the nickel current collectors. The completed model is shown in Figure 2.

III. Test Procedures

In all the tests reported here, the working regime for the cells and modules was as follows. During working hours (40 h/week),

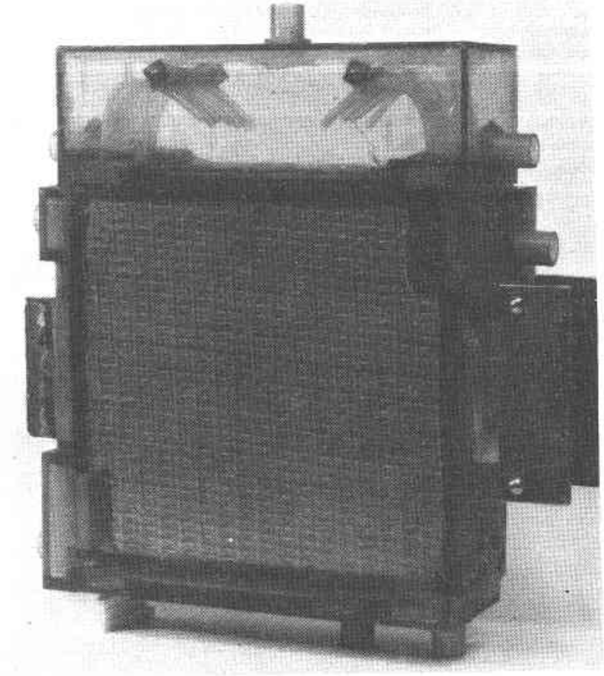

Figure 2. Alkaline hydrogen/air fuel cell module dimensions excluding terminals 26.5 cm x 21.5 cm x 7.5 cm. Dry weight 3.64 kg.

the cells were maintained at a temperature of 65°C and discharged at a current density of 100 mA/cm^2. At night and on weekends, there was no electrolyte in the cell and the cell was allowed to return to ambient temperature. Polarization curves were taken periodically.

IV. Results and Discussion

Single Cells

Figure 3 shows a set of performance curves that were obtained over a seven-week period at weekly intervals. There was some random scatter in the results at higher currents. Performance data for Union Carbide alkaline cells from the late sixties[7] are shown for comparison. The T-3 air electrodes resulted in a significant increase in performance.

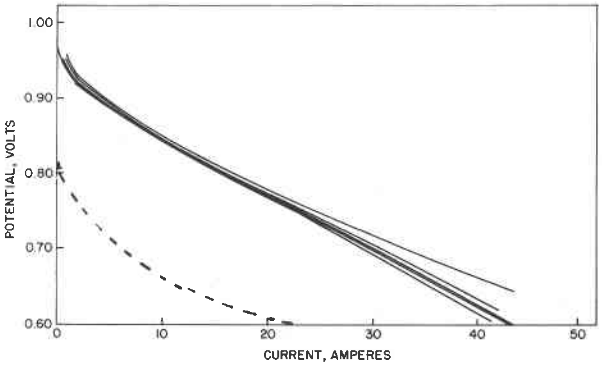

Figure 3. Performance data for a single cell over a seven-week period. Data of Kordesch[7] (broken line) is shown for comparison. Electrode area for both cells is 289 cm^2, temperature 55°C.

Improved Air Flow Field

Figure 4 shows performance data for two cells in series with improved air electrode flow fields. The further improvement of performance is evident. The performance on pure oxygen is shown for comparison.

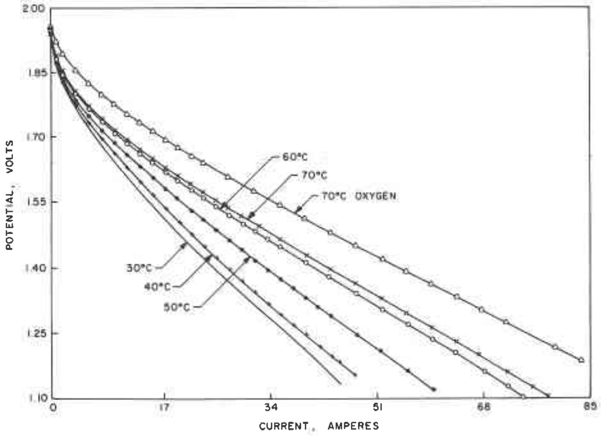

Figure 4. Performance data for two cells in series with improved air flow field. Electrode area 289 cm^2.

0.5 kW Module

The performance of the 16-cell 0.5 kW module on air and oxygen is shown in Figure 5. The results are very similar to those found in single cell tests.

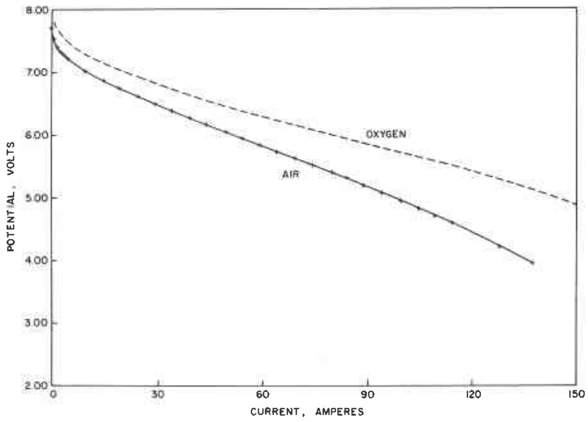

Figure 5. Comparison of 0.5 kW module performance with air and oxygen. Module had eight bicells in series. Single cell electrode area 289 cm^2.

Figure 6 shows the performance variations of the 0.5 kW module over an 11-week period. After about eight weeks there was sloughing of the carbon layer on the hydrogen electrodes which yielded a dark color in the electrolyte. No degradation of the air electrodes was observed. The Union Carbide T-2 hydrogen electrodes have a design point of 50 mA/cm^2. Operation at higher current densities 100 to 250 mA/cm^2 degrades the structure. This may be due to dilution of KOH in the electrolyte pores at high current densities. The prospects of making improvements in hydrogen electrodes, similar to those made in air cathodes are extremely good. The T-2 electrodes are palladium catalyzed. Plans are underway to develop improved hydrogen electrodes with a low Pt loading, as well as with no noble metal loading.

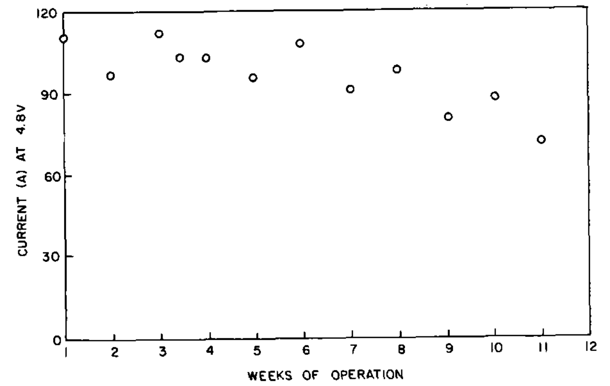

Figure 6. Performance variation of 0.5 kW module with time.

V. Implications for Vehicular Application

In the past, the fuel cell has been discounted for vehicular applications because of its weight, bulk, cost and the unlikely prospect of the availability of a suitable fuel. The major contributors to weight and bulk are low operating power densities and chemical complexity of the fuel. For instance, the GM Electrovan was 100% overweight (3227 kg).[8] Kordesch was able to reduce the overall power plant weight by the simple expedient of a fuel cell/battery hybrid power plant.[7] Any increase in fuel cell power density will yield even a lighter power plant. Figure 7 is a Ragone plot for various batteries and fuel cells. In the case of alkaline fuel cells, the 1969 data are based on the results of Kordesch.[7] The 1978 data are based on the results of the present work, and the 1985 data are based on a projected power density of 180 mW/cm^2. Allowances have been made for increased weight of heat exchangers, pumps, etc. Projected phosphoric acid fuel cell data are for a reformed methanol/air power plant and are based on data from Energy Research Corporation.[9] The present prospects for the wide availability of suitable fuels from coal and renewable sources, and the demonstrated improvements in fuel cell performance make the fuel cell/battery hybrid a strong contender for vehicular applications.

Fuel cells with a specific power of 50 to 60 W/kg are well within the range of near-term technology. While this power level is more than adequate for cruising, an auxiliary power source such as a battery will be needed for acceleration. Several benefits accrue from such a hybrid power plant. An electric/electric hybrid is inherently much simpler than a mechanical/electric hybrid. The battery accelerates startup and simultaneously prevents cell reversal in the stack. Batteries have much longer life in the shallow cycling regimes in hybrid cycling. A fuel cell/battery hybrid power plant offers good performance, long range and fast refueling. No breakthrough in battery development is needed. Presently available lead-acid or nickel-zinc batteries will suffice. Materials problems in fuel cells are more tractable than in batteries because of the absence of a charge cycle, and as a result, considerable progress has been made in operating life over the past decade.

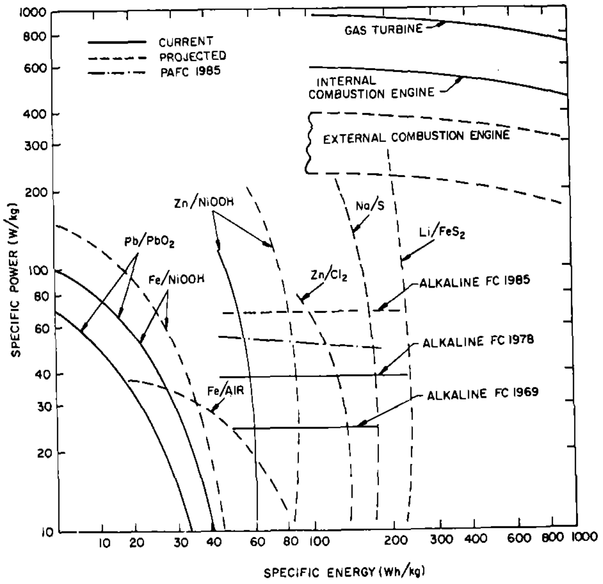

Figure 7. Ragone plots for batteries, fuel cells and various heat engines.

Even though many of the technical obstacles to fuel cells have been overcome, economic viability is still uncertain. Resolution of this question will require further work on assessing initial costs, fuel costs and maintenance costs. The latter would require experience with fuel cells in vehicular environments.

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OPTICAL CONSTANTS OF SINGLE CRYSTALS IrO_2 AND RuO_2 AND THEIR RELATION TO ELECTRONIC STRUCTURE

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Abstract

A novel design for water electrolysis using a solid polymer electrolyte is being developed by General Electric. Ruthenium is one of the best electrocatalysts for the oxygen evolution reaction. There are problems connected with the significant loss in electrocatalytic activity with time. This performance degradation is presumably due to the gradual formation of an RuO_2 film.

In addition to investigation of variations of catalytic activity, the intrinsic reflectivity of RuO_2 and IrO_2 is of considerable interest. Measurements of the spectral dependence are extremely valuable in elucidating the electronic properties. Results of reflectivity measurements of single crystals are compared with the band structure calculations of Mattheiss and thus give valuable information concerning the nature of the d-electrons in these materials.

I. Introduction

At the present time there is considerable interest in developing high efficiency and low cost water electrolyzers to meet the demands of hydrogen required by the chemical industry and as a fuel in fuel cells and gas turbines. The development of advanced technology for water electrolysis is essential to minimize the cost of hydrogen. The efficiency of water electrolysis systems depends critically on the behavior of the oxygen electrode. For oxygen evolution reaction (OER) on metals or alloys at constant potentials, the continuous decrease of current densities with time is one of the more difficult problems in water electrolysis. The time variation of current density has been pointed out by Schultze[1] in the anodic evolution of oxygen on platinum. More recently, similar behavior has been observed on iridium[2] and on nickel[3] anodes. It has been suggested that the current decay with time is connected with the continuous growth of a poorly conducting oxide film, which retards the electron transfer or inhibits the radical on the film surfaces[2,3,4]. Based on electrochemical and ellipsometric methods Srinivasan et al have concluded that the performance degradation for oxygen evolution on RuO_x catalyst is presumably due to the gradual accumulation of a RuO_2 film on the surface of the RuO_x particles by a dissolution/precipitation process.[4]

The OER always takes place on electrodes which are covered with an oxide layer. Little is understood about the properties of the oxide phase and, especially, about the properties of the oxide-electrolyte interface which are required to achieve improved performance on the OER. Evaluation of a number of metals and alloys as electrocatalysts for the oxygen evolution reaction, leads to nickel as a preferred anode material for the OER in alkaline solutions and to noble metals and their alloys as electrocatalysts for the OER in acid solutions. Among the nobel metals, the performance of Ru, Ir and their alloys was found to be much superior to that of a pure Pt anode. Thus, the potential at which a steady state oxygen evolution current density of 1 mA cm^{-2} (real) is obtained on Pt at room temperature is about 1.8 vs. RHE, while at a Ru or an Ir anode this potential is only about 1.4V (Ru) or 1.5V (Ir).[5,6] It is obvious, therefore, that analysis of the surface layer formed on Ru or Ir prior and during the evolution of oxygen, revealing the relationship between properties of this layer and the performance of the Ru (Ir)/aqueous solution interface in the OER, may be an important key to the role of oxide layers in electrocatalysis. In addition the work of Srinivasan et al[4] has shown the significance of our understanding the properties of RuO_2 and IrO_2.

A novel design for water electrolysis is being developed by the General Electric Company using solid polymer electrolytes.[7] In this type of water electrolysis cell a solid sheet of perfluorinated polymer (Nafion) serves as the electrolyte. The electrocatalysts are platinum on the cathode side and iridium, ruthenium or binary and ternary alloys of these metals with transition metals on the anode side. Hence there is considerable interest from a practical point of view in gaining a better understanding of nature of electrocatalyst/electrolyte interface for these particular materials.

II. Experimental Details

We have measured the near-normal incidence intrinsic reflectivity of single crystal IrO_2 and RuO_2 for light polarized $\perp$ and $\parallel$ to the c-axis in the range 0.5 - 9 eV. Measurements were made using the rotating light pipe reflectometer (RLPR) method which has been described in detail elsewhere.[8] The single crystals were grown by the chemical vapor transport method.[9,10,11] The IrO_2 material was kindly supplied by F. M. Reames while the RuO_2 was prepared by L. I. Berger.

Work supported by Brookhaven National Laboratory Contract EC77-S-02-4590 & by NATO

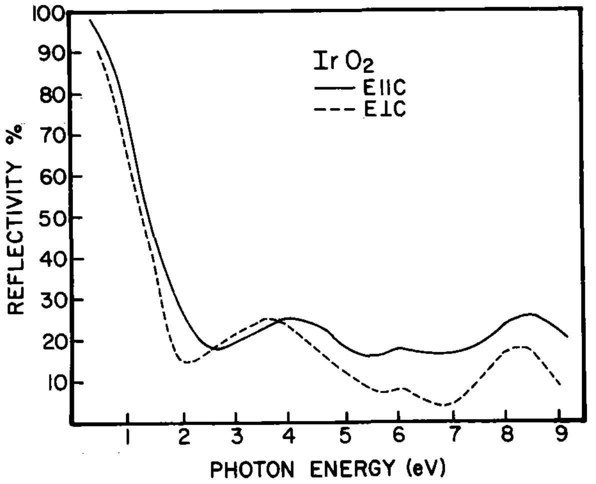

Figure 1. Spectral dependence of the reflectivity, R, of IrO_2 for light polarized ⊥ and ∥ to the c-axis.

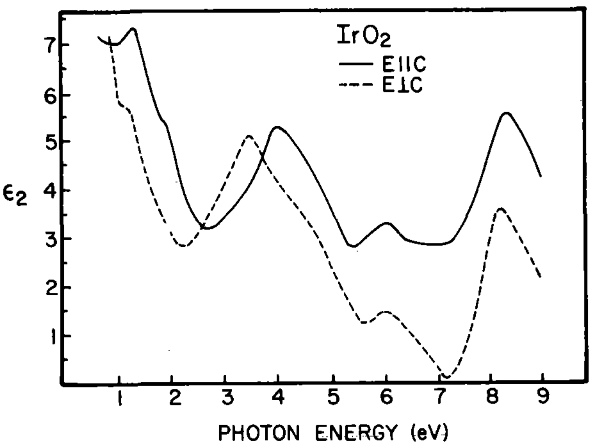

Figure 2. Spectral dependence of the imaginary part of the complex dielectric constant, ϵ_2 , for IrO_2 for light polarized ⊥ and ∥ to the c-axis.

III. Experimental Results

Shown in Fig. 1 is the near-normal incidence reflectivity, R, for single crystal IrO_2 for light polarized ⊥ and ∥ to the c-axis in the range 0.5 - 9 eV. By a Kramers-Kronig analysis[12] of the reflectivity in this range we have obtained the spectral dependence of the real (ϵ_1) and imaginary (ϵ_2) parts of the complex dielectric constant.

In addition angular dependent reflectance at He-Ne and Argon ion laser lines was measured. The values of ϵ_2 obtained from the solution of the Fresnel equations using this data then determine the choice of parameter used to extrapolate the reflectivity data beyond 9 e.v.[13] The quantity ϵ_2 is of particular interest since it is related to optical transitions between various electronic states of the material.

In Fig. 2 we have plotted ϵ_2 for IrO_2 as a function of photon energy for light polarized ⊥ and ∥ to the c-axis. The imaginary part of the dielectric constant is given by

$$\epsilon_2(E) \propto \frac{1}{E^2} \sum_{m,n} \int |M_{mn}|^2 \, \delta(E_n - E_m - E) \, d\vec{k}$$

where E is the energy and m and n label the occupied and unoccupied states respectively; the interband oscillator strength

$$M_{mn}(\vec{k}) = -i \int \psi^*_{\vec{k}m} \nabla \psi_{\vec{k}n} \, d\Omega .$$

Since the joint density of states

$$J(E) \propto \sum_{m,m} \int \delta(E_m - E_m - E) \, d\vec{k}$$

we expect agreement in peak positions of $\epsilon_2(E)$ and $J(E)$ as long as the matrix elements remain constant. The polarization dependence of ϵ_2 results from differing matrix elements.

The results for IrO_2 compare well to the band structure and density of states calculation of Mattheiss.[14] In Fig. 3 is shown the density of states of IrO_2 for both the oxygen p- and Ir d-electronic states. The oxygen p- states are completely occupied and the Fermi level lies in the t_{2g} d-electron states. The octahedral component of the ligand fields splits the five-fold-degenerate d- level into e_g and t_{2g} sublevels. The orthorhombic component of the ligand field causes further splitting of the e_g and t_{2g} subbands. There exists relatively little hybridization between the e_g and t_{2g} subbands.

In general, the metallic conductivity of IrO_2 (d^5) appears to be accounted for by the Goodenough model[15] in which the t_{2g} orbital is assumed to be filled with a consequent lack of bonding. The metallic conductivities of IrO_2 are consistent with the partially filled metal(m) - Oxygen (O) bond. Mattheiss has achieved a more detailed identification of the various subbands in terms of these combinations. For example, the (t_{2g}) subband is below the Fermi energy, E_F, and almost completely occupied in IrO_2. The $(t_{2g})_2$ state involves a covalent mixture of M-atom t_{2g} and O-atom (x,y) orbitals while $(t_{2g})_3$ subband involves M-atom t_{2g} and O-atom z orbitals. Therefore, in the case of IrO_2, the Fermi surface is determined by the partially filled $(t_{2g})_2$ subbands in the

$$\Gamma M X (k_z = 0) \text{ and } Z A R (k_x = \tfrac{\pi}{c})$$

planes in Brillouin zone. The presence of three independent t_{2g} subbands in the rutile structure suggests that the Fermi surface topology will depend on the relative position of each subband relative to E_F. As a result, we can anticipate the crystallographic dependence in the catalytic activity of IrO_2 crystal. In particular, these results in the conduction band density of states are due primarily to the (t_{2g}) subbands.

The spectral dependence of ϵ_2 for IrO_2 (see Fig. 2) shows several interesting features. The structure for both polarizations is fairly similar, the perpendicular peaks occurring at somewhat lower energies below about 5 eV. Below about 2.5 eV both polarizations show a large peak. There are also large structures at about 3.5 eV and 8 eV, a smaller feature at about 6 eV and a shoulder on the low energy side of the 3.5 eV peak.

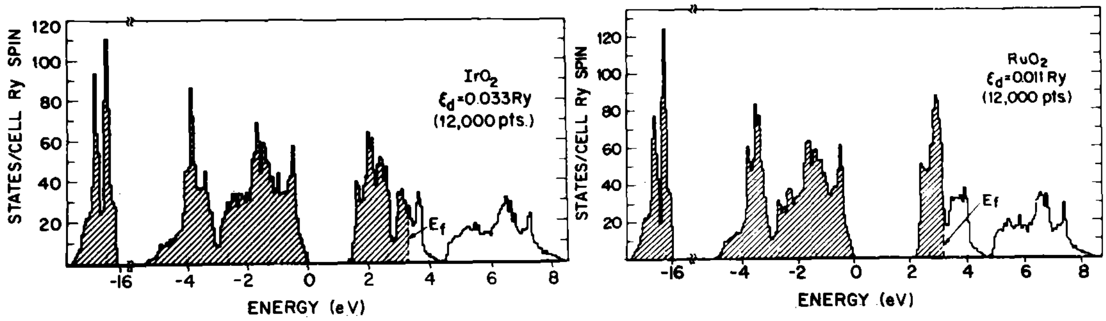

Figure 3. Valence and conduction band density of states for a) IrO_2 and b) RuO_2 (Ref. 14).

The peaks in ϵ_2 below 3.0 eV can be identified with conduction band excitations, i.e., $(t_{2g})_1 \rightarrow (t_{2g})_{23}$. The shoulder at about 3.4 eV can be identified with $t_{2g} \rightarrow e_g$ transitions. The onset of valence to conduction band transitions occurs at about 3.5 eV. The higher energy peaks, i.e., 6 and 8 eV, are identified with p- to d- electronic transitions.

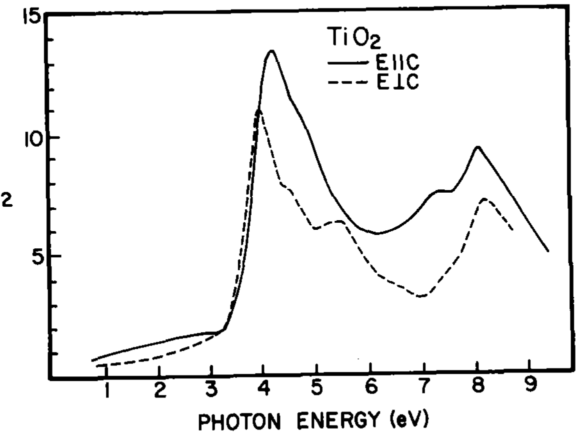

Figure 4. Spectral dependence of the imaginary part of the complex dielectric constant, ϵ_2, for TiO_2 for light polarized ⊥ and ∥ to the c-axis. (Ref. 16,17).

Further conformation of this interpretation can be obtained by a comparision of the spectral dependence of TiO_2[16,17] (see Fig. 4) and rutile phase NbO_2[18]. Since TiO_2 is a semiconductor the complete spectrum arises from oxygen p- to metal d electronic transitions. The overall shape of the single density of states for all three materials is quite similar. Differences in the spectra can be expected because of differing p - d band gaps, band widths and the position of the Fermi level.

All structure below 3 eV corresponds to d-d transitions. In particular the height of the low energy peak corresponds to the number of d- electrons i.e. TiO_2 with no d electrons has nothing, NbO_2 with 1 d electron has a small peak and IrO_2 with 5 - d electrons has a very large peak. The joint density of states calculation of Posternak[18] indicate that the higher energy peaks represent p - d transitions. The intermediate energy peak at about 3.4 volts is the result of p - d and d - d transitions, consequently its exact shape and position is material dependent.

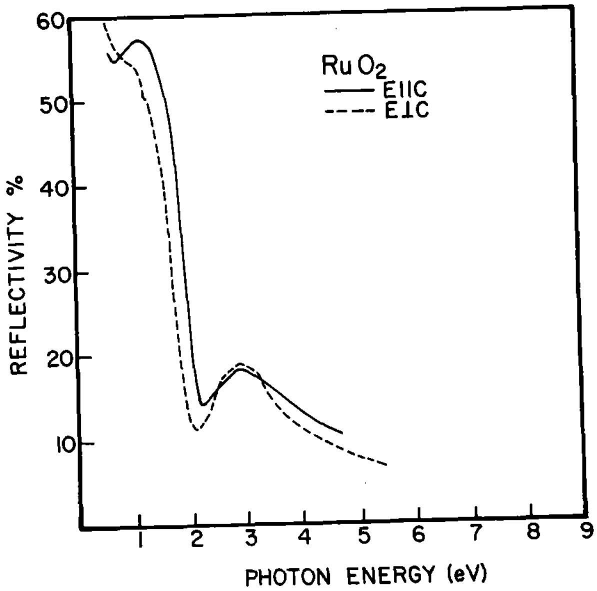

Figure 5. Spectral dependence of the reflectivity of RuO_2 for light polarized ⊥ and ∥ to the c-axis.

Measurements of the reflectivity of RuO_2 have been made. Preliminary results are shown in Fig. 5. The reflectivity at 2 eV is less than that of IrO_2, consistent with the number of metal d- electrons. Preliminary work indicates that the higher energy spectrum due to p to d transitions is similar to that of IrO_2 and TiO_2, consistent with the theoretical calculations of the density of states (see Fig. 3a).

IV. Summary of Results

We have measured the near-normal incidence reflectivity of IrO_2 and RuO_2 in the range 0.5 - 9 eV. From this data we have obtained the spectral dependence of the real and imaginary parts of the dielectric constant. Thus, we have been able to make a detailed comparison to a theoretical calculation of the band structure and density of states of the oxygen p and the metal d- electronics states. The agreement of theoretical and experimental determinations of the nature of electronic states (and hence orbitals) provides important information toward the understanding of electrochemical behavior of these materials.

V. Future Work

We plan to grow larger single crystals of IrO_2 and RuO_2 in order to develop further the electrochemical and optical work.

Additional electrochemical studies will be performed on oriented single crystals of IrO_2 and RuO_2. This includes measurements using the rotating disc electrode method to be done in collaboration with Brookhaven National Laboratory.

Optical investigations have been performed on single crystal IrO_2 and preliminary work has been done on RuO_2. We propose to continue the detailed study of this area in order to gain information concerning their detailed electronic structure.

Our ultimate goal is to relate the observed electrochemical behavior of single crystal IrO_2 and RuO_2 with the fundamental electronic structure.

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MICROCAVITY STORAGE UPDATE - 1980

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Abstract

Last year, two microsphere grades were evaluated for hydrogen storage in automotive applications (3M-D32/4500 and Fillite 200/.7). The 3M grade came the closest to meeting the automotive requirements. The hydrogen weight density attained was 0.053. This year, test procedures were standardized and eight grades were evaluated. Two new grades (Emerson & Cuming HAS and HASY) appear to be superior in strength to the 3M grade studied last year. Both grades were subjected to 5500 psig nitrogen pressure. The Emerson-Cuming Grade HAS had 80 wt. percent survivors and Grade HASY had 92 percent survivors. Tests on the 3M-D-32/4500 grade indicated 56 percent survivors. Crush tests were performed in hydrogen, nitrogen and helium atmospheres. Some grades appeared to be more resistant to crushing in hydrogen and helium than in nitrogen. Judging from the glass composition, the two Emerson Cuming grades may have difficulty in retaining hydrogen at ambient temperatures. The aspect ratio (diameter to wall thickness) of the eight grades of microsphere beds were measured and correlated to the crush test survivor results. These studies indicated that an average microsphere aspect ratio of about 30 is needed to survive a 6000 psi crush. Measured average aspect ratios on survivors of 6000 psig crush were between 31 and 39. A two cu. ft. bed of a new lot of 3M-D32/4500 was prepared. The new lot of microspheres did not have the same properties as the original lot used in tests last year. The hydrogen storage density attained was .042. The results of fill-dispense tests and the selection of two grades for further study will be available by the end of the fiscal year. Engineering estimations of hydrogen storage costs will also be available.

Introduction

The use of micron size, hollow, glass spheres (microspheres) as a container for high pressure hydrogen (microcavity hydrogen storage) was proposed by Robert J. Teitel Associates in 1978. Hydrogen is admitted and dispensed from the spheres by permeation through its glass walls. The rate of hydrogen transfer depends upon the glass composition and microsphere dimensions. The strength of the glass and microsphere dimensions limit the maximum storage pressure. The first DOE sponsored study (1978) established that the concept, when designed for automotive hydrogen storage, had economic and weight advantages over an advanced metal hydride storage system.[1] On the other hand, the microcavity system would require a greater volume. An engineering study of the automotive hydrogen storage system and the associated microsphere filling plant was performed. In 1979, two commercial grades of microspheres were selected and evaluated experimentally (3M-D32/4500 and Fillite 200/.7). Heat treated 3M D32/4500) came close to meeting the requirements for automotive applications.[2,3] Additional fill plant economic studies were performed. They indicated that filling costs could be halved.

This year, the experimental investigation has been extended to eight commercial grades. Standard characterization tests are being developed and applied. Two of the most promising grades will be selected for optimization studies and cyclic attrition tests. Economic studies will be updated by performing an engineering plant study to determine projected cost of microspheres. RJTA was asked to fill a 2 cu. ft. bed of microspheres. These beds have been prepared and sent to BNL. The large beds are to be used in safety tests and engineering dispension tests by Brookhaven National Laboratory.

Experimental Results

Microsphere Selection

Eight grades listed in Table 1 were selected for screening tests. The selection was based on the results of prior studies and new vendor information.

Microsphere Crush Strength

Microspheres received from the vendor were submitted to a sink-float test to ascertain the quantity of whole spheres prior to crush tests. Beds of microspheres were exposed to gases (nitrogen, hydrogen, and helium) at pressures up to 6000 psig. After the crush treatment, the fraction of spheres surviving were determined by a iso-propanol sink-float test.

Table 1 gives some of the results of the crush test studies. The tests were duplicated on the same sample (up to 3 cycles) and in duplicate samples. The agreement between tests on the same grade and crush pressure were within a few percent. The variations in crush pressure, as indicated in the table, did not affect the results appreciably as deduced from other unreported tests. Aside from the variation in crush strength from grade to grade, the gas composition also contributed significant changes. The difference between hydrogen and nitrogen were striking and unexpected (Table 1). An explanation of this phenomenon is not available without more study. Crush strengths of two lots of 3M D32/4500 and their heat treated samples are included in Table 1. The onset of sintering prevented the treatment of Lot 1516-6 at 580°C. Consequently, the improvement brought about by heat treatment on this grade was limited. As noted in the table, the bracketed results are corrected for debri in the "as received" microspheres. These crush test results will be discussed further along with other screening test results.

Chemical Analyses

Chemical analyses of the eight microsphere grades employed atomic absorption analytical techniques. The results are summarized in Table 2. All results were averages of duplicate samples and duplicate tests on each sample. They were adjusted for oxygen assuming the oxide formulas given in the table and normalized.

The 3M grades appear to be made of lime-soda-boro-silicate glasses compositions. Emerson and Cuming grades consisted of sodium-boro-silicate compositions. Fillite 'fly-ash' grades were made of an alumino-silicate glass. The iron oxide in the later grade was present predominately as a separate phase inclusion. From these results, the mole percent non-network formers for each grade were obtained for comparison. The glass composition implied other well established glass properties: softening point, anneal temperature, general strength and hygroscopic behavior. Mole percent non-network formers results derived from the chemical analysis are included in the screening test results (Table 3).

Particle Size

Prior to the particle physical measurements, the whole microspheres of each grade were separated and washed in an iso-propyl alcohol sink-float operation. Surface weighted diameters and glass wall thicknesses were calculated from measured bed properties: average particle density, average glass wall density and particle area. The average particle sizes were calculated using the following equations (symbols designated in Table 3).

$$d = \frac{6}{\rho_p S}, \qquad w = \frac{1}{\rho_g S}, \qquad A = \frac{6\rho_g}{\rho_p}$$

The measured values were substantiated in duplicate and triplicate analyses on the same samples or on separate samples. Consequently, the variations are considered substantiated. Samples of each grade were crushed in high pressure gas to obtain a sample for chemical analyses and glass densities. Area analyses were performed on the samples used in particle density analyses. In order to avoid uncertainties of duplicate samples, where possible, the same sample was used to make several measurements. Microscopic analyses were used to measure the extent of the particle size distribution and particle shape deviations.

Fill-Dispense Tests

To complete the screening test program, the eight candidate microsphere grades will be subjected to a standard fill-dispense cycle to determine the bed storage capacity, breakage of microspheres, and hydrogen availability at 200, 250, and 300°C. These results are not complete at this writing, but will be completed by the end of this fiscal year.

Screening Test Results

Screening test results are summarized in Table 3 including the mole percent of non-network formers derived from the chemical analyses (Table 2) and the crush strengths (Table 1). Fill-dispense test results will be available by the end of the fiscal year to complete the survey. The wide variations in particle dimensions, chemical compositions and strengths available from commercial grades of microspheres are apparent.

Specimens from each of the eight grades were crushed in a 5500 psig nitrogen atmosphere and the survivor microspheres analyzed for particle dimensions. In all cases, the crush survivors had a lower aspect ratio (diameter to wall thickness) than the 'as received' microspheres. This would be expected since the lower aspect ratio microspheres should be stronger. At the same time, the average diameter increased in some grades and diminished in others. The average aspect ratio for the crush survivors ranged from 30-40 in all grades except the Fillite 200/7 and EC-HASY. The latter grades had lower values in the 'As received' condition. The Fillite grade is basically strong. Microscopic studies last year indicated that failure in this grade was not caused by glass strength limitations but by the presence of FeO inclusions or chemical non-uniformity in the microsphere walls. The EC HASY grade was very strong (92% survivors in a 5500 psig nitrogen crush). Its average aspect ratio was already lower than the crush survivors of other grades. A plot of the aspect ratio of all the 'as received' microspheres vs % survivors after a 5500 psig crush test was made excluding the two very strong microsphere grades (Fillite 200/7 and EC HASY). An extrapolation, using the best straight line through the data points, indicated a target for improved microsphere development might be an aspect ratio between 25 and 30.

On the basis of microsphere strength either Fillite 200/.7 or EC-HASY may be capable of containing high pressure hydrogen. However, this is not the sole consideration. The fill-dispense test results are equally important. Fillite 200/.7, as established last year, will require higher temperatures for hydrogen permeation. EC-HASY grade is on the other side of the spectrum. Judging from the low non-network composition of this grade, the hydrogen permeability will be high and there may be difficulties with ambient temperature storage life.

Large Bed Filling Operations

RJTA has assembled a 0.25 cu. ft. high pressure vessel to fill microspheres. The vessel consists of seven 316 stainless steel, heavy wall tubes measuring 2.5 in. OD by 1.25 in. ID. Plugs in the ends provide connections to a gas manifold. A stainless steel frit was press fitted into the plug at each end to confine the microspheres. Temperature control was provided by thermocouples attached to the fill vessel wall. The basic procedure was to evacuate the vessel, heat the tubes using external heaters to 350°C, and increase the hydrogen pressure to 3000, 6000 and then to 8000 psig. using a gas compressor. The pressure was maintained at the 3000 and 6000 psig level for one hour each and three hours at the 8000 psig level. Under these conditions, the microsphere walls were not subjected to crush pressures greater than 3000 psig.

Lot 1516-6 of 3M D32/4500 microspheres were used in the preparation of large beds. This lot was weaker than the earlier lot. The crush strength of the two lots are compared in Table 1. The lower strength of the new lot of microspheres was very likely due to the lower anneal temperature, which was limited by the onset of sintering and to the lower particle density (0.287 gm/cc). The annealing treatment also had an effect on the permeation properties reported last year.[2] As a result, the maximum hydrogen storage density was 0.042. Breakage during the fill and dispense cycle was $\sim$15%.

Microsphere Optimization Studies

Two most promising microsphere grades will be

TABLE 1 - MICROSPHERE CRUSH TEST RESULTS

Grade	Medium	Pressure	Wt% Sur.*
3M-D32/4500			
(P5427-1)	N_2	6000	54 (56)
	H_2	5500	88 (93)
	He	6000	75 (77)
Treat.**	N_2	5900	77 (79)
(1516-6)	N_2	5500	57 (59)
Treat.***	N_2	5500	69 (71)
3M-B38/4000	N_2	6000	37 (44)
	H_2	5500	85 (86)
3M-A38/4000	N_2	6000	76 (77)
	H_2	5500	85 (86)

Grade	Medium	Pressure	Wt% Sur.*
Fil.-200/.7	N_2	6000	46 (66)
E&C-SI	N_2	6000	17 (17)
	H_2	5500	30 (30)
E&C-202	N_2	6000	30 (30)
	H_2	5500	37 (37)
E&C-HAS	N_2	5600	75 (77)
	H_2	5500	90 (93)
E&C-HASY	N_2	5500	89 (92)

* Weight % survivors corr. for debri in brackets

** 580°C anneal. *** 500°C anneal.

3M-3M Corporation, Fil.-Fillite Corporation, E&C-Emerson & Cuming Company

TABLE 2 - CHEMICAL ANALYSES RESULTS

Grade	Metal (Wt%)						Oxide (mole% normalized)					
	Al	Fe	SI	Na	B	Ca	Al_2O_3	FeO	SiO_2	Na_2O	B_2O_3	CaO
3M-D32/4500			43.56	4.54	0.83	5.73			84.7	5.4	2.1	7.8
3M-B38/4000			41.60	6.22	0.30	5.20			84.3	7.6	0.7	7.4
3M-A38/4000			43.19	6.05	0.40	5.35			84.4	7.3	1.0	7.3
EC-202			47.59	3.04		0.72			94.5	3.7	1.8	
EC-SI			46.37	4.10		0.62			93.3	5.1	1.6	
EC-HAS			45.38	4.37		0.62			92.9	5.5	1.6	
EC-HASY			40.07	3.29		0.57			93.6	4.7	1.7	
						K						K_2O
Fillite 200/.7	15.48	2.55	30.46	0.36	~.3	~.8	19.7	3.2	74.5	0.6	1.0	1.0

TABLE 3 - SCREENING TESTS RESULTS

Grade	S (m^2/g)*	ρ_p(g/cc)*	ρ_g(g/cc)*	A*	d*(μm)	w*(μm)	M*(%)	%Surv.*
D32/4500								
AR (clean)	.670	.302	2.11	42.1	29.7	0.707	13	
C-5500 (N_2)	.740	.336	2.11	37.7	24.1	0.641	13	56
A38/4000								
AR (clean)	.390	.353	2.09	35.5	43.6	1.230	15	
C-5500 (N_2)	.276	.400	2.09	31.3	54.4	1.737	15	77
B38/4000								
AR (clean)	1.055	.292	2.16	44.4	19.5	0.439	15	
C-5500 (N_2)	.603	.338	2.16	38.3	29.4	0.768	15	44
Fillite 200/.7								
AR (clean)	.198	.562	2.27	24.3	54.1	2.229	25	
C-5500 (N_2)	.216	.547	2.27	24.9	50.7	2.038	25	66
EC-202								
AR (clean)	.933	.224	2.05	54.9	28.7	0.523	4	
C-5500 (N_2)	.619	.313	2.05	39.3	31.0	0.789	4	30
EC-SI								
AR (clean)	.538	.232	2.11	54.6	48.1	0.881	5	
A-5500 (N_2)	.372	.334	2.11	37.9	48.2	1.272	5	17
EC-HAS								
AR (clean)	1.129	.374	2.17	34.7	14.2	0.409	5.5	
C-5500 (N_2)	.930	.395	2.17	32.9	16.3	0.496	5.5	77
EC-HASY								
AR (clean)	.723	.467	2.06	26.5	17.7	0.670	5	
C-5500 (N_2)	.839	.511	2.06	24.2	14.0	0.578	5	92

* S-particle area, ρ_p-particle density, ρ_g-glass density, A-aspect ratio d-ave. diameter, w-ave. wall thickness, M-mole % of non-network formers, % Surv.-5500-6000 psig N_2 crush survivor wt. % of cleaned whole microspheres.

selected upon completion of the screening tests for optimization studies. Sizing separations, surface treatments, heat treatments and over pressurization treatments will be applied to improve the 'as received' microspheres. The improvement will be evaluated and the impact of the operation costs on microsphere costs estimated.

Storage Cost Estimates

An engineering plant study will be performed on a microsphere production plant to estimate the results of a projected cost for microspheres. All of the above information, and additional information obtained from vendors will be incorporated in previous studies to re-estimate the cost of hydrogen storage. These results are not available at this writing. They will be completed by the end of the fiscal year.

Cyclic Tests

Cyclic testing on the two improved, most promising microsphere grades are planned for Fiscal 81 to assess breakage under repeated fill-dispense cycles. Cost impact of any losses will be assessed and incorporated into estimations on hydrogen storage costs.

CONCLUSIONS

The principal accomplishments of the program anticipated at the end of this year are:

(1) A two cu. ft. bed of filled microspheres has been supplied to BNL for engineering large scale studies.

(2) Screening tests on eight candidate microsphere grades will be complete.

(3) The results of crush tests on lime-soda-boro-silicate glass microspheres and sodium-boro-silicate glasses indicate that the microsphere particle densities of strong microspheres should have an aspect ratio (diameter to wall thickness) between 25 and 30. The aspect ratio of most commercial grades are above this range.

(4) Two most promising grades will be selected for improvement studies and cyclic fill-dispense tests.

(5) Engineering evaluations of projected microsphere costs and storage costs will be completed.

Acknowlegements

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AMMONIA AS A HYDROGEN ENERGY-STORAGE MEDIUM

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Abstract

Liquid Hydrogen (LH_2), Methanol (MeOH), and Ammonia (NH_3) are compared as hydrogen energy-storage media on the basis of reforming the MeOH to produce H_2 and dissociating (cracking) the NH_3 to release H_2. The factors important in this storage concept are briefly discussed. Results of the comparison show that, in terms of energy input for media manufacture from natural gas, hydrogen energy content of the medium, and energy cost (\$/10^6 Btu), NH_3 has a wide advantage and comes the closest to matching gasoline. The tasks required in developing a safe and practical hydrogen energy-storage system based on the storage and cracking of NH_3 are listed. Results of the technical and economic evaluation of its concept will provide the basis for continued development.

I. Introduction

Hydrogen's value is based on its use as an essential chemical commodity and as a consituent of common fuels. By itself, it is a non-polluting fuel because combustion can be controlled to limit NO_x formation to very low values. Hydrogen can also be used in fuel cells for the efficient generation of electrical energy. In nature it exists in the form of compounds which are not always suited to the end-use. Various alternate methods of storing energy in the form of hydrogen have been examined and tested; however, all of them have problems which presently limit their use. The problems for mobile storage are more acute because of weight and volume limitations, and the direct involvement of persons. Of the current methods, compressed gas (in metal cylinders or hollow glass microspheres), liquid hydrogen, metal hydrides, or liquid chemical compounds, the latter appear to be best because of their ease of handling and comparatively low cost in terms of \$/10^6 Btu. Ammonia and methanol are the primary choices, and both release hydrogen by catalytic decomposition.

The purpose of this preliminary study is to point out the advantages of ammonia as a hydrogen energy-storage medium, and to describe a program dealing with the pertinent problems involved in developing safe and economical storage systems.

In the comparisons made here, only liquid hydrogen (LH_2), methanol (MeOH), and ammonia (NH_3) are considered because they presently appear to be the most attractive for both stationary and mobile storage. Compressed gas cylinders are suitable for moderate-size stationary systems, but are too heavy for mobile applications—unless vehicle range is severely limited. Glass microspheres may prove to be suitable for stationary applications; however they are presently too bulky and thus range-limited for mobile applications. Increasing the available hydrogen content from the current value of $\sim$5 wt% to at least 10 wt% would be advantageous. Metal hydrides were not included because of their weight and cost penalties. On the other hand, methanol and ammonia are attractive because of their high hydrogen content, ease of handling as liquids, and low-cost mass production with much established technology. All of the candidates require heat input to release gaseous hydrogen, as explained later.

II. System Factors

A wide range of factors must be considered in evaluating hydrogen storage media.

- Storage Properties
- Energy Input
- Energy Content
- Energy Cost
- Release of Hydrogen
- Distribution
- Safety and Handling
- Environmental
- Social

In relation to the current technology for ammonia and methanol, the factors in the left-hand column concern well-known quantities; whereas the other factors require further development effort when these liquids are used as hydrogen storage media.

Storage Properties

Values for some physical properties related to storage are provided for the three candidate liquids in Table 1; gasoline is included for reference. Although liquid hydrogen has, by far, the highest gravimetric heat content, its volumetric heat content is comparatively low because of its very low density; and a cryogenic container is required. Methanol has modest heat contents, and is easily stored at ambient temperatures. Ammonia's heat contents are slightly less; and it requires a pressure vessel of moderate rating (250 psig is minimum allowable) for storage. The high heat contents of gasoline and its simple storage requirement are not available in alternate fuels (except synthetic gasoline).

Table 1

STORAGE PROPERTIES OF SELECTED MEDIA

	LH_2	MeOH	NH_3	Gasoline[a]
Wt % H_2	100	12.6	17.8	15
B.P., °F[b]	-423	148	-28	-
ρ, lb/ft^3	4.43	49.7	42.6[c]	45.5
Btu/lb	51,600	8,640	8,000	18,800
Btu/Ft^3	229,000	429,000	341,000[c]	855,000
V.P., psia	d	2	129[e]	f

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[a] Included for reference
[b] Boiling point
[c] At -28°F
[d] Cryogenic liquid, vented container
[e] Vapor presssure at 70°F
[f] Variable, but low

Energy Input

The candidates may also be compared on the basis of energy input during production. All three are presently mass produced using natural gas (largely methane, CH_4); so their requirements are well established and suitable for comparison. The heat inputs, for CH_4 used as feed and fuel, were obtained from recent publications and are shown in Table 2.[1-7] Note that the values are in units of Btu/lb H_2 content. The advantageously low value for NH_3 is due to the heat contributed in the exothermic reaction between N_2 and H_2.

Table 2

ENERGY INPUT FOR MANUFACTURE
OF CANDIDATE STORAGE MEDIA

Medium	Btu/lb H_2[a]
LH_2	106,500[b]
MeOH	102,400[c]
NH_3	88,300[d]
Gasoline	20,900[e]

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[a] CH_4 is used for feed and fuel
[b] Average of two values, including liquifaction energy as 25% of lower heating value[1-2]
[c] Average of three values[3-4]
[d] Average of three values[6-7]
[e] Based on an average energy content of five times <u>more</u> than the energy to find, produce, and process crude oil to gasoline, on 114,000 Btu/gal, and on 15 wt% H_2

Energy Content

The system requirements for hydrogen release vary considerably for the three candidates. Simple heating is sufficient for LH_2, but MeOH and NH_3 require elevated temperatures and catalysts to promote the decomposition reactions which release H_2. Low-grade waste heat and a heat exchanger are sufficient for LH_2. In steam reforming of MeOH, a third of the hydrogen produced can be supplied by the steam in a catalytic reaction at 600°F (316°C).

$$CH_3OH + H_2O \longrightarrow CO_2 + 3H_2 \qquad (1)$$

If waste heat can be used to promote the reforming reaction, it is effectively converted to useful chemical energy, and the energy enhancement will be 13.6%. For the thermal dissociation of NH_3 to N_2 and H_2, the enhancement is 14.5%. Although there is significant energy enhancement in the steam reforming of MeOH, there is a weight penalty due to the requirement for 0.56 lb H_2O/lb MeOH; thus the gravimetric energy density is greatly reduced. A comparison between MeOH and NH_3, shown in Table 3, points out the substantial advantage that NH_3 has.

Energy Cost

Current market prices for the storage media are given in Table 4.[8-9] Using the energy content values in Table 3 in combination with the prices provides the energy cost in $\$/10^6$ Btu. These values are based on decomposing MeOH and NH_3 with waste heat to obtain hydrogen; and in the case of MeOH, the effect of the required water is included. The comparison, in terms of $\$/10^6$ Btu for delivered LH_2, MeOH, and NH_3, is for H_2 at the point of use. Ammonia provides the best competition for gasoline, being only 24% higher in price. Methanol is 79% higher than NH_3, and LH_2 is over three times more costly than NH_3.

Table 3

ENERGY CONTENT of MeOH and NH_3

Lower Heating Value, Btu/lb

MeOH	MeOH Reformed	NH_3	NH_3 Cracked	Gasoline
8640	9740[a] 6250[b]	8000	9160	18,800[c]

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[a] On Basis of MeOH weight only
[b] On basis of MeOH and H_2O weights
[c] Average value

Table 4

CURRENT PRICES AND ENERGY COSTS FOR LH_2, MeOH AND NH_3 PRODUCED FROM NATURAL GAS

	LH_2	MeOH	NH_3	Gasoline
Price, F.O.B.	\$1.85/lb[a]	\$0.71/gal[b]	\$160/ton[b]	-
Price, Delivered	2.45/lb[c]	0.81/gal[d]	200/ton[e]	\$1/gal[f]
\$/lb, F.O.B.	1.85	0.107	0.080	-
\$/lb, Delivered	2.45	0.122	0.100	0.165
$\$/10^6$ Btu, F.O.B.[g]	35.90	17.10[h]	8.73[i]	-
$\$/10^6$ Btu, Delivered	47.50	19.50[h]	10.90[i]	8.80
Relative $\$/10^6$ Btu[j]	5.40	2.22	1.24	1.00
	4.35	1.79	1.00	0.81

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[a] At Alabama
[b] At Gulf coast
[c] Delivered to BNL
[d] Estimated
[e] Delivered to East coast
[f] Excluding taxes
[g] Based on L.H.V. and H_2 release
[h] For MeOH reformed with H_2O
[i] For cracked NH_3
[j] For delivered material

Release of Hydrogen

Ammonia is used as a source of high-purity hydrogen, or nitrogen, by thermally decomposing it in the presence of a catalyst. Conventional equipment for ammonia disociation operates at temperatures above 700°C, using the iron-oxide type of catalyst employed for ammonia synthesis. In promoting ammonia as a hydrogen energy-storage medium, it is essential to use a catalyst which will function at much lower temperatures and to make the equipment more compact.

Distribution

Established channels for the distribution of ammonia consist of pipelines, barges, tank cars and trucks, as well as various sizes of cylinders. The pipelines serve nine central states ranging from Texas to Minnesota, where ammonia is mainly used seasonally as a fertilizer. Thus these states could easily expand their use of ammonia by cracking it to use the hydrogen chemically, or as a fuel for farm machinery.

Safety and Handling

Ammonia, like most liquid chemicals, including fuels, has properties which require specific handling techniques that are now well developed and provide safe containment. Although ammonia is very irritating and has a pungent odor, it has some desirable properties. Ammonia is classed as nonflammable because of its high ignition temperature 1204°F (651°C). It is difficult to ignite and has a narrow flammable range (16-25 vol % in air). In this respect ammonia differs from ordinary fuels and has a unique advantage.

Ammonia is commonly stored as a refrigerated liquid (at -28°F, or -33.4°C) although it is classed as a compressed gas. The pressure vessel required for non-refrigerated storage is much more rugged than hydrocarbon fuel tanks; so there is a considerably lower probability of ammonia release resulting from container impact. Further consideration of safety and handling measured will be required for the use of ammonia as a hydrogen energy-storage medium.

Environment

Ammonia also has several environmental advantages. It is not classed as a toxic pollutant, is non-carcinogenic, does not bio-concentrate, and is not persistent in the environment; it is rapidly degraded (if released) and is readily dispersed by water. For combustion applications, cracked ammonia has the environmental advantages of not releasing carbon oxides at its point of use; and lean burning of the released hydrogen will result in NO_x values below those now mandated.

Social

Ammonia is an acceptable industrial and agricultural commodity which is mainly used for its chemical values. In promoting ammonia as a hydrogen energy-storage medium, the degree of acceptability will most likely depend upon safety, cost, and environmental factors in comparison with the alternatives. Most essential will be the development of systems which demonstrate a record of safe operation.

III. Project Description

The favorable factors cited above make ammonia worthy of further examination as a viable hydrogen energy-storage medium for stationary and, perhaps, mobile applications. Accordingly, the project goal is to develop safe and economic systems based on the storage and cracking of ammonia. Emphasis will be on the storage systems rather than on the end-use devices. The program tasks are briefly described below.

1. Initially, the prior work will be reviewed in order to guide the analytical and experimental program and avoid non-essential repetition of effort.

2. A bench-scale ammonia cracker will be designed, constructed, and tested to obtain essential kinetic data.

3. A safe and practical stationary storage and conversion system for producing hydrogen from ammonia will be developed.

4. The combustion and environmental characteristics of cracked ammonia will be studied experimentally in order to determine the effects of partial cracking.

5. The information obtained will be used in making a technical and economic evaluation so that a decision can be made on continuing development of the concept for stationary and mobile applications.

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MODIFICATION AND OPERATION OF THE HYDROGEN HOMESTEAD HYDRIDE VESSEL ENERGY STORAGE SYSTEM

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Abstract

In researching the aspects of hydrogen energy, an important area of study is the safe storage of the hydrogen fuel. The performance characteristics of bulk hydride storage is the subject of current research being performed at the Billings Energy Corporation, under the direction of Brookhaven National Laboratory. A description of the experimental design and operating proceedings is the subject of this report. The description includes hydrogen production, drying, purification and safety system drying, as well as the monitoring of flow, temperature, pressure data and girth measurement.

Progress Report

During this report period the hydrogen storage system design has been completed, including several important modifications. The major modifications are in the hydrogen production phase, primarily in the areas of hydrogen drying and pressurization. A new swing dryer system has been installed to meet dry hydrogen requirements, and a hygrometer has now been installed to monitor the moisture content of the dried hydrogen. An X-Y plotter is now included in the data acquisition system to provide graphical representation of experimental data.

Operating Design

Purification and Pressurization. In order to interface with the existing hardware, the 16 pound per day solid polymer electrolyzer will produce hydrogen at a reduced pressure from the original design specifications. To maintain equalized pressure across the electrolytic cells, hydrogen is produced at a pressure of 150 psi rather than the 600 psi indicated previously. The product hydrogen is then fed through a Pall filter to remove any suspended water particles and promote cooling of the hydrogen prior to the swing dryer. The new swing dryer system is actuated by a solid state timing mechanism rather than the earlier pneumatic system, and will provide more dependable and more consistent levels of dryness than obtained previously. However, due to the pressure sensitive characteristics of the dessicant material, any reduction in operating pressure will cause a decrease in the swing system efficiency. The product hydrogen exiting the dryer mechanism, is expected to be of the same quality as mentioned in the previous progress report, a hydrogen purity in excess of 99.999%. A Panametrics Model 2000 hygrometer has now been mounted after the swing dryer to measure product hydrogen moisture content. Hygrometer readings will be monitored continuously by the computer and will be included as part of the experimentally recorded data. After drying, the hydrogen gas enters a pneumatically driven Haskel pump and is compressed to pressures ranging from 500 to 2200 psi for storage in the hydride vessel or for gaseous storage in the high pressure tube trailer.

During charging, flow meter #1 will be used to monitor flow rates and total hydrogen storage. Immediately before entering into the hydride vessel, the dried hydrogen enters a three-stage dessicant tank which removes any final amounts of oxygen or water (See Figure 1). The three stages are composed of first - molecular sieve material to maintain very low moisture content in the hydrogen gas, second - platinized catalyst to react any remaining oxygen with process hydrogen forming water, and third - molecular sieve material to absorb any catalytically formed water. This three-stage vessel is a final protection for the stored hydride in the event of a system malfunction or leak. After the hydride vessel has received a complete charge, and sufficient time is allowed to achieve equilibrium, the outgassing phase of the experiment is begun.

During outgassing, hydrogen passes back through the three stage dessicant tank, removing any trapped water, and then passes through two flow meters which are positioned in series. These flow meters provide a redundant check of all outflow data. The integrating capacity of the data acquisition system provides a record of stored hydrogen at any given instant.

During normal outgassing, valves 5 and 6 are closed to prevent any hydrogen backflow into the electrolyzer area (See Figure 2). Valve 7 may direct flow to the atmosphere or to the low pressure tube trailer for later use. Charging the hydride vessel requires valve 5 to be open, and 6 and 7 to be closed. In the event of an emergency, valve positioning is not important due to the placement of solenoid valves.

Safety System Design. In the event of a hydrogen leak, the hydrogen sniffers signal the shutdown of all electrolyzer power and send the solenoid valves into their "normal" mode. Solenoid valve 5 opens to release stored hydrogen from the hydride vessel while solenoid valve 6 closes to prevent any hydrogen release within the laboratory area (See Figure 2). Solenoid valves 7 and 8 close to seal off the tube trailer storage from the building. In the event that a power outage were to accompany an actual emergency, an additional valve (V9) has been installed, and may be opened manually to vent the hydride vessel.

Two hydrogen sensors have been installed in the laboratory, one in the ceiling above the hydride vessel, and one above the electrolyzer control panel. A third sniffer has been positioned inside the electrolyzer cabinet, but is operational only when the electrolyzer is on. These sensors automatically signal the electrolyzer and safety control system in an emergency.

In the emergency mode, the air conditioning/heating system is shut off, and an audible alarm is sounded to warn personnel of the danger. The alarm sounds in two modes - a beeping tone to signal the detection of trace amounts of hydrogen, and a steady tone signalling a dangerous level of hydrogen concentration. The audible alarm is powered by 110 volt building power. In the event of a power outage, while all other emergency systems are in the safety mode, the warning alarm will not be operable. Since a power outage itself represents no real danger, the lack of the warning system is acceptable as a non-hazardous condition. An exhaust fan remains on in all modes of operation to remove any hydrogen from the laboratory.

Data Acquisition System. The computerized data acquisition system has been set up to monitor 16 data channels. This includes 2 pressure transducers, 2 strain gauges, and 8 thermistors positioned as shown in Figure 3. Three flow meters and a linear output hygrometer are also monitored by the system. Two integrating channels may be used to monitor any of the 16 mentioned above. The integrating channels display high, low, and average values as well as the integral values, and elapsed time. An internal clock provides a relative time base for all resultant data. The experimental data may be printed out, stored on diskette, or both at the option of the user. A plot program has been developed to show results graphically, allowing a visual comparison of any two channels, or any channel versus time.

Summary

The project is now in a final phase of preparation. Upon completion of a last system purge and final flow meter calibration, initial testing will begin. There have been some problems in the computer system analog to digital (A/D) board. The system has now been repaired and is in complete working order. A thorough explanation of planned experimental tasks has been made in the previous progress report. A copy is found in the appendix to this report.

FIGURE 1

HYDROGEN PURIFICATION

1. FROM ELECTROLYZER
2. 1 P.S.I CHECK VALVE
3. PRESSURE GAUGE
4. VALVE
5. VENT TO ATMOSPHERE
6. FILTER
7. WATER TRAP
8. TO WATER DRAIN
9. DESSICANT CYLINDER
10. MOLECULAR SIEVE MATERIAL
11. SOLENOID VALVE
12. NEEDLE VALVE
13. BACK PRESSURE REGULATOR
14. HYGROMETER HEAD
15. HYGROMETER
16. TO HYDRIDE STORAGE SYSTEM
17. 2 MICRON FILTER

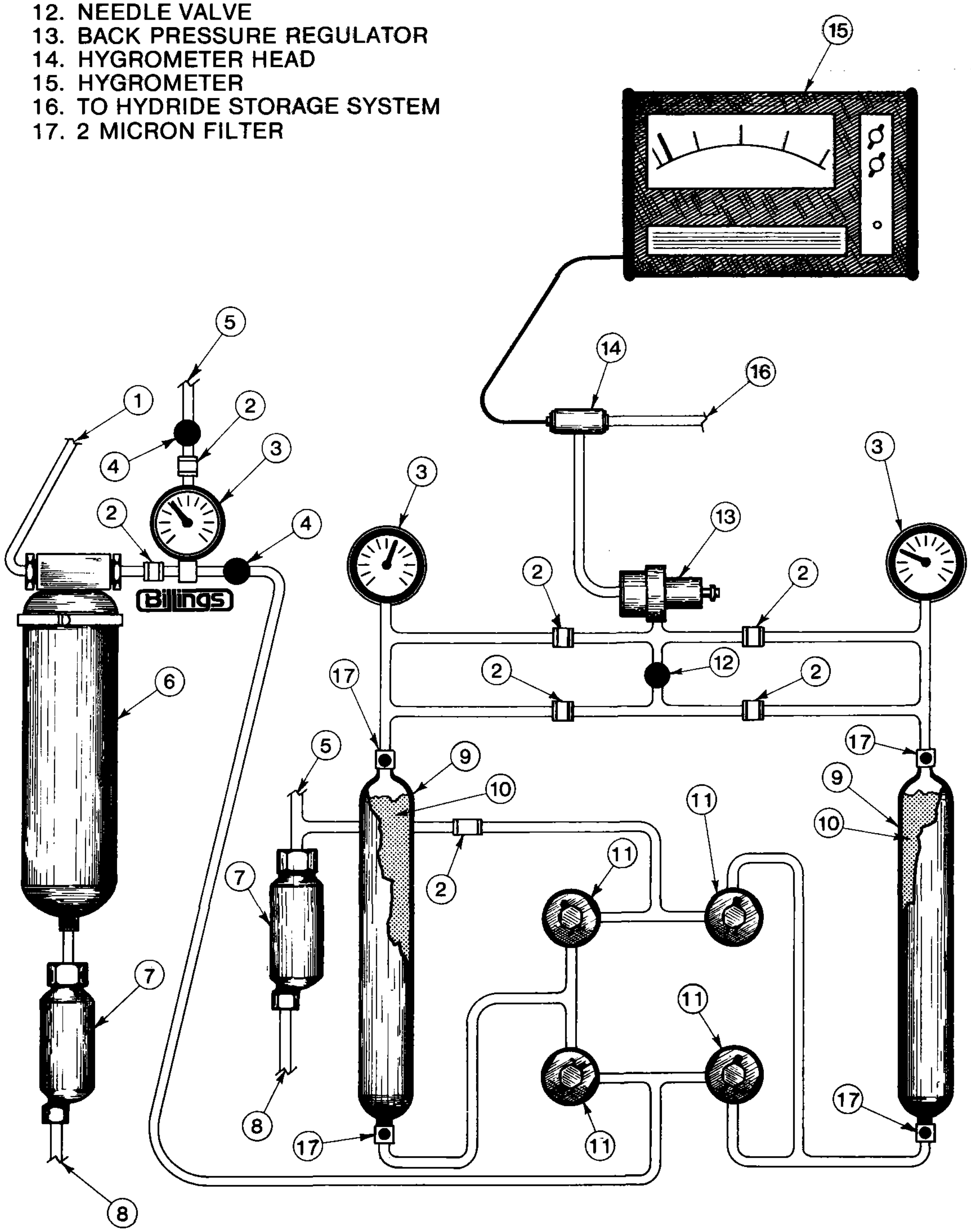


FIGURE 2

HYDRIDE STORAGE VESSEL LAYOUT

1. FROM ELECTROLYZER
2. TO BUFFER TANK
3. PRESSURE GAUGE
4. VALVE
5. VENT TO ATMOSPHERE
6. PRESSURE SWITCHES (ELECTROLYZER CONTROL)
7. PNEUMATIC COMPRESSOR, 2200 P.S.I. MAX.
8. HIGH PRESSURE TANKS
9. HIGH PRESSURE TUBE TRAILER
10. 3-WAY VALVE
11. LOW PRESSURE TUBE TRAILER
12. FLOW METERS
13. SOLENOID VALVE (NORMALLY OPEN)
14. SOLENOID VALVE (NORMALLY CLOSED)
15. NEEDLE VALVE
16. DESSICANT TANK
17. MOLECULAR SIEVE MATERIAL
18. CATALYST
19. HYDROGEN FILL PORT
20. EMERGENCY VENT LINE
21. 650 P.S.I. PRESSURE RELIEF VALVE
22. METAL HYDRIDE
23. HEATING COILS
24. INSULATION
25. STEEL CONTAINMENT VESSEL
26. PUMP
27. WATER HEATER
28. WATER VALVES
29. 1 P.S.I. CHECK VALVES
30. HYDRIDE VIEW PORT

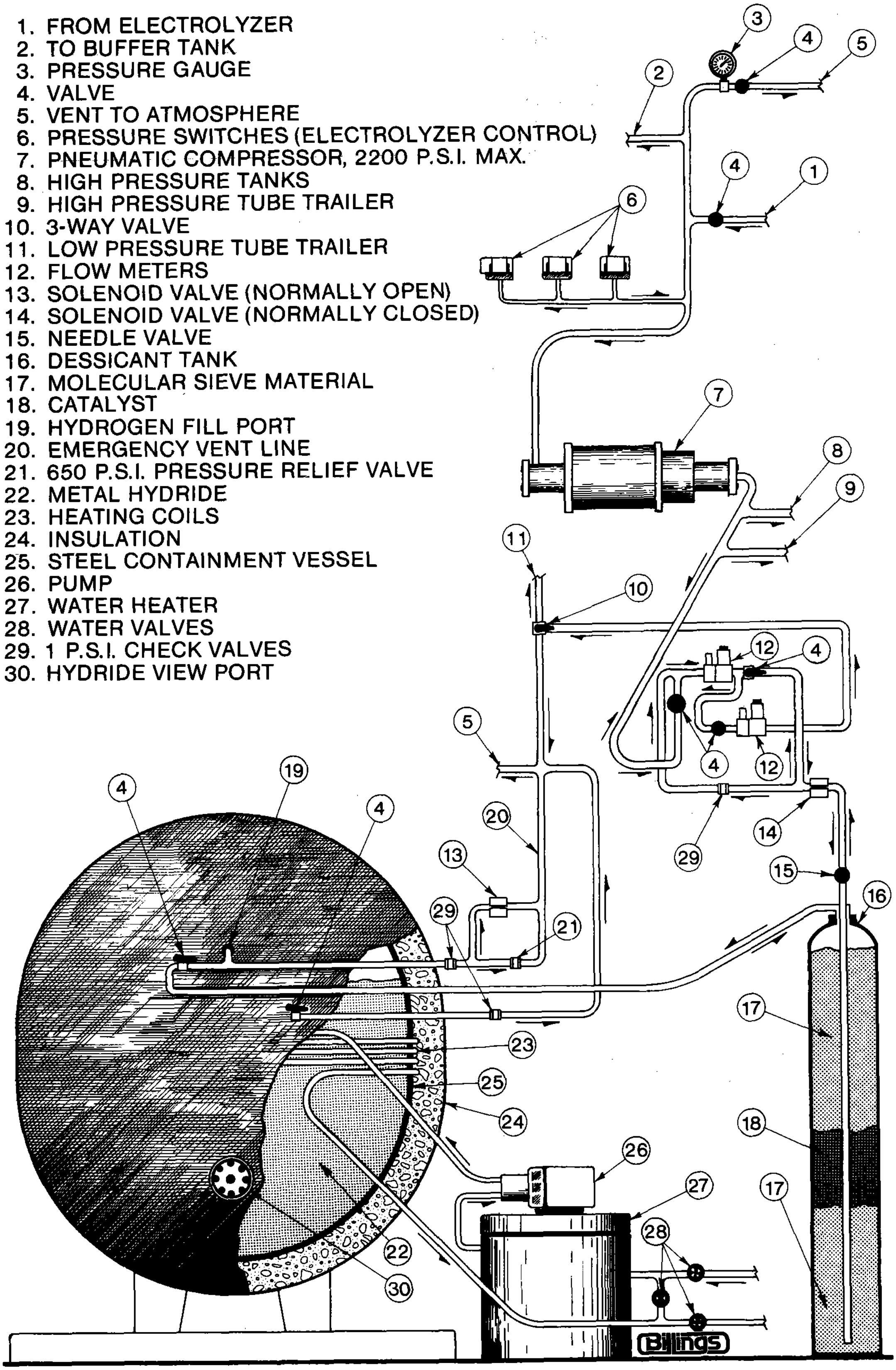


FIGURE 3

HYDRIDE VESSEL SENSOR LAYOUT

A/D CHANNELS

1. HYGROMETER (SEE FIGURE 1)
2. STRAIN GAUGE (TOP)
3. STRAIN GAUGE (BOTTOM)
4. PRESSURE TRANSDUCER HD4
5. PRESSURE TRANSDUCER HD3
6. FLOW METER 1 (SEE FIGURE 2)
7. FLOW METER 2 (SEE FIGURE 2)
8. THERMISTOR 1
9. THERMISTOR 2
10. THERMISTOR 3
11. THERMISTOR 4
12. THERMISTOR 5
13. THERMISTOR 6
14. THERMISTOR 7
15. THERMISTOR 8
16. THERMISTOR 9

A. VALVE
B. BILLINGS COMPUTER
C. PRINTER
D. FLOPPY DISK STORAGE
E. X-Y PLOTTER
F. PRESSURE GAUGE

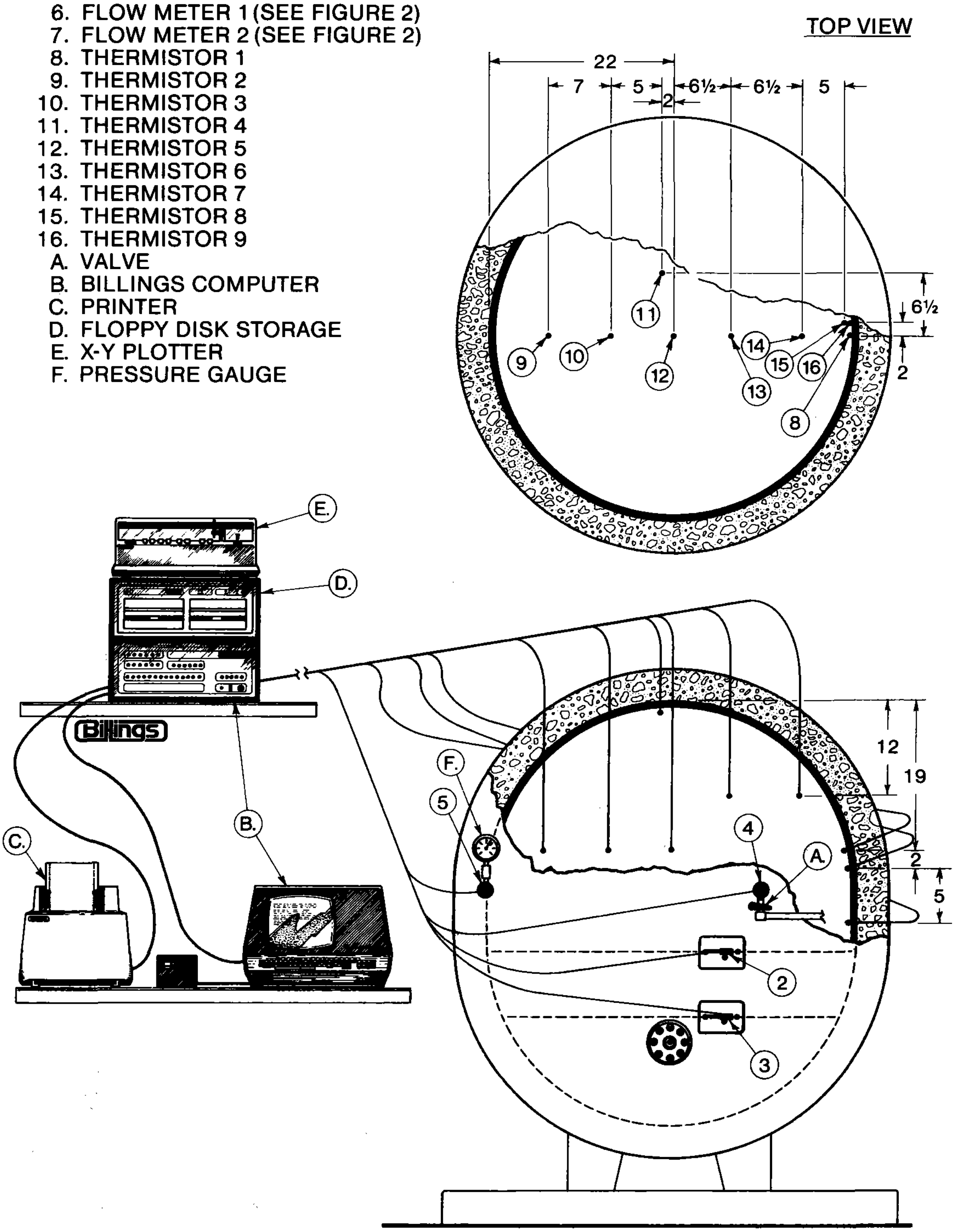
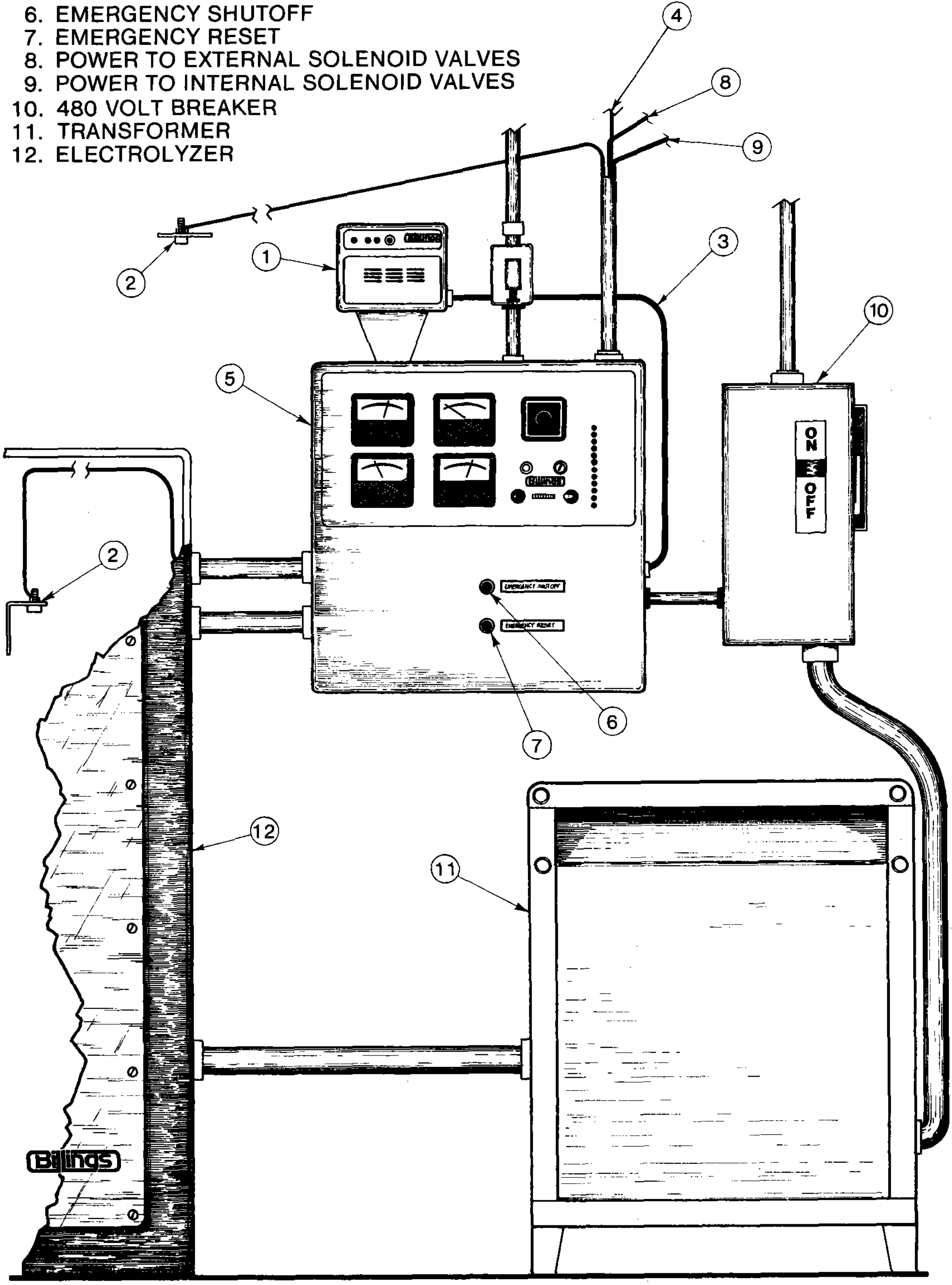


FIGURE 4

SAFETY CONTROL SYSTEM

1. HYDROGEN SENSOR & AUDIBLE ALARM
2. HYDROGEN SENSOR
3. ELECTRIC SHUTOFF SIGNAL
4. HEATING SYSTEM
5. ELECTROLYZER CONTROL PANEL
6. EMERGENCY SHUTOFF
7. EMERGENCY RESET
8. POWER TO EXTERNAL SOLENOID VALVES
9. POWER TO INTERNAL SOLENOID VALVES
10. 480 VOLT BREAKER
11. TRANSFORMER
12. ELECTROLYZER



Experimental Data Collection Procedure

Task 1 - Hydrogen Vessel Performance Test. The first series of tests are designed to establish hydrogen charging and discharging limits for the metal hydride system. This will be accomplished by supplying hydrogen at 600 psi to the hydride vessel from the electrolyzer and from the fully charged high pressure tube trailer. It is anticipated that in this charging mode the vessel charging rate will be the limiting system parameter due to the limited heat transfer capability of the vessel. By monitoring hydrogen flow via FM1 the maximum charge rate will be established. It is anticipated that the hydrogen charge rate will decrease as the vessel approaches a full charge due to the longer path of heat transfer required. Various plots of this data overlaying charge rates with pressure differentials within the vessel should provide some very interesting data for analysis.

The next test will establish maximum discharge rate. Prior to the initiation of this test the hydride vessel will be allowed to achieve equilibrium by sustaining the 600 psi charging condition 24 hours after absorption process has discontinued. At this point, assuming equilibrium, the weight percent of the hydride material will be determined. Then the hydrogen discharging phase will begin by allowing hydrogen to flow through FM2 and FM3. After the initial pressure release, the hydrogen withdrawal rate should be limited by the capacity of the heat exchanger to supply the necessary dissociation of energy. This procedure will be continued until hydrogen flow has ceased and until the tank has achieved a temperature equilibrium. The maximum withdrawal rate data will be plotted and analyzed as appropriate. Again, a decrease in withdrawal rate is anticipated as the discharging experiment proceeds.

The previous two steps will be repeated twice to determine that the metal hydride material is in good condition and to establish that repeatable data can be collected. Any flaws in the quality of the hydride or the test procedure will then be scrutinized and an attempt will be made to rectify the same.

Task 2 - Hydrogen Vessel Continual Performance Test. The next series of tests will be performed to determine what sustained withdrawal rates can be supported by the hydride vessel heat exchanger design. This will be accomplished by controlling hydrogen charge and discharge rates external to the hydride vessel. Three separate hydrogen flow rates will be selected based on data provided during Task 1. At each flow rate the hydride vessel will be completely charged and discharged. The resulting plot of hydrogen flow should remain level until the point that the system is no longer able to sustain the flow rate under consideration. At this point deterioration in the flow rate will indicate the heat exchanger's inability to sustain flow conditions.

Task 3. In this task a definitive evaluation of all data collected during Tasks 1 and 2 will be evaluated, including girth measurements, temperature and pressure differentials, hydrogen flow rates, etc. will be analyzed to identify any unfamiliar phenomia or unusual characteristics. An attempt will be made to prepare the data in various graphical forms to illustrate pertinent information. Based on this assessment an additional set of test runs will be performed as necessary.

Items to be monitored during the data collection as Tasks 1 through 3. The following parameters will be recorded throughout the collection of data as described in the above tasks:

1. Date
2. Time of Day
3. Technician
4. All temperature readouts
5. All pressure readouts
6. All girth measurement readouts
7. All flow meter readouts
8. Barometric pressure
9. Electrolyzer water purity
10. Electrolyzer hydrogen purity
11. Pressure in the high pressure tube trailer
12. Water inlet temperature
13. Water exit temperature
14. All control operation sequences
15. Any abnormalities or observations

Additionally, an attempt will be made to collect photographic data of the condition of the hydride material as the experiment progresses. This will be attempted utilizing the 2 inch glass window which has been installed on the side of the hydride vessel.

HYDROGEN MICROSPHERE HAZARD EVALUATION

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Abstract

Progress on a preliminary hazard evaluation of hollow glass microspheres for hydrogen transport and storage is reported here. Most of the work to date has involved laboratory testing to assess the flammability and explosibility of representative hydrogen-filled microspheres. The tests included dust cloud explosion tests, flame propagation tests, impact sensitivity tests, spark ignition tests, and autoignition furnace tests. Test results reveal that the microspheres can be ignited and propagate flame either in the quiescent bulk form or as a suspended cloud. A preliminary comparison with reported flammability data for gaseous hydrogen and iron titanium hydride powder indicates that the auto-ignition temperature of hydrogen-filled microspheres is comparable to that for the other forms of hydrogen, but suspended clouds of microspheres produce lower explosion pressures than hydride dust or hydrogen gas. Safety codes and government regulations pertinent to hydrogen filled microspheres are also reviewed briefly.

I. Introduction

R. J. Teitel Associates, under contract to Brookhaven National Laboratory, have been developing a novel and potentially attractive technique for hydrogen storage and transport. Teitel's technique, called the Microcavity System[1], involves filling micron-sized thin-walled glass cavities with high-temperature, compressed hydrogen gas. Since the microcavities or microspheres are only permeable to hydrogen at high temperatures (the permeation rate typically is reduced by four orders of magnitude as the the temperature drops from 200°C to 20°C), hydrogen can be stored within room temperature or refrigerated microspheres for relatively long periods of time. Reheating of the microspheres will release the hydrogen for use in a hydrogen fueled automobile, or for some other application.

The eventual commercial acceptance of the microcavity hydrogen storage system will depend in part upon the cost and convenience of handling and transporting the filled microspheres. This in turn depends upon the safety measures required to control the inherent hazards of the microspheres. Factory Mutual Research Corporation (FMRC) has contracted with Brookhaven to conduct a preliminary hazard evaluation of the microspheres. The evaluation consists of four tasks: 1) Review of Pertinent Standards, 2) Laboratory Flammability and Explosibility Tests, 3) Analysis of Miscellaneous Hazards, and 4) Hazard Comparisons with Alternative Hydrogen Storage Modes. Progress to date is described below with the emphasis placed on laboratory tests and their results.

II. Laboratory Flammability and Explosibility Tests

R. J. Teitel Associates provided, via Brookhaven, a sample of hydrogen-filled microspheres for the laboratory tests. The glass microspheres were 3M brand designation D32/4500, denoting a mean particle size of 32 microns. The microspheres were hydrogen filled by R. J. Teitel Associates to an equivalent room temperature pressure of 232 atmospheres. Since the filled microspheres were refrigerated during storage, there was no significant leakage of hydrogen gas prior to the tests.

Dust Cloud Explosibility of Hydrogen Microspheres

A series of standard experiments to measure the explosibility of hydrogen microsphere particles dispersed in air was carried out. The Hartmann dust explosibility apparatus was used for this purpose. The Hartmann apparatus is a 7-cm dia. x 30-cm long cylindrical body equipped with nichrome wire ignition source, a pressure transducer, and a sample dispersion assembly. Hydrogen microsphere powder deposited in the dispersion assembly cup was dispersed within the cylinder by a measured blast of air just prior to firing the ignition source. The concentration of hydrogen microspheres was approximately 0.78 g/ liter assuming the entire sample was evenly dispersed within the cylindrical volume. This is the standard sample concentration used at Factory Mutual Research for dust explosion tests[2], since most combustible dusts produce the highest explosion pressure near this concentration. Experiments with two separate batches of hydrogen microspheres indicate explosion pressures in the range 8 to 10 psig for one sample and 16-18 psig for the other sample. These measured pressures (maximum of 18 psig) are lower than the reported maximum deflagration explosion pressures for hydrogen-air mixtures (about 101 psig), and for FeTi hydride dust (73 psig) and $LaNi_5$ hydride dust (59 psig)[3].

Hydrogen Microsphere Combustibility (Flame Propagation) Test

To measure the fire hazard potential of hydrogen microsphere deposits, a flame propagation test was carried out. Hydrogen microsphere powder was deposited in a ceramic channel measuring 18 cm x 3 cm x 1 cm. The channel was fabricated from 2 mm thick ceramic paper. A nichrome wire coil embedded in the hydrogen microsphere deposit at one end of the channel served as the ignition source. The temperature of the nichrome wire was raised to approximately 900°C within 10 sec using a Chemical Data System pyrolyzer controller. The temperature of the hydrogen microsphere powder in the vicinity of the ignitor coil and midway through the length of the channel was recorded. As the temperature of the ignitor was raised, there was vigorous sputtering of the hydrogen microsphere powder in the vicinity of the ignitor; this was soon followed by a light orange-colored flame propagating along the microsphere bed. Fumes of hydrogen (microsphere particles apparently kicked off by rapidly burning powder) were also observed. Occasionally, a fraction of the hydrogen microsphere powder was ejected from the channel as burning progressed. The flame velocity as measured from 16-mm color movies, was about 22 cm/sec. The results of this experiment demonstrate that hydrogen microsphere deposits are susceptible to hot-spot ignition and subsequent flame propagation.

Impact Sensitivity

The effect of sudden crushing of hydrogen microspheres was examined via the ASTM Drop-Weight Impact Sensitivity Test[4]. In this test, a small sample (0.03 ml) of hydrogen microsphere powder is enclosed in a cavity (0.06 ml) formed by a steel cup, an elastic ring, and a steel diaphragm. A piston rests on the diaphragm and carries a vent hole which is blocked by the steel diaphragm. A 6-kg weight lifted to a height of 50 cm was dropped onto the piston. There was no puncture of the steel diaphragm nor any loud bang indicative of an explosive reaction upon impact. This negative result, i.e., no explosion, is the same as that previously reported for FeTi hydride powder[3]. However, microscopic examination of the hydrogen-filled microspheres following the present tests indicated that many of the microspheres had ruptured upon impact, thus releasing hydrogen gas.

Electrostatic Spark Susceptibility Test

Electrostatic spark ignition sources are a concern in future transport and handling of hydrogen microspheres. It is well known that static discharges can easily ignite hydrogen-air mixtures. Therefore, to assess the susceptibility of hydrogen microsphere powder, the following test was carried out.

Approximately 2 g of hydrogen microsphere powder was placed into a ceramic crucible. A capacitance spark source delivering 11 Joules of spark energy was discharged across electrodes embedded in the sample. Upon discharge, one of the test samples burned vigorously in the crucible before self-extinguishing. The results of this experiment demonstrated that a static spark source of sufficient energy can ignite hydrogen-filled microsphere in bulk form. Metal hydride powders are also susceptible to electrostatic spark ignitions, with reported spark ignition energies less than 1 Joule[3]. No attempt was made here to measure the minimum spark ignition energy for hydrogen microspheres.

Autoignition Temperature Experiments

Autoignition tests of the type previously reported[3] for metal hydrides have also been carried out with hydrogen microspheres. A 2-g sample of microspheres was placed into a ceramic boat, and a chromel-alumel thermocouple was embedded in the sample. The sample was then inserted into a tubing furnace purged with a 1-liter/min air flow. Furnace temperatures in the range 300°C-900°C were employed.

With a furnace temperature of 700°C, flames were observed when the sample temperature reached 170°C. This is only slightly lower than the reported ignition temperature of 188°C for FeTi hydride powder in the equivalent test[3]. It should be noted that no ignitions were observed with the microspheres when the furnace temperature was lower than about 500°C. This is consistent with reported[5] hydrogen gas-air autoignition temperatures of 400°C for near stoichiometric mixtures and higher temperatures at other compositions.

III. Review of Relevant Safety Regulations

The experimental results described in the preceding section demonstrate that hydrogen microsphere powder is a potentially explosive and combustible material even without significant accumulation of hydrogen gas from the microspheres. The storage and transport of hydrogen microsphere will require compliance with appropriate federal, state, and local regulatory standards for flammable materials. Furthermore, because hydrogen microspheres are small glass particles in the range of 5-200 microns, compliance with OSHA Standards for respirable dusts may also be required.

We have reviewed Federal regulations to identify the following standards which are potentially applicable to hydrogen microsphere safety in filling, storage, and transport operations:

1) OSHA Standard 1910-1000, Table Z-3, for silica dust appears to be applicable to hydrogen microsphere powders since microspheres are glass. This standard specifies that quartz (silica dust) concentration exposure be limited to 10 mg/m^3 for eight hours per day over 40 hours per week. According to OSHA officials, OSHA Ventilation Standard 1910.94 on abrasive blasting operation appears applicable for ventilation requirements to maintain hydrogen microsphere cloud concentrations below this limit. Standards Z9 2-1960 and ANSI Z33.1-1961 for the design and operation of ventilation systems were suggested as being applicable to cope with the dust cloud problem.

2) EPA National Ambient Air Quality Standards (40CFR50, 1976) for particulate emission appears applicable for possible emission control of hydrogen microsphere particles in the vicinity of manufacturing and storage facilities. This standard requires that concentration of emitted particles should not exceed 75 μg/m^3 as an annual geometric average and certainly no more than 260 μg/m^3 for a 24-hour period not to be exceeded more than once per year.

3) Hazardous Materials Regulations 49CFR, Part 171-177 of the Department of Transportation were reviewed for their applicability to the transport of hydrogen microspheres. This review in consultation with the DOT Office of Hazardous Materials Operations indicated that DOT shipping requirements will depend on: 1) the packaging of the H_2 microsphere powder; and 2) the rate of loss of hydrogen from the microspheres at the postulated extreme ambient temperature of 55°C (130°F). An application for an exemption from compressed gas shipping requirement should be filed with DOT when hydrogen microspheres are to be shipped in packaged volumes over 0.118 liters (7.2 in.^{3}).

4) NFPA Pamphlet No. 50A (ANSI Z292) which also appears as OSHA Standard 29CFR 1910.103(c) - Standard for Gaseous Hydrogen Systems at Consumer Sites is applicable where the volume of hydrogen is in excess of 400 SCF. This code specifies requirements for isolation of hydrogen systems from other structures, acceptable designs for hydrogen gas containers, and specifications for buildings containing hydrogen equipment.

Analysis of Accident Scenarios

If requests for exemptions from the preceding regulations are eventually to be filed, hydrogen microsphere flammability and toxicity data will have to be analyzed in the context of potential accident scenarios. A preliminary analysis of this nature will be conducted in the next few months with regard to the relative safety of various possible packaging containers. A final report on the completed study will be submitted in January 1981.

References

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3) Lundin, C.E., and Lynch, F.E., "Safety Characteristics of FeTi Hydride," University of Denver, Final Report to Brookhaven National Laboratories, December 1974.

4) American Society of Testing and Materials Test D2540-G6T, "Drop-Weight Sensitivity of Liquid Monopropellants," ASTM Book of Standards, 1967.

5) Zabetakis, M.G., "Flammability Characteristics of Combustible Gases and Vapors," Bureau of Mines Bulletin 627, 1965.

HYDROPOWERED ELECTROLYSIS IN NEW YORK STATE

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Abstract

An inventory of New York State's hydropower potential conducted by the New York State Energy Research and Development Authority has located more than 1,000 sites with dams in the state which could be refurbished to produce power. It is estimated that these facilities can be made to generate 3.8-billion kilowatt hours of (firm) electrical power per annum. The present low rates which the utilities are willing to pay for excess dumped energy have motivated hydropower developers to find more lucrative means of utilizing excess power. Specifically, the Village of Potsdam has found that the use of excess power to operate an advanced technology solid polymer electrolyzer can produce research grade hydrogen whose kilowatt-hour equivalent value is more than 10 times greater than that of dumped electrical energy. To achieve this goal, the Village's hydropower facility will be equipped with two, 350-kilowatt tube turbines and a 200-kilowatt electrolyzer. The latter will produce approximately 18-million standard cubic feet of hydrogen annually which will be sold for $.50 per hundred cubic feet.

I. Introduction

A considerable amount of the state's hydro potential remains unutilized for power production. An inventory of the state's hydro potential conducted by the New York State Energy Research and Development Authority has located approximately 1,700 sites in the state which could generate power. Seven hundred fifty-four (754) of these sites have been categorized by size and presence or absence of dams as shown in the table below:

Tabulation of Undeveloped Capacity 50 Kw Minimum

Capacity Range Mw	Undeveloped Capacity in Kw			
	# of Sites	With Dams	# of Sites	Without Dams
100-50	4	284,000	4	343,000
50-30	2	78,000	6	203,000
30-15	17	324,000	18	381,000
15-10	14	168,000	15	176,000
10-5	38	270,000	26	190,000
5-1	114	286,000	77	178,000
1-.5	44	37,000	38	26,000
.5-.25	80	38,000	40	14,000
.25-.10	101	16,000	37	6,000
.10-.05	54	6,000	25	2,000
	468	1,507,000	286	1,519,000

Analysis of the hydropower statistics for New York State indicates that while 3,000 megawatts of hydropower potential may be harnessed, only about one-third of this power is estimated to be economically attractive at this time.

Some of the hydropower sites that could undergo feasibility examination for expansion of hydroelectric production are now operated by industries that can create more jobs if increased power at a reasonable stable cost is made available.

II. Alternative Hydropower Concepts

The alternate use of hydropower is one of several strategies being studied by the Authority in its efforts to broaden its hydropower program and accelerate the redevelopment of other facilities.

The development of the hydropower site at the Village of Potsdam is one of several examples. In this instance, the power at the site will be used to operate an electrolyzer, which will create hydrogen and oxygen from water via dissociation. In this respect, the water will serve a dual purpose, namely that of the driving force used to power the electrolyzer, and the fuel which will be used to generate hydrogen gas. Hydrogen is conventionally produced from fossil fuels.

The Village of Potsdam's power house was built in 1926 as an addition to the existing Village water treatment plant. It contained two flumes, each designed for 9.5-feet of head and 268-cubic feet per second of flow. A 42-inch, 238-HP, Type B James Leffel and Company turbine was installed in one of the flumes and the other left for future turbine installation. A second turbine was never installed, however, and the plant operated until 1971 with only one machine which at that time, was decommissioned.

The Village expressed an interest in redeveloping the old site in 1978 thus initiating a feasibility study to assess what opportunities existed at the site. The Village of Potsdam suggested in the first instance that four of its existing facilities: the water treatment plant; the police station; the sewage treatment plant; and the ice skating arena would be candidate recipients of the electrical energy generated by the hydroelectric facility. During 1976-77, the average annual electrical energy consumption for these four facilities totalled 2,000,000 kilowatt hours, with a peak demand of 550 kilowatts. With a proposed expansion of the existing water treatment plant, and the conversions of the heating system in the police station to electrical resistance heating, it was anticipated that the maximum demand would rise to 690 KWs and that the annual energy consumption would consequently rise to 2,250,000 Kw hours.

Because of the time variations in supply and demand it became clear that a significant amount of excess electrical energy produced by the facility would have to be dumped into the utility's grid. The five-mil per kwh rate which the utility (in this case the Niagara Mohawk Power Corporation) would pay for dumped energy motivated the Village to explore other and more lucrative means of utilizing this excess power. Solid polymer electrolysis, a high-efficiency electrolytic process being developed by the General Electric Company proved to be an economically viable option tailored to meet the Village's needs. At an 85 percent conversion efficiency it may be shown that one kwh of electrical energy may be used to produce 8.8 rcf of research grade hydrogen whose present market value ranges from $.75 to $1.25 per hcf. This price represents an equivalent value ranging from 132 to 220 mils per kwh (electrical).* On this basis, the Village decided to couple the hydroelectric facility to a 200-kw electrolysis module and convert excess electrical energy to hydrogen (and oxygen) gas.

Excess power produced over that needed to operate the four village facilities and the hydrogen production system will be sold to the Niagara Mohawk Power Corporation as dump power of the plant's 700-KW total; approximately 500 KW and 200 KW will be dedicated to electrical and hydrogen production, respectively. For the case of hydrogen production, the power needed to run the electrolyzer will be deducted from the excess available and the rest sold as dump power. Two of the five facilities are not located in the immediate vicinity of the power plant, and must have power transmitted (or "wheeled") to these facilities over Niagara Mohawk power lines.

III. Project Development

The total construction cost for the 700-KW plant with the hydrogen production system is approximately $2,480,000, of which $299,000 and $1,900,000 include the cost of the hydrogen production system and the redevelopment cost of the hydroelectric plant, respectively. The balance will be used to rehabilitate the dam. The reactivation of the hydroelectric plant will cost $2,714/KW. Over the useful life of the facility, total costs amount to slightly less than $12,000,000 while benefits amount to just over $31,000,000, resulting in a net benefit of approximately $19,000,000. Nearly all the benefits are a result of displacing power that would have to be purchased from Niagara Mohawk for the four village facilities. A present worth analysis is performed by using a rate of return of eight percent. The present worth of the costs is computed to be slightly greater than $3,400,000, while the present worth of the benefits is nearly $5,700,000, indicating a rate of return exceeding eight percent. The project's total cost is $2,929,100.

Construction costs include rehabilitation of the dam, modifications to the powerhouse, purchase and installation of turbine/generator units, and engineering. The costs of dam rehabilitation and the building renovation are estimated on the basis of similar projects, while turbine/generator costs are obtained from equipment manufacturers. Engineering costs are derived by taking a percentage of the total construction cost. Construction costs include the electrolyzer and gas storage facilities as well. These costs were obtained from data supplied by General Electric (the electrolyzer manufacturer). It is further assumed that the village will pay for the construction through a bond issue to be repaid over a 25-year period at six percent interest.

Operation and maintenance costs for the hydroelectric plant are assumed to require one man-year annually. An operator's wage is estimated and multiplied by a factor to account for parts and contractual repair work. Operating costs for the electrolyzer are taken as the loss in revenues for the dump power used by the unit. Maintenance costs are derived from data supplied by the manufacturer.

IV. Project Economics

A 40-year period is used for the analysis of the proposed project as this is the expected useful life for similar facilities. The Potsdam plant is expected to begin operation in 1981. The prices for purchased power and "wheeling" and dump power are, therefore, adjusted to reflect expected costs at that time. Construction costs include a contingency factor for the same purpose.

A decreasing factor of inflation is used to account for future price changes except for the sales of hydrogen gas which have a constant inflation factor over the entire period. Also, the

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*The Village did not choose to exclusively produce hydrogen because such a project would have proven to be extremely capital intensive. The prototype price of the electrolyzer is estimated at several thousand dollars per installed kw.

revenues for dump power sales are held constant over five-year periods in accordance with Niagara Mohawk's policy of negotiating five-year contracts for dump-power purchases.

V. Assumptions

1. The hydropower plant has a capacity of 700 kilowatts and an average annual output of 5,600,000 kilowatt-hours. 2,250,000 kilowatt-hours will be used by the Village at its various buildings; 2,016,000 kilowatt-hours will be used by the electrolyzer; and 1,334,000 kilowatt-hours will be sold as dump power. 1,550,000 kilowatt-hours used by the Village has to be transmitted, or "wheeled" from the plant to other locations by way of lines owned by the area electric utility company.

2. The Village will bond $938,600 at six percent interest for 25 years.

3. Hydrogen gas production will average 180,000 HCF per year. The gas will sell for $0.50/HCF and will increase four percent per year.

4. Operation and Maintenance for the power plant will start at $12,000 per year. Operation and Maintenance for the electrolyzer (which will include an annual cost for the cell replacement costs, cost of annual maintenance for the cells, and costs of power to run the plant at dump power rates) starts at $21,000.

5. Operation and Maintenance costs, "wheeling" costs, and the cost of the displaced power increase annually at the following rates:

1981 to 1985	12 percent
1986 to 1990	10 percent
1991 to 1995	8 percent
1996 to 2000	6 percent
2001 to 2020	4 percent

6. Dump power rates are re-negotiated every five years and are assumed to increase as if they had increased annually according to No. 5 given above.

7. Costs in 1981 dollars are:

Operation and Maintenance	$ 33,000
Purchased Power	$100,125
Dump Power Sales	$ 7,951
"Wheeling"	$ 2,325
Hydrogen Gas Sales	$ 90,000

VI. Summary of Benefit - Cost Analysis

TOTAL COSTS

Debt Service	$ 4,550,600
Operation and Maintenance	$ 6,914,891
"Wheeling"	$ 487,129
TOTAL	$11,952,620

TOTAL BENEFITS

Hydrogen Gas Sales	$ 8,552,292
Dump Power Sales	$ 1,608,175
Value of Power Used if Purchased	$20,980,500
TOTAL	$31,140,967

POTENTIAL SAVINGS

Total Benefits	$31,140,967
Total Costs	$11,952,620
TOTAL	$19,188,347

VII. Summary of Present Worth Analysis

BENEFITS

Hydrogen Gas Sales	$ 1,752,758
Dump Power Sales	$ 250,382
Value of Power Used if Purchased	$ 3,684,008
TOTAL	$ 5,687,148

COSTS

Debt Service	$ 2,106,875
Operation and Maintenance	$ 1,214,197
"Wheeling"	$ 85,540
TOTAL	$ 3,406,612

VIII. Summary

It is expected that the 18-million standard cubic feet of hydrogen that will be produced at the site annually will sell at prices under current market quotations. Furthermore, the oxygen will produce ozone which will be used to purify the local water supply at the Village of Potsdam's water treatment plant adjacent to the hydropower facility.

Rehabilitation of the site will produce both hydrogen and an increased amount of electricity for local use. Current production of about 150 kilowatts will increase to more than 700 kilowatts.

Of the new total, about 500 kilowatts will be used by the town of Potsdam and about 200 kilowatts will be used for the hydrogen production process.

The oxygen gas will be used in the purification process at the adjacent water treatment plant. The village expects to manufacture ozone, which will be used in water treatment, more economically from oxygen than it currently does from air.

Results of the Potsdam experiment are expected to be equally applicable at some 50 other sites in the state. The installation of similar equipment at the other sites would dedicate a total of 47 additional firm megawatts of electrical power at a 90 percent capacity factor. This power potential is equivalent to a state-wide hydrogen production of 3.2 billion cubic feet of hydrogen per annum. This in turn translates into a 30 million dollar per year business for New York State.

This demonstration, in addition to producing hydrogen, is also part of the overall plan to increase production of hydroelectric power across the state as outlined above.

IX. Present Status

The contract for this project is currently in effect as of August 1, 1980. The scope of work consists of phases described as follows:

1) Phase I - program plan
2) Phase II - site description and engineering design
3) Phase III - construction
4) Phase IV - operation and monitoring

A program plan has already been submitted to USDOE. This plan describes phase II in detail. A similar program plan for phases III and IV will be given as part of the final task (task 5) of phase II in March of 1981. Currently work has already been initiated in phase II. A fixed price contract has been negotiated with the firm of Rist Frost Associates (RFA) of Glens Falls, New York. RFA will be the Authority's principal contractor throughout the project. The firm's major responsibilities will encompass the performance of all engineering design and acting as liaison between the Authority and its subcontractors namely General Electric, NCG Industrial Gases and the Village of Potsdam. Phases I and II will cost $320,000 of which USDOE will contribute $174,900. The termination of phase II will constitute a major decision point regarding the continuation of the project into phase IV or the construction phase. It is presently projected that operation will begin in the Spring of 1982.

STUDY OF THE BEHAVIOR OF GAS DISTRIBUTION EQUIPMENT IN HYDROGEN SERVICE — PHASE II

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Abstract

To study the characteristics of gas distribution pipe in hydrogen service, a series of test loops and experiments were designed. In experiments with three types of commercially available polyethylene natural gas piping, hydrogen permeation was found to be 4 to 6 times greater than methane permeation. Ring tensile tests showed no significant difference in apparent strength of exposed and as-received pipe samples, although the exposed specimens show greater elongation after testing to failure. Leakage experiments with methane-hydrogen blends showed no selective leakage of hydrogen via Poiseuille, turbulent, or orifice flow through leaks. Leak rates increased with increasing pressure and decreasing specific gravity. Analyzing these results along A.G.A. data, the investigators concluded that 13.7 X 10^6 SCF of natural gas could be lost annually in the U.S. by permeation; if hydrogen were distributed, the comparable loss would be 67.4 X 10^6 SCF. Similarly, a total conversion from natural gas to hydrogen would produce an increase in unaccounted-for gas loss from 236 X 10^9 SCF to 693 X 10^9 SCF annually. This conclusion is based on the worst-case assumption that all unaccounted-for gas loss is leakage.

Introduction

This program is part of a multiyear effort to supply needed information about hydrogen delivery in natural gas distribution equipment. The overall program will identify operating, safety, and materials problems associated with the use of hydrogen in conventional distribution systems. One of the major incentives behind nonfossil-based hydrogen as a future supplement and eventual replacement for natural gas is the expectation that the existing gas delivery system can be used without major modifications.

In Phase I, under DOE Contract No. EY-76-C-02-2907, IGT conducted an experimental study with contemporary gas distribution equipment in hydrogen service.[1] The observations and results of two test loops initially operated on natural gas (baseline) and then on cylinder-grade hydrogen for 6 months indicate no major incompatibilities in performance. Existing in-place components and piping (with the possible exception of meters) should be adequate for hydrogen delivery. The observed overall hydrogen-to-natural gas volumetric leak ratio ranged between 3.00 and 3.35 and the overall energy loss ratio ranged between 1.00 and 1.04. In isolated situations, the difference in pipe-flow characteristics of hydrogen may necessitate a small increase in delivery pressure to provide equivalent energy delivery. Experiments in a third test loop demonstrated that the Joule-Thomson hydrogen effect of heating upon expansion is minute, and does not affect distribution operations. Hydrogen leaks to the atmosphere will not ignite spontaneously without an ignition source; hydrogen escaping from a leak expands somewhat adiabatically and cools. Short-term (6 months) exposure to hydrogen did not significantly affect the properties of the metallic materials of system components. Some plastic products, lubricants, and adhesives were affected by the exposure.

In general, the results and observations in Phase I indicate that, for short-term exposure, contemporary distribution equipment is suitable for hydrogen service (except for certain lubricants and adhesives and for meter capacity to deliver an equivalent amount of energy). However, before hydrogen can be utilized as a universal fuel, or as supplemental fuel, a number of problems must be addressed. Among the problems to be addressed by Phase II are a) experimentially determining the absolute and relative permeabilities of commercially available plastic gas distribution piping for hydrogen and methane, b) experimentally characterizing leakage of hydrogen-methane blend through orifices (simulated leaks), and c) assessing the impact of selective leakage via permeation and/or orifice flow on the distribution of hydrogen and blends of hydrogen and methane.

Permeability Investigations

Mass Transfer Mechanism

The transmission of gas through a plastic material has been studied and described by many investigators. Gas flow is visualized as a complex transport process caused by a partial pressure differential between the two sides of the material. It requires a) adsorption and solution of a component on the high-pressure side, b) diffusion through the material under a concentration gradient, and c) desorption and evaporation on the low-pressure side. Diffusion is the rate-determining process, and under steady-state it obeys Fick's law. The flow through a polymeric material is expressed as —

$$q = \frac{DSA\ (p' - p'')t}{\ell} = \frac{PA\ (p' - p'')t}{\ell}$$

where —

q = amount of gas diffusing

D = diffusion constant

S = solubility constant

A = area

p' = high pressure

p'' = low pressure

t = time

ℓ = thickness

P = DS = permeability constant

Materials

Acrylonitrile-butadiene-styrene (ABS), cellulose-acetate-butyrate (CAB), polyethylene (PE), and polyvinyl chloride (PVC) are the only plastic materials used in significant quantities for gas distribution. CAB pipe was introduced in 1942 when steel pipe was in short supply. PE pipe was developed in 1948, and in 1949 it became the fastest growing plastic pipe material. ABS pipe appeared around 1954, and it offered higher tensile strength and heat distortion temperatures than CAB. ABS pipe soon forced CAB pipe off the market, except for some very special applications, among them gas service relining.

PVC pipe appeared around 1955 in Europe and began to compete with ABS. Test data showed that PVC could be assigned a 2000-psi design stress rating, while ABS earned only 1000 psi. This eliminated ABS as a pressure pipe contender, except where its unique properties were required. PVC pipe was not accepted readily. Factors that deterred its use were a) difficulty with achieving sound solvent joints; b) suspect ductility; c) lack of availability in coiled lengths.

Currently, PE is the only plastic pipe material of interest in North America for gas distribution. DuPont, Phillips, and Gulf (under Phillips' license) are the primary polyethylene pipe resin manufacturers. DuPont extrudes pipe from its own resins. Phillips both produces pipe from its own resins and sells resins to other pipe extruders, whereas Gulf only sells resins. Plastic pipe designated as PE-2306, PE-3406, and PE-3408 is currently available for gas distribution applications. PE-3306 is now primarily used as irrigation piping.

Permeability Apparatus

Figure 1 shows various subassemblies of the permeability cell. The cell was designed to accommodate a 2-inch ips SDR-11 plastic pipe; OD averages 2.375 inches, and the minimum wall thickness is specified as 0.216 inches. The cell is constructed from 6061-T6 aluminum pipe, bar stock, and tubing; joining was accomplished by dip brazing. A plastic pipe specimen (item D) is inserted into the housing (item C). Preinstalled EPR O-rings (item B), in the two collars of the housing, seal the annular space between the housing and the pipe OD. Two identical plugs with EPR O-rings (items A and E) are inserted into the pipe specimen and then fastened to collars of the housing with lock washers and cap screws. One-quarter-inch pipe taps in the plugs facilitate flushing and pressurization of the specimen with the test gases, whereas 1/4-inch tubes on the housing facilitate flushing of the annular space, collection/sampling of permeated gas, and measurement of annulus pressure.

Figure 2 shows the permeability test setup. Six cells are being utilized for hydrogen and two cells for methane. Common manifolds supply hydrogen, methane, and nitrogen from gas cylinders. Each cell has its own sample collection bottle, pressure gauge, and mercury manometer.

Test Procedure

Samples of regular production PE gas pipe were cut to an appropriate length, and the OD and wall thickness were measured. The samples were assembled into the apparatus and leak-tested. Then, the volume of the annular space was determined using the gas law relationship $P_1V_1 = P_2V_2$.

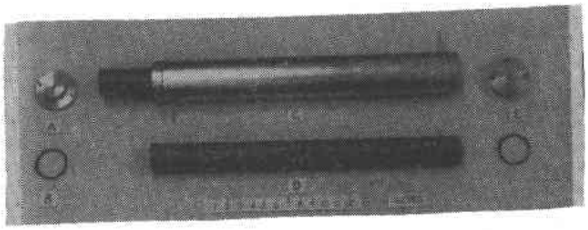


Fig. 1 Permeability cell subassemblies.

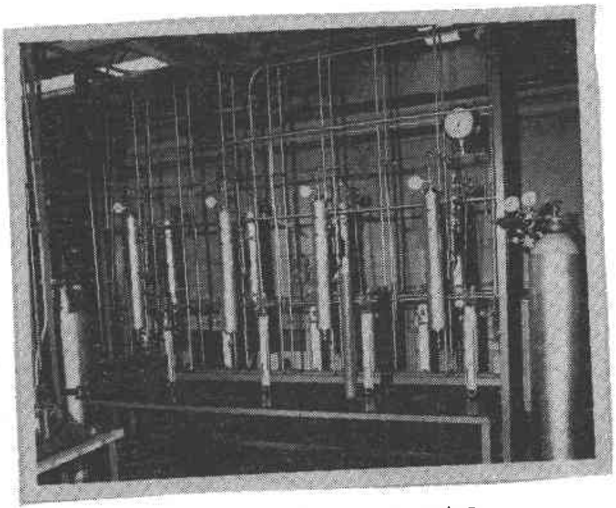


Fig. 2 Permeability test setup.

The permeation cells were connected to a single pressure-regulated source of hydrogen or methane and flushed. At the same time nitrogen was used to purge the annular space of air. The pressure of the annular space was reduced to atmospheric and the pipe sample pressurized to 60 psig with hydrogen or methane. The pressure in the pipe samples was maintained at 60 ± 0.5 psig and the temperature was maintained at 70 ± 2°F, throughout the testing.

Permeability Results

Table 1 presents the permeability constants of various PE pipe specimens as determined by gas law relationships and gas analysis of the annular space with a mass spectrometer. The data correlate with values reported in the A.G.A. Plastic Pipe Manual for Gas Service[2] for PE-2306.

Ring Tensile Tests

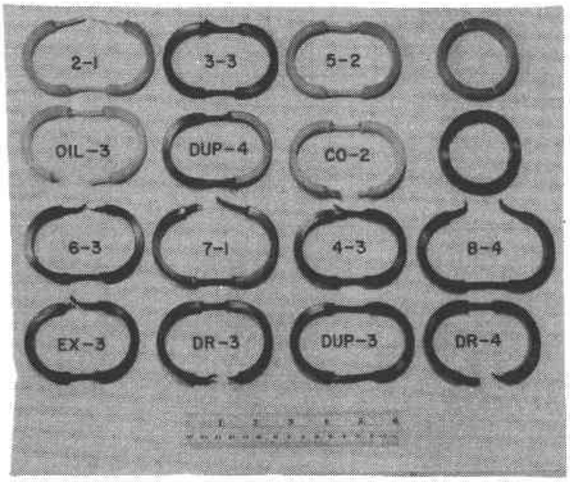
Procedure

Ring tensile test specimens were prepared from permeability-exposed PE pipe samples and from as-received (virgin) PE pipe samples. Four rings of each specimen were prepared. Ring tensile tests per ASTM D 2290-76, "Standard Test Method for Apparent Strength of Ring or Tubular Plastics by Split Disc Method," were performed on the specimens of plastic

Table 1 Permeability constants

PE pipe sample	Gas permeability constant, $\frac{ft^3\text{-mil-day}}{ft^2\text{-atm-day}} \times 10^{-3}$ H_2	CH_4
Continental Industries 2306	20.5	ND
DuPont 2306	25.6	5.6
DuPont 3406	17.2	4.1
Nipak 2306	19.6	ND
Nipak 3406	20.4	3.2
Oil Creek Plastics 2306	25.6	ND
Phillips 2306	17.6	3.1
Phillips 3406	30.8	6.8
Phillips 3408	28.7	7.1
Plexco 2306	20.4	3.4
Plexco 3406	16.1	2.8
Tex-Tube 2306 (black)	19.3	ND
Tex-Tube 2306 (orange)	18.6	ND

ND = Not determined.



Identification Key

2-1	Oil Creek Plastics 2306, H_2-Exposed
Oil-3	Oil Creek Plastics 2306, As-received
3-3	DuPont 3406, H_2-Exposed
DUP-4	DuPont 3406, As-Received
5-2	Continental Industries 2306, H_2-Exposed
CO-2	Continental Industries 2306, As-Received
6-3	Plexco 3406, H_2-Exposed
EX-3	Plexco 3406, As-Received
7-1	Phillips 3408, H_2-Exposed
DR-3	Phillips 3408, As-Received
4-3	DuPont 3406, CH_4-Exposed
DUP-3	DuPont 3406, As-Received
8-4	Phillips 3408, CH_4-Exposed
DR-4	Phillips 3408, As-Received

Fig. 3 Ring sample comparisons after failure.

pipe. The tests were run in a 10,000-lb capacity Instron Universal testing machine that makes chart records of load versus displacement.

Ring Tensile Test Results

Comparison of apparent strength data shows few differences of any statistical significance between as-received and exposed samples. Differences in apparent strength are greater between different types of plastic than between as-received and exposed samples.

Figure 3 compares the elongation observed after failure with permeability-exposed and as-received specimens. The exposed pipe samples show more elongation than the corresponding as-received samples, for both hydrogen and methane exposure. The results verify the greater elongation of exposed PE pipe samples previously observed in Phase I.

Hydrogen/Natural Gas Leakage Investigations

Mass Transfer Mechanism

If there is a pressure difference across a microporous solid, mass transport can proceed by several mechanisms: a) molecular effusion, b) molecular streaming or Knudsen flow, c) streamline or Poiseuille flow, d) turbulent flow, and e) orifice flow. Poiseuille, turbulent and orifice flow are the most common types, being a function of micropore geometry, gas density, gas viscosity, and mean pressure; they are classified as nonseparative.

Knudsen flow and/or molecular flow are separative flows. The difference in flow rates of the various gaseous species depends upon the relative frequency with which molecules of the various components strike the surface; that is, the more frequently they strike the surface, the greater the probability of their entering a micropore. Because each component of a gaseous mixture has the same average kinetic energy, this frequency is directly proportional to their molecular weights. Hence, in a mixture of gaseous molecules, the lighter component will permeate more rapidly than the heavier component. The lighter and heavier molecules will both pass through the microporous medium, but in a given time interval more lighter molecules will permeate, and the abundance of lighter molecules will be greater on one side of the microporous medium than the other.

Microporous Structure

Separative flows depend upon the relation between the capillary diameter of the microporous medium and the mean free path, λ, of gas molecules. The pores must be of such size and relation to the mean free paths of the gaseous components that intermolecular collisions are avoided as much as possible. The pore diameters must therefore be appreciably less than λ. At standard conditions of temperature and pressure, the λ of CH_4 is about 165 angstroms, and the λ of H_2 is about 3000 angstroms. The microporous medium must have pore sizes considerably smaller to produce molecular flow and the separation phenomenon.

If the pore diameters are small in comparison with λ, flow takes place by molecular effusion following Knudsen's law. A λ/d ratio of 2.5 is often the practical limit; however, reasonably good separations have been achieved at a ratio of 1. In a microporous solid with capillaries of various diameters both Knudsen and Poiseuille flow may occur.

Adsorptive Flow

Microporous solids are capillary systems, and therefore exhibit varying degrees of adsorptive activity. This gives rise to adsorbed or surface flow from concentration gradients due to excessive adsorption of, usually, the heavier molecules within the porous matrix. The process produces flow rates that are greater than those predicted on the basis of molecular weight, thus partially nullifying the Knudsen effect. Investigators have shown by experiments that vapor mixtures and gas-vapor mixtures cannot be expected to separate in the direction predicted by the square root of the inverse ratio of component molecular weights.

Leakage Test Setup

The residential commercial test loop (RCL) developed in Phase I was modified and refurbished; see Figure 4. A single-stage compressor circulates gas through the closed loop system at a rate of about 900 SCF/hr with an intake pressure of 5 inches w.c. and a discharge pressure of 65 psig. Surge tanks are provided on either side of the compressor to dampen pressure pulsations.

Flow from the compressor is regulated from 65 psig at a regulator station to 54 psig and then flows into a 1-1/2-inch steel manifold with four parallel branches. One of the four branches is the primary bypass. The flow through the primary bypass is controlled by valves and is metered using a glass tube flowmeter at 54 psig. Pressure is dropped to 8 inches w.c. through a regulator prior to joining up with the compressor intake piping.

Two of the four branches feed into two different service regulators that reduce the pressure to 8 inches w.c. and 9 psig prior to being routed through two diaphragm meters. Flow is controlled by adjusting spring tension on the service regulator. Three capillary tubes with diameters of 0.003 inch, 0.010 inch, and 0.030 inch, and a 15 micron-sized sintered stainless steel disc were potted in four different Swagelok male connectors and then attached to the branches at three different pressures: 54 psig to simulate high-pressure distribution, 9 psig to simulate medium-pressure distribution, and 8 inches w.c. to simulate low-pressure distribution.

Test Procedure

The modified RCL was initially purged with nitrogen and then purged and filled with a mixture of hydrogen and methane (for example, 40% hydrogen and 60% methane). After about 1 hour of operation, the four potted test fittings were connected to one of the three pressurized loops (54 psig). The simulated leaks (test fittings) were opened (allowed to leak) via a valve, samples of leaking gas were collected for analysis, and leak rates of the simulated leaks were measured. A sample of the gas circulating in the RCL was also collected for analysis.

After the sample collections and leak-rate determinations were completed at one pressurized loop, the four potted test fittings were removed and connected to another pressurized branch (9 psig). Then, gas samples were collected and leak rates were determined for the sintered disc and capillaries at this pressure. The procedure was repeated again at the last pressure condition (8 in. w.c.). After the leakage tests were completed, the RCL was vented to the atmosphere and purged with nitrogen.

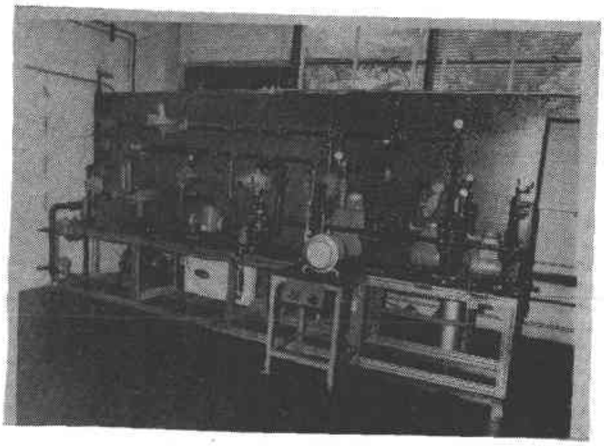


Fig. 4 Modified residential/commercial loop

The procedure of purging the RCL initially with nitrogen, and then purging and filling with another mixture of hydrogen and methane (20% H_2 and 80% CH_4, or 10% H_2 and 90% CH_4) was repeated. The same set of simulated leaks (test fittings) was utilized and the same procedure of collecting leakage samples and determining leak rates was repeated, until the leakage investigations were completed.

Samples of the gas circulating in the test loops and samples of the gas leaking from the simulated leaks were collected in 150 ml stainless-steel sampling cylinders and then analyzed by mass spectrography. Leak rates from the simulated leaks were measured with a wet-test meter and/or with a bubble piston.

Leakage Test Results

Table 2 presents the results of the leakage tests with circulating mixtures of hydrogen and methane (approximately 10%, 20%, and 40% hydrogen). The data show that there is no selective leakage of hydrogen via orifice flow on the distribution of blends of hydrogen and methane — the composition of the gas circulating in the test loop and the composition of the gas leaking through the simulated leaks did not change. As expected, the leak rates of the simulated leaks increased with increasing pressure and increasing hydrogen content (decreasing specific gravity).

Analysis and data correlations show that the ratios of flow rates of the simulated leaks are equivalent to the ratios of the square roots of their specific gravities. Thus, the leakage (volumetric) of one gas can be estimated by multiplying the known volumetric leakage of another gas by the appropriate inverse square root specific gravity ratio.

Table 2 Flow rates and gas compositions of simulated leaks with RCL tests

		40% H_2 — 60% CH_4			20% H_2 — 80% CH_4			10% H_2 — 90% CH_4		
Simulated Leaks	Pressure	Flow Rate, cm^3/s	% H_2	% CH_4	Flow Rate, cm^3/s	% H_2	% CH_4	Flow Rate, cm^3/s	% H_2	% CH_4
Sintered Disc	54 psig	786.6	38.98	60.49	723	19.38	80.22	720.6	9.35	90.35
0.03 in.	54 psig	449.5	39.11	60.33	425.8	19.31	80.26	393	9.34	90.37
0.01 in.	54 psig	48.5	39.07	60.05	45.3	19.31	80.28	42.3	9.10	90.58
0.003 in.	54 psig	11.1	39.00	60.47	10.4	19.35	80.23	9.6	9.29	90.42
Sintered Disc	9 psig	252.8	39.30	60.48	240.1	19.40	80.33	235.8	9.37	90.33
0.03 in.	9 psig	172.7	39.25	60.58	153.9	19.06	80.29	142.8	9.43	90.27
0.01 in.	9 psig	17.8	39.36	60.45	16.7	19.36	80.40	14.4	9.33	90.36
0.003 in.	9 psig	2.2	39.34	60.51	2.0	19.39	80.38	1.8	9.76	89.97
Sintered Disc	8 in. w.c.	29.7	39.22	60.34	29.2	19.41	80.37	28.8	9.21	90.53
0.03 in.	8 in. w.c.	24	39.21	60.46	23.6	19.34	80.42	23.4	9.32	90.35
0.01 in.	8 in. w.c.	1.8	39.60	60.08	1.7	19.43	80.3	1.7	9.46	90.23
0.003 in.	8 in. w.c.	0.07	39.19	60.62	0.07	19.44	80.37	0.06	9.37	90.33
Test Loop			39.30	60.54		19.39	80.40		9.35	90.35

Analysis/Assessment

Permeability

A recent survey reports that the total plastic pipe mileage installed by U.S. gas distribution utilities is now 154,276 miles.[3] Of this total piping installed, 46.9% is 1 inch and under in size, 41.5% is in the 1-1/4-inch to 2-inch range, 7.5% is 3 inches, 3.4% is 4 inches, and 0.7% is larger than 4 inches. Polyethylene dominates the market; PE is used by 95.1% of all companies installing plastic pipe today.

From the above data the log mean circumferential area of the installed plastic piping was calculated. Using the hydrogen permeability data developed in Phase II and A.G.A. data, the quantities of hydrogen and methane permeating the piping were calculated. Assuming an operating pressure of 60 psig and assuming PE-2306 piping, the losses by permeation of various gases could be as shown in Table 3.

Leakage

The A.G.A.'s Gas Facts reports that unaccounted-for gas ranged between 0.2369% and 1.934% in the period 1968 to 1977 inclusive, and averaged 1.363%.[4] Unaccounted-for gas is the difference between purchases and sales; it includes losses and inaccuracies resulting from time lag between meter-reading dates or sales, and the border-station or city-gate readings representing purchases. Assuming the "worst-case condition," that unaccounted-for gas represents leakage, and utilizing the square-root specific gravity relationship with an annual consumption of 17,328,767 X 10^6 SCF of natural gas, the U.S. distribution losses of various gases could be as shown in Table 3.

Table 3 Losses by the U.S. gas distribution system by permeability and unaccounted-for gas

	Gas losses, 10^6 SCF/yr	
Gas	Permeation	Unaccounted-for gas
Natural gas (CH_4)	13.4	236,191
Hydrogen	67.4	693,530
10% H_2 - 90% CH_4	H_2 = 6.8	H_2 = 25,727
	CH_4 = 12.0	CH_4 = 231,548
20% H_2 - 80% CH_4	H_2 = 13.5	H_2 = 51,114
	CH_4 = 10.7	CH_4 = 216,455
40% H_2 - 60% CH_4	H_2 = 26.9	H_2 = 121,920
	CH_4 = 8.04	CH_4 = 182,880

Acknowledgements

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Continental Industries
Tulsa, Oklahoma

E. I. DuPont de Nemours and Company
Wilmington, Delaware

Nipak, Inc.
Dallas, Texas

Oil Creek Plastics
Titusville, Pennsylvania

Phillips Products Co.
Dallas, Texas

Plexco
Franklin Park, Illinois

Tex-Tube Division of Cyclops Corporation
Houston, Texas

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CONTAINMENT MATERIALS: STATUS AND SUMMARY

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Abstract

The final summary of the hydrogen containment materials program accomplished under the technical leadership of NASA-Ames Research Center for the DOE is presented. The safe, reliable, and economic containment of hydrogen is essential to the success of virtually any hydrogen energy transport and storage scheme. The potential problems associated with hydrogen containment are great. A brief review of some of these problems is also presented.

Hydrogen Containment

The well known ability of hydrogen to degrade almost all containment materials together with our lack of information on detailed aspects of hydrogen degradation makes the reliable, long-term containment of hydrogen a difficult task. Containment problems are most apparent in high pressure gaseous hydrogen storage systems where hydrogen is in intimate contact with the containment vessel and temperatures are sufficient to impart significant mobility to the hydrogen molecule or atom. Problems conceivably can exist in liquid hydrogen containment systems or with hydride beds where catalytic influences, long-term exposure, and other such considerations are presently unpredictable.

The process of hydrogen degradation of containment materials is a very complicated process and is influenced by a large number of variables. Virtually all metallic structural materials can be degraded by hydrogen. Most forms of degradation are time-dependent and are influenced by the specific aspects of the service environment. Time is a factor because hydrogen must move in sufficient quantities to a point on or within the containment material where degradation will occur--the required time may be a day, a month, a year, or ten or more years. The service environment is important because it can influence both hydrogen movement as well as the severity and form of hydrogen degradation--the important aspects of the service environment include mechanical, thermal, and chemical considerations. To quantify and predict the process requires much detailed information. Figure 1 is a montage to illustrate the complexity of hydrogen degradation. To reliably predict the safe, long-term containment of hydrogen is to understand and predict long-term, individual influences based upon a specific containment material exposed to a specific service environment.

In terms of hydrogen containment for hydrogen-energy schemes, economic factors will almost certainly require a major use of carbon and low alloy steels rather than austenitic stainless steels. Although austenitic stainless steels are, in general, much less susceptible to hydrogen degradation, the relatively high cost will preclude their use for all but the most critical applications. Of commonly used containment materials, probably the least well understood in regard to hydrogen degradation are carbon and alloy steels. Much of what is known has been gained through the DOE Containment Materials effort, yet much remains to be understood.

Based on our present state of knowledge, a major area of concern is the use of carbon and low alloy steels in cyclic loading and the subsequent hydrogen-enhanced fatigue damage. Any large storage or transport system, a pipeline for example would most probably require large welded sections which could potentially contain numerous flaws. Operating pressures could be in excess of 2000 psi with in-line compressors. Cyclic stresses could not be avoided. A primary question which remains to be answered is what will be the long-term degrading effect of hydrogen under these operating conditions?

Containment Materials Program

The containment materials program had the overall objective of helping to develop the understanding required for the economic, safe, long-term containment of hydrogen. Specifically, through the use of model environments, a detailed knowledge of hydrogen degradation of carbon and low alloy steels was to be developed. These tests determine the influences of both metallurgical and environmental parameters, such that existing low cost materials, having intermediate to long-term hydrogen compatibility, could be identified; new, inexpensive and highly compatible alloys could be developed; and reliable accelerated testing techniques and life prediction methods could be established. The program contained both fundamental and applied elements including an experimental pipeline-loop on which service experience was gained.

Although the containment materials program has had a relatively short life, a significant increase in our understanding of hydrogen degradation of carbon and low alloy containment steels has been attained. Probably the most significant finding is that these containment steels can be severely degraded by the presence of hydrogen, but, in a manner considerably different than that observed for the extensively studied, higher strength, martensitic steels. Our findings indicate that the primary mechanism of hydrogen degradation in low-strength steels is different than in the high-strength steels and, therefore, much of the information available on degradation of high-strength steels does not appear to be applicable to the behavior of low strength steels in hydrogen.

A few of our more notable findings are as follows:

- Surface cracks can initiate more easily in the presence of gaseous hydrogen.

- Unlike high strength steels, a crack initiated in a low-strength steel will not grow if the stress is held constant.

- If the stress is cycled, an initiated crack will grow very rapidly in gaseous hydrogen--up to 100 times more rapidly than in dry air.

- The fatigue crack growth threshold is lowered in hydrogen: a crack may grow at low cyclic loads in hydrogen but may not grow in an air environment.

- For high stresses and short cracks or low stresses and long cracks, the fracture toughness (onset of unstable crack growth) is greatly reduced by the presence of gaseous hydrogen or a hydrogen-containing environment.

- In hydrogen/methane blends, hydrogen degradation is directly related to the concentration of hydrogen present and is unaffected by the presence of methane--methane is inert to these containment materials at all temperatures up to 375°C.

- Degradation of a containment material in contact with a hydride ($FeTiH_x$) is no greater than degradation as the result of an equivalent hydrogen partial pressure in the gase phase.

- Other chemical species in the environment can reduce the severity of hydrogen degradation--notably O_2, H_2O, SO_2, and CO.

- Stress state should be considered in the design of a vessel--materials may be more susceptible to "delayed hydrogen degradation" as the stress state changes from uniaxial to biaxial to triaxial.

- It is possible to improve the fatigue resistance of a commercial containment material by proper heat treatment (selection of microstructure)--the martensitic structure is more fatigue-resistant than the ferrite/pearlite structure.

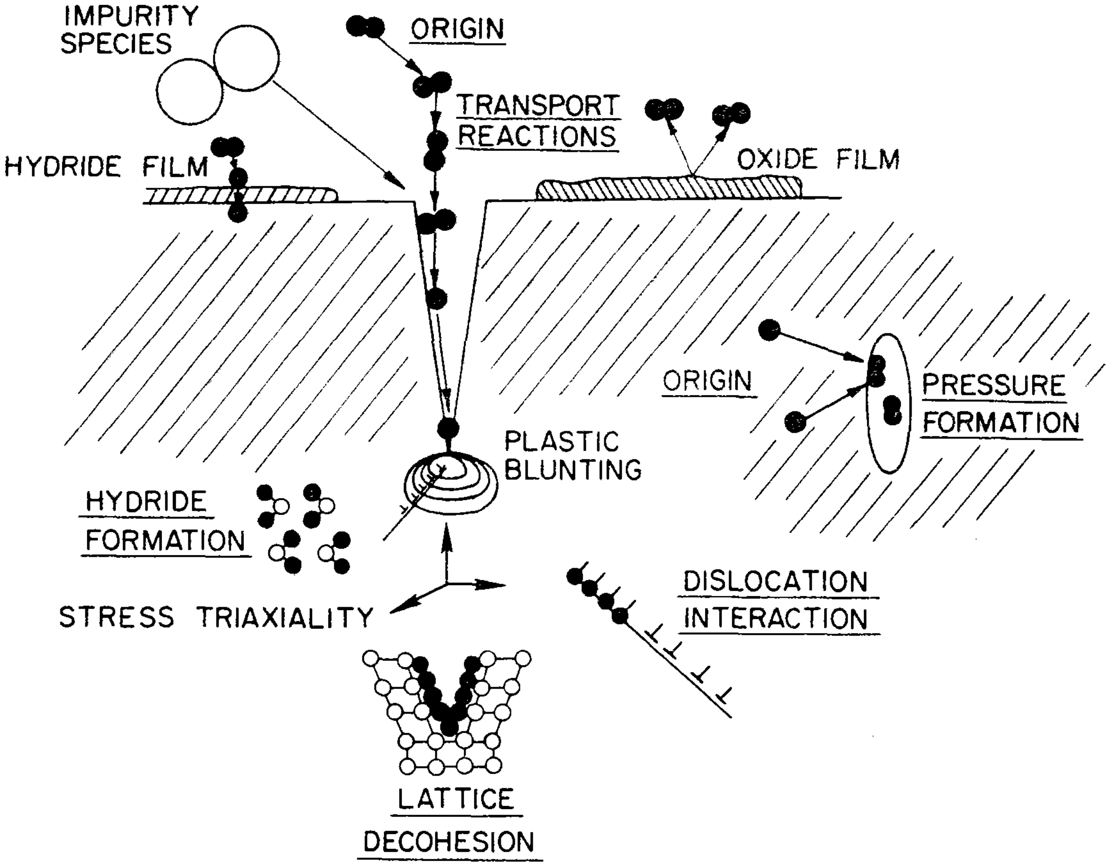
- Laser beam welding can produce weldments of comparable quality to those produced by gas-tungsten arc and electron beam welding. Laser beam welding is at least as compatible with hydrogen as the more commonly used techniques.

- Finally, extensive and invaluable experience has been gained from the exposure of flawed carbon and low alloy steels to a simulated service environment--experimental pipeline-loop.

In conclusion, much information has been gained from the NASA-lead, DOE Containment Materials Program. However, the economic, safe, long-term containment of hydrogen is not yet possible.

FIGURE 1

MONTAGE OF HYDROGEN CONSIDERATIONS



PRODUCTION COST COMPARISONS OF HYDROGEN FROM FOSSIL AND NUCLEAR FUELS AND WATER DECOMPOSITION*

by

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Abstract

At the present time, hydrogen is produced almost exclusively from petroleum residual oils and natural gas, and used primarily in petroleum refining product upgrading and as a feedstock in chemical processes. However, since these conventional feedstocks can be expected to escalate greatly in price over the next two decades, alternative methods of producing hydrogen must be developed that are less affected by the dwindling of fossil fuel supplies, particularly petroleum and natural gas. As the relative price movements continue, the alternative methods, coal conversion and hydrogen produced from decomposition of water, begin to offer hydrogen, first, at prices that are competitive in feedstock applications and eventually at prices that will make the use of hydrogen on a large scale, as a general purpose fuel, feasible.

This study examined the comparative costs entailed in producing hydrogen by major technologies that rely on petroleum, natural gas, coal, thermochemical cycles, and electrolysis.

Since the different sources of available data and published studies could not be assessed directly due to differences in size and in economic and technical bases, techniques were developed for comparing these processes by formulating the process data and economic assessments on a uniform and consistent basis. These data were then normalized to permit a meaningful comparative analysis of product costs of these processes through the year 2020. These cost projections are shown in Figure 1, Hydrogen Production Costs.

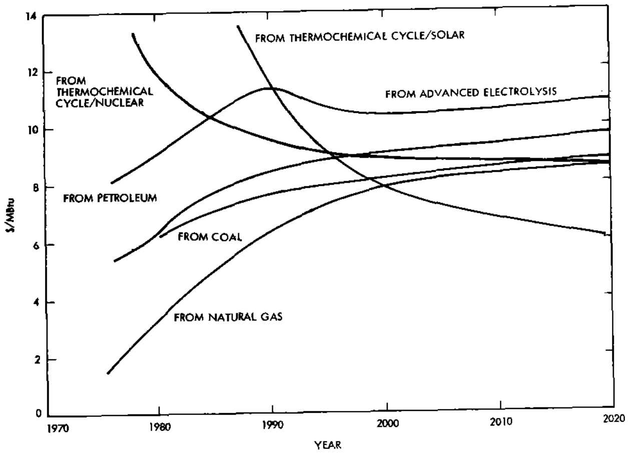

Figure 1. Hydrogen Production Costs (1979$)

Table 1. Hydrogen Production Costs (1979$/MBtu)*

	1980	1985	1990	2000	2020
Natural gas	3.2	5.0	6.3	7.8	8.5
Petroleum	6.3	7.7	8.4	9.1	9.7
Coal	6.1	7.0	7.6	8.2	8.8
Advanced electrolysis	9.0	10.4	11.4	10.4	10.8
Nuclear (HTR) thermochemical	12.0	10.3	9.5	8.9	8.5
Solar thermochemical	-	-	11.6	7.8	6.0

Summary

Hydrogen production from natural gas is and remains the least expensive option through CY 2000, although limited availability may preclude its large scale use. Hydrogen costs from petroleum increase in the same ratio as natural gas, starting to level off about 2000.

If hydrogen were produced from coal today, it would cost about $6/MBtu, about the same as petroleum-derived hydrogen.

Thermochemical cycles can be expected to become cost competitive with fossil fuels around 1995, assuming substantial process development and demonstration work continues and the economies of large scale facilities are realized. The production costs for hydrogen of less than $9/MBtu by the year 2000 are obtainable from thermochemical cycles utilizing a captive high temperature helium cooled nuclear reactor for process thermal heat. The cost goals for solar-thermochemical cycles show a hydrogen cost of $6/MBtu by 2020. These costs are not calculated but are cost goals which have been set and can only be realized if the capital costs of the solar processes meet these anticipated projections.

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*The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, and was sponsored by the U.S. Department of Energy through an agreement with NASA.

The cost of producing hydrogen by electrolytic processes will remain high, over $10/MBtu, and will increase more as electricity rates escalate with fossil fuel prices. By 1990, production of energy by high-temperature nuclear reactors may reach commercial feasibility and begin to provide a good share of the electrical energy required. This new energy source will then tend to stabilize overall production costs for electrolytic hydrogen at about $10/MBtu.

Hydrogen production costs versus time, for the various processes considered in the study, are presented in Figure 1 and Table 1.

Background

Basis for Study

1. Energy Pricing

The developed costs for energy are shown in Figure 2, Energy Costs (1979$), for the different forms of energy through the year 2020. The energy price levels for fossil fuels and electricity were developed from base data contained in the JPL Reference Scenario on Energy Prices. These projections were adjusted in line with current and historical pricing trends in world energy prices. The basic assumption is that petroleum and natural gas will continue as the dominant energy sources until the year 2000 when coal conversion, now a mature technology, becomes dominant thereafter. The price increases for petroleum bring oil costs up to a more realistic inflated value, in line with other worldwide commodities and should stabilize by 1990 when new oil finds and secondary recovery methods are in full production. Petroleum prices escalate at about 5%, decreasing to about 2% per year near the end of the decade. Natural gas prices follow oil in price but at a more accelerated pace and approach petroleum pricing levels over the next decade. Natural gas prices will escalate about 10% per year through 1990, then slowing down and reaching parity with petroleum about the year 2000.

Electrical energy prices are expected to continue rising at a constant rate with fossil fuel prices until 1990. At this time, energy from high temperature reactors should be available and stabilize electrical energy costs at about $10/MBtu.

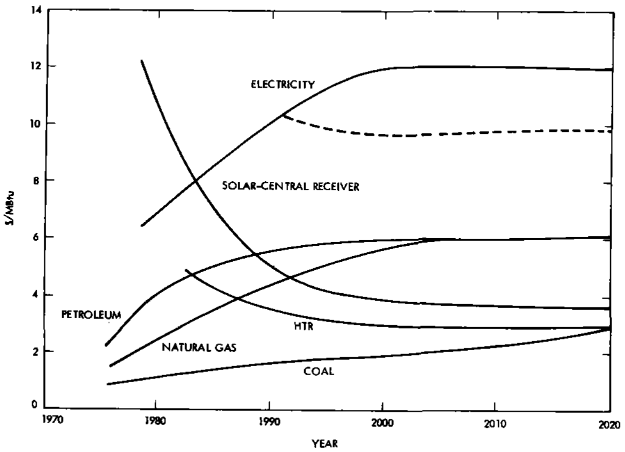

Figure 2. Energy Costs (1979$)

Projection of the cost of energy from coal, which is currently priced very low compared to European prices and the derived hydrogen energy from petroleum (less than half), should increase at about 5% per year, doubling by the year 2000. Projected coal prices, because of the many factors involved, are decidedly in a speculative and unclear position.

The cost of energy from high-temperature central-receiver solar systems is based on current second-generation facility evaluations and the expectation of important technological breakthroughs in increased process efficiency. The projected cost goal for the year 2000 is about $4/MBtu.

It is expected that thermal energy will be produced commercially and competitively from high temperature reactors by the year 1990. High temperature thermal nuclear reactors, operating captively, in conjunction with hydrogen production processes such as thermochemical processes or advanced electrolysis systems, offer the potential of unlimited amounts of clean energy by the year 2000.

2. Production Costs

Figure 1 shows the projected unit cost of hydrogen, as produced by various methods. Detailed studies were made of two technologies, coal conversion and nuclear-thermochemical cycles. For petroleum and natural gas, sufficient data from existing plants were available. Since solar-thermochemical and advanced electrolysis processes are still in an early stage of development, projected cost estimates are quite speculative and are based wholly on published literature.

To determine the cost of coal-derived hydrogen, 36 cost studies and economic evaluations were assessed and normalized to common design and economic parameters. A base case formula was then developed from the generalized data and used in this study.

As mentioned above, in developing the capital investment and production costs for hydrogen from thermochemical processes, a detailed cost study was made. A specific thermochemical process, General Atomics iodine-sulfuric acid cycle, was chosen primarily because the process design has been demonstrated on a laboratory scale and the process shows high overall process thermal efficiencies. Capital cost data and the economic parameters were developed from similar published cost studies. Although the cost data, by definition, is not definitive, the values are considered to be accurate within -10%, +25%.

Petroleum-Derived Hydrogen

The hydrogen production costs presented in this section are based on economic parameter assessments of existing commercial facilities. These manufacture hydrogen from petroleum residual and heavy oils. They use well-established partial oxidation processes, and have been in operation for a number of years.

Capital investments, based on mid-1979 figures, are \$6-9/MBtu/yr. The hydrogen production cost is about \$6/MBtu. This cost is very sensitive to the cost of feedstock, which amounts to 65-85% of the total operating cost. By 1990, the cost of producing hydrogen will be over \$8/MBtu. By the year 2000, total operating costs should stabilize at about \$8-8.50/MBtu.

Hydrogen cost factors, as related to petroleum-derived hydrogen, are as follows:

Partial Oxidation Process

	% of Production Cost
Feedstock cost	83%
Capital recovery cost	13%
Operation and maintenance cost	4%

Maximum size single-train plants, as dictated by economic and shop-fabrication limitations, would have a hydrogen production capacity equivalent to about 20-25 x 10^9 Btu/day. Larger size plants, if required, could be built in multiple trains; investment costs would increase in almost direct proportion.

Natural Gas-Derived Hydrogen

Production costs for hydrogen manufactured from natural gas or other light hydrocarbons are based on current data from existing commercial facilities. The technology is well established; medium-sized plants have been in operation for a number of years. The capital investment for these plants, based on mid-1979 figures, is about \$3-5/MBtu/yr, and the hydrogen production cost is about \$3/MBtu.

For this type of facility, the hydrogen production cost figure is very sensitive to the cost of feedstock, since the latter makes up 70-90% of the total operating cost. Future price projections are therefore heavily dependent on energy prices and escalate in the same proportion. By 1990, production cost will have risen, in line with energy costs, to over \$6/MBtu and by the year 2000, to about \$8/MBtu.

Hydrogen cost factors, as related to natural gas-derived hydrogen, are as follows:

Steam Reforming Process

	% of Production Cost
Feedstock cost	89%
Capital recovery cost	8%
Operation and maintenance cost	3%

The maximum capacity of the optimal steam-reforming facilities is about 20 x 10^9 Btu/day as compared with 350 x 10^9 Btu/day for economical coal conversion units.

Hydrogen From Advanced Electroytic Processes

The cost of producing hydrogen by electrolytic processes is expected to remain high - over \$10/MBtu - and to go even higher as electricity rates escalate with fossil fuel prices. Electricity accounts for 80% of the total operating cost of producing hydrogen electrolytically; achievement of overall efficiencies exceeding 35-40% is doubtful. However, by 1990, the production of energy by high-temperature reactors (HTR) may reach commercial feasibility. This thermal energy, which will become competitive in cost with other energy sources, will tend to stabilize overall production costs for electrolytic hydrogen at about \$10/MBtu. Energy costs, as a function of total operating costs, would decrease from 80-85% to about 30% of total operating costs. These production costs would still remain high, however, because the total plant investment for the HTR energy-coupled plants would increase and make manufacturing costs very capital cost-sensitive.

Total plant investments would be, in 1979 dollars, \$30-45/MBtu/yr. With increased process and mechanical efficiencies, evolved from further development and technology, overall investments could decrease, before the year 2000, to about \$25/MBtu/yr.

Hydrogen from Thermochemical-Solar Energy Sources

Thermochemical hydrogen costs, for processes utilizing solar energy sources, are very speculative and are based on solar energy cost projections of about \$4/MBtu in the year 2020. Adjusting this figure back to CY1979 dollars shows solar energy costs of over \$12/MBtu (see Figure 2). These projections are based on decreased capital and operating costs attributable to ultimate mass production of solar components, lower cost materials, and substantial technology gains over the next two decades. The total investment cost for solarthermochemical coupled processes, based on mid-79 prices, will be \$75-100/MBtu/yr. By 1990, the total capital investment could decrease to \$25/MBtu/yr, and by the turn of the century, to about \$8/MBtu/yr.

Coal-Derived Hydrogen

An initial assessment of published coal conversion process studies was made, which included 36 separate economic evaluations of 23 different processes. Twenty studies were eliminated because of extreme dissimilarities in the baseline parameters used. The remaining cases consisted primarily of processes for which process development was complete, or nearly so, having been proved commercially or tested in pilot plant or demonstration units. These cases showed good economic reliability, with most of the cost data on a firm basis. The data were then normalized to a common basis, using the EPRI Technical Assessment Guide as the format.

Development of a standardized format was predicated on a normalization of the data on the following basis:

(1) The plant is a large, self-contained coal conversion facility placed on a previously undeveloped site and hydrogen gas is its principal product.
(2) All costs are in mid-1979 dollars.
(3) Construction commences in 1979; the plant is completed and on-stream in 1984.
(4) Hydrogen purity - 95% by volume.
(5) Capacity - 350 x 10^9 Btu/day.
(6) Capacity factor - 0.9.

(7) Overall thermal efficiency - 55%.
(8) Contingency factor - 30% of total capital cost.

The capital cost, on the above basis, averaged

- o $18/MBtu/yr for the industrial financing case, with 40/60 debt-equity ratio, and
- o $20/MBtu/yr for the utility financing case, with 75/25 debt-equity ratio.

The annual operating cost, on the above basis, averaged

- o 7% of the total capital requirement for the industrial financing case, and
- o 6.5% of the total capital requirement for the utility financing case.

The annual capital recovery and fuel feedstock costs were calculated, based on assumed and defined financial parameters as follows:

Coal cost	$1/MBtu
Inflation rate	9% per year
Debt-equity ratio	
Industrial financing	40/60
Utility financing	75/25
Debt cost	9% per year
Discounted rate of return	15%
Income tax	50%
Taxes and insurance	2% per year
Plant life	20 years
Capital factor	
Industrial financing	15%
Utility financing	9%

Results

Table 2 presents the results of the study of the production cost of coal-derived hydrogen.

Table 2. Production Cost of Coal-Derived Hydrogen

Production Cost Based on Utility Financing (Debt-Equity Ratio = 75/25).
Total capital requirement = $2,200M.

		Annual Production Cost as:	
		% of Total Capital Requirement	% of Total Production Cost
o Annual Production Costs			
Feedstock	$200M	9%	37%
Capital Recovery	$200M	9%	37%
Operation & Maintenance	$140M	7%	26%
Total	$540M	25%	100%
o Total Annual Hydrogen Production		110×10^{12} Btu	
o Hydrogen Production - Unit Cost		$4.90/MBtu	

Hydrogen From Nuclear-Thermochemical Processes

The cost of producing hydrogen in a large-scale plant through the thermochemical decomposition of water was based on the following.

The source of energy for the process was a helium-cooled nuclear reactor having a 1283°K (1850°C) outlet temperature and rated at an energy output of 3,345 MW (thermal). The process chosen for the capital cost estimate is the General Atomic iodine-sulfuric acid cycle. The plant assumed produces 394 x 10^6 SCFD of hydrogen (37.4 x 10^{12}Btu/yr) and operates at an overall thermal efficiency of 46.9%. This very high efficiency was the overriding reason for selecting the General Atomic process; another important consideration was the fact that the total capital requirement, as calculated, was well within 20% of estimates made of two simpler, less capital-intensive, purely thermochemical processes.

Capital Cost Determination

Process Description. Water splitting, as developed by General Atomic, consists of a three-step process employing liquids and gases. The three chemical reactions are

$$2H_2O\ (\ell) + SO_2\ (g) + xI_2 \rightarrow H_2SO_4\ (aq.) + 2HI_x\ (aq.)$$

$$H_2SO_4(g) \rightarrow H_2O(g) + SO_2(g) + 1/2\ O^2(g)$$

$$2HI_x(g) \rightarrow xI_2(g) + H_2(g)$$

The first reaction is conducted at low temperature (230°F) in an aqueous solution. Excess I_2 causes formation of two distinct liquid phases, which are separated by decanting. The lighter phase is primarily H_2SO_4 plus unreacted SO_2; the heavier phase contains hydroiodic acid (HI_x).

The second reaction in this cycle is a high temperature (1600°F) endothermic decomposition of H_2SO_4, a reaction well documented in the literature.

The third reaction is an intermediate-temperature process involving the drying and separation of excess iodine from the HI solution, utilizing concentrated phosphoric acid as a drying agent, and the low-temperature (250°F) catalytic decomposition of HI to product hydrogen and I_2, which is recycled.

The total installed cost for the nuclear heat source with a thermal heat rating output of 3,345 MW, including associated offsite facilities, is $443M in mid-1974 dollars. The total plant investment, including the allowance for funds during construction, has been increased by approximately 50% to account for inflation from mid-74 to mid-79. The plant is based upon a conceptual design proposed by Westinghouse.

The capacity of the thermochemical plant is 394 x 10^6 SCFD (130 x 10^9 Btu/day) as 100% hydrogen. The installed cost of the process equipment was developed for each process area based on the equipment cost for similar conventional chemical plants. For two of the Process Areas these costs were multiplied by 2.5 to allow for additional unknown costs arising from the high level of internal recycling of process streams (much greater than in coventional chemical plants) and also for the requirement for highly corrosion-resistant materials. The total direct capital cost was $900M, which is almost double the amount estimated for a conventional chemical plant.

Hydrogen Production Cost

The hydrogen production cost is shown in Table 3. The cost is given for both utility financing (60/40 debt-equity ratio), at $14.20/MBtu, and industrial financing (30/70 debt-equity ratio), at $17/MBtu.

These costs are "today's gate price" for hydrogen, based on an 80% capacity factor and a hydrogen purity of 99.9% by volume.

Sensitivity Analysis

As Table 3 indicates, the hydrogen production cost is strongly affected by the amount of capital investment required and, to a lesser extent, by operation and maintenance costs and nuclear fuel cost. It is also affected significantly by the type of plant ownership (i.e., utility or industrial). Industrial type financing increases the hydrogen production cost by more than 20%.

To determine if hydrogen could be produced commercially by thermochemical cycles at a cost competitive with fossil fuels, a sensitivity analysis of the hydrogen production cost as a function of several plant design variables was made. Starting from the base case (Table 3), changes in these variables were applied successively, and with cumulative effect, in the following order: (1) a decrease in the capital equipment installed cost, (2) a reduction in indirect costs, (3) a change in the method of financing, (4) a reduction in the contingency allowance, and (5) a decrease in total plant investment. Such changes as these are expected to result from more detailed and accurate designs and cost estimates, as well as higher process efficiencies through increased R&D. The cost effects of the changes are summarized in Table 4.

Table 3. Production Cost of Thermochemical Hydrogen

Base Case: (General Atomics I_2, H_2SO_4 Thermochemical Cycle)

	Utility Financing	Industrial Financing
o Annual Production Cost		
Capital Recovery(1)	$309M	$429M
Operations and Maintenance	$180M	$167M
Nuclear Fuel ($0.50/MBtu)	$ 40M	$ 40M
Total	$529M	$636M
o Annual Hydrogen Production (as 100% Hydrogen)	37.4 x 10^{12} Btu/yr	
o Hydrogen Production Cost		
Utility Financing	$14.20/MBtu	
Industrial Financing	$17.00/MBtu	

(1) Capital Recovery Factor:
- o Utility financing (60/40 debt-equity ratio) - 12% of total capital requirement.
- o Industrial financing method (30/70 debt-equity ratio) - 18% of total capital requirement.

Table 4. Production Cost of Thermochemical Hydrogen - Summary of Results of Sensitivity Analysis

Note: The changes to the parameters are applied successively, going down the table, with cumulative effect on the hydrogen production cost. Exception: In case (6) the contingency factor is restored to its base case value of 40% of total capital cost.

Case	Parameter Changed	Change from Base Case (see Table 3)	Hydrogen Production Cost ($/MBtu)
(1)	(Base Case)	-	14.20
(2)	Materials of Construction Cost	-7.5%	13.90
(3)	Indirect Costs	To 15% of Direct Capital Cost from 25%	13.30
(4)	Debt-Equity Ratio	To 75/25 from 60/40	11.33
(5)	Contingency Factor	To 10% of Total Capital Cost from 40%	9.78
(6)	Total Capital Investment	To 75% from 100%	8.82

RECENT WORK IN ADVANCED HYDROGEN PRODUCTION CONCEPTS

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Abstract:

A technical and programmatic overview of the Advance Hydrogen Production Concept activities during the past year will be presented. The presentations will include a description of the activities and results with comments on the limiting or pacing technology.

Introduction:

The Advanced Hydrogen Production Concepts Element has supported further development of the innovative and unusual technological findings that derive from creative basic research. It is not the intent of this activity to do fundamental or basic research, but only to extend work that has been described (literature, technical reports or by private communication) and to bridge the technology gap between very basic concepts and true larger scale applications. The activities have been divided into two topic areas:

Hydrogen Produced by Solar Radiation

1. The hydrogen photoelectrolytic conversion activity (EIC Conf Newton MA) has investigated practicability of semiconductor-electrolytic devises (similar to Honda-Fujishima) that use solar energy to decompose water into hydrogen and oxygen in an apparent single step process.
2. The photocatalytic decomposition of inorganic hydrogen compounds; i.e., hydrobromic and hydriodic acids (Prof. Gray, CIT) using rhodium organic bridge complexes.
3. Studies were conducted on the feasibility of direct high temperature thermal decompositions of water with diffusion processes for separation of the equilibrium mixture of hydrogen and oxygen into usable energy sources (Battelle-Geneva).

Conservation Activities

1. A study (SRI) on the recovery of hydrogen from hydrogen sulfide were conducted. It developed a base line in terms of markets, economics and chemistry of the recovery of hydrogen from hydrogen sulfide streams in situations where hydrogen would otherwise be wasted.
2. Preliminary comments on the low temperature decomposition of sulfuric acid by high sulfur content coal to yield sulfur dioxide and carbon dioxide (JPL).

PRODUCTION OF HYDROGEN BY ELECTRON TRANSFER CATALYSIS USING CONVENTIONAL AND PHOTOCHEMICAL MEANS

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Abstract

This paper presents alternate methods of generating hydrogen from the sulfuric acid thermal or electrochemical cycle. A number of processes requiring chemical, electrochemical or photochemical methods are presented. These include the design of potential photoelectrodes and photocatalytic membranes using $Ru(bpy)_3^{2+}$ bpy = 2,2'-bipyridine, impregnated nafion tubing and the design of experiments to study the catalyzed electrolytic formation of hydrogen and sulfuric acid from sulfur dioxide and water using quinones as catalysts. Experiments are currently being carried out to determine the value of the new approaches to energy conversion.

Introduction

The thermal splitting of sulfuric acid has been coupled with other chemical reactions to produce hydrogen and oxygen from water. Reactions for the H_2SO_4/HI thermodynamic cycle are:

$$H_2SO_{4(aq)} \xrightarrow{850^{0}C} SO_{2(g)}+H_2O_{(g)}+\tfrac{1}{2}O_{2(g)} \qquad (1)$$

$$SO_{2(g)}+2H_2O_{(l)}+I_{2(s)} \xrightarrow{900C} H_2SO_{4(aq)}+2HI_{(aq)} \qquad (2)$$

$$2HI_{(aq)} \xrightarrow{150oC} I_{2(s)}+H_{2(g)} \qquad (3)$$

The net reaction is simply the splitting of water into higher energy products - hydrogen and oxygen. Sulfuric acid and iodine can be regarded as "catalysts" for the process.[1]

Westinghouse Electric Company has replaced steps 2 and 3 by an electrochemical process.[2] Their process embodies conversion of $SO_2(g)$ into sulfurous acid (eq. 4) followed by electrolysis to give

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)} \qquad (4)$$

sulfuric acid and hydrogen (eq. 5). The reactions initially thought to

$$H_2SO_{3(aq)} + H_2O_{(l)} \xrightarrow{elec.} H_2SO_{4(aq)}+H_{2(g)} \qquad (5)$$

occur at the anode and cathode were, respectively.

$$\text{anode: } H_2SO_{3(aq)}+H_2O_{(l)} \rightarrow H_2SO_{4(aq)}+2H^+(aq)+2e^- \qquad (6)$$

$$\text{cathode: } 2\ H^+_{(aq)}+2e^- \longrightarrow H_{2(g)} \qquad (7)$$

Acceptable cell currents at low potentials (200 ma at 0.5V) have been difficult to achieve by this process. Recent evidence[3] suggests that the actual reaction occurring at the anode involves a dithionic acid intermediate limiting the rate at which H_2SO_4 is produced. Formation of the intermediate requires additional steps to account for sulfuric acid formation. Reation 6 is replaced by 8. The dithionic acid

$$\text{anode: } 2H_2SO_{3(aq)} \rightarrow H_2S_2O_{6(aq)}+2H^+_{(aq)}+2e^- \qquad (8)$$

formed in equation 8 undergoes disproportionation to produce sulfuric acid and sulfur dioxide (eq. 9).

$$H_2S_2O_{6(aq)} \rightarrow H_2SO_{4(aq)}+SO_{2(g)} \qquad (9)$$

The direct electrochemical route to formation of H_2SO_4 without passing through the dithionic acid[3] intermediate has been discovered and enhanced cell currents were obtained. The simple addition of iodide ions to the anode solution catalyzed the reaction. The electroactive species in the solution is iodide ion which is oxidized to iodine (I_3^-) at the anode (eq. 10) instead of sulfurous acid to dithionic acid. The iodine then reacts with dissolved sulfurous acid (H_2SO_3)

$$\text{anode: } 3I^-(aq) \longrightarrow I^-_{3(aq)} + 2e^- \qquad (10)$$

to produce sulfuric acid (eq. 11).

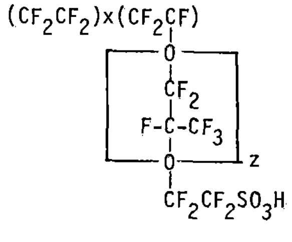
$$I^-_{3(aq)}+H_2SO_{3(aq)}+H_2O_{(l)} \rightarrow H_2SO_{4(aq)}+2HI_{(aq)}+I^-_{(aq)} \qquad (11)$$

Work[4] carried out by the Institute of Gas Technology (IGT) indicates that catalysis conditions best suited for the electrochemical conversion of SO_2 to sulfuric acid and hydrogen with iodide ion present in the anode solution are in 30-35% sulfuric acid. Their work further shows that is is difficult to obtain 200 ma currents at the desired 0.5V operating condition.

Cost effectiveness requires greater currents at lower than 0.5V potentials and preferably in more concentrated acid solutions. Otherwise an addtional process should be found which would reconcentrate the acid at lower costs than thermal methods require.

Potenial Photoelectrodes and Photocatalytic Membranes - Impregnation of Nafion Tubing with Photosensitive Materials

Nafion is a perfluorosulfonic acid substituted polytetrafluoroethylene in which each repeating unit has a molecular weight of about 1000 and has the following structure:



Subscripts x and z are integers such that the polymer has a molecular weight from 500,000 to 1,000,000 and a minimum sulfonic acid contest of 1.0 to 1.5 millequivalents /gram. The material behaves as a cation exchange resin and hydrogen ions contained in the sulfonic acid groups are replacable by other cations.

It was found that $Ru(bpy)_3^{2+}$ and UO_2^{2+} were incorporated into nafion after exposing it to one molar solutions of the cations. The $Ru(bpy)_3^{2+}$ was slowly found to diffuse into the material of 1/4 mm thickness over a peroid of three days. The degree of incoporation of $Ru(bpy)_3^{2+}$ was rather suprising due to the molecules large diameter (14A°).[5] The luminescence of both $Ru(bpy)_3^{2+}$ and UO_2^{2+} in nafion was similar to that found in solution. Thus, it seemed reasonable that the properties of the compounds in solution be extended to the compounds in nafion. This would suggest that $Ru(bpy)_3^{2+}$ and UO_2^{2+} impregnated nafion be investigated for use as photoelectrodes, cell membranes, or oxidation catalysts.

The excited state of $Ru(bpy)_3^{2+}$ behaves as an electron acceptor or an electron donor (eq. 12-14)[6]. Themodynamically, the

$$Ru(bpy)_{3(aq)}^{2+} \longrightarrow Ru(bpy)_{3(aq)}^{2+*} \qquad (12)$$

$$Ru(bpy)_{3(aq)}^{2+*} + e^- \longrightarrow Ru(bpy)_{3(aq)}^{+} \quad E^0 = 0.82V^7 \qquad (13)$$

$$Ru(bpy)_{3(aq)}^{2+*} \longrightarrow Ru(bpy)_{3(aq)}^{3+} + e^- \quad E^0 = 0.82V^8 \qquad (14)$$

excited state of $Ru(bpy)_3^{2+}$ is capable of splitting water into hydrogen and oxygen. In most reports the excited state of $Ru(bpy)_3^{2+}$ has been used to produce hydrogen and oxygen separately.[9] Only recently has a hybrid system been developed which reportedly will split water in one step.[10] The primary difficulty in applying excited state technology to chemical reactions is avoiding extremely rapid back reations between the electron donor and acceptor pairs. It seems reasonable that generation of $Ru(bpy)_3^{2+}$ (and hydrogen) and $Ru(bpy)_3^{2+}$ (and oxygen) in close proximity (a membrane) could counteract the donor/acceptor back reation difficulty due to the very exothermic $Ru(bpy)_3^{3+}$ /$Ru(bpy)_3^{+}$ "neutralization" reaction producing 2 $Ru(bpy)_3^{2+}$ (2.7V). Electron exchange between $Ru(bpy)_3^{3+}$, $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{+}$ is reported to be extremely facile[7,11] providing a mechanism for electron transfer from one side of the membrane to the other. This same concept can be applied to use of $Ru(bpy)_3^{2+}$ /nafion for use as photoelectrodes.

To test whether or not the above hypothesis was reasonable, two experiments were carried out based on the following solution reactions.[6,8]

$$Ru(bpy)_{3(aq)}^{2+*} + Co(NH_3)_5Cl_{(aq)}^{2+} \xrightarrow{H^+} Ru(bpy)_{3(aq)}^{3+} + Co^{2+}(aq) + 5NH_4^+{}_{(aq)} + Cl^-{}_{(aq)} \qquad (15)$$

$$Ru(bpy)_{3(aq)}^{2+*} + PQ_{(aq)}^{2+} \longrightarrow Ru(bpy)_{3(aq)}^{3+} + PQ_{(aq)}^{+} \qquad (16a)$$

$$Ru(bpy)_{3(aq)}^{3+} + TEOA \longrightarrow Ru(bpy)_{3(aq)}^{2+} + \text{Irrev. Prod} \qquad (16b)$$

In reaction 16a and 16b, PQ^{2+} is methyl viologen and TEOA is triethanolamine.

Sunlight photolysis of $Ru(bpy)_3^{2+}$ /nafion in the presence of PQ^{2+}, TEOA, and NaCl resulted in the formation of blue PQ^+ as expected (eq. 16). However, it was noted the $Ru(bpy)_3^{2+}$ was released from the tubing into solution rendering the experiment inconclusive.

Photolysis of $Ru(bpy)_3^{2+}$/nafion in the presence of $Co(NH_3)_5Cl^{2+}$ and H^+ (eq. 15) resulted in the nafion changing color from orange to black instead of green as expected.

The experiments point out that additional work must be done to define the metal ion incorporated - nafion system for use in photochemical and catalytic applications.

Photolytic Conversion of SO_2 to SO_3

The combination of reactions 17 and 18 results in a process which

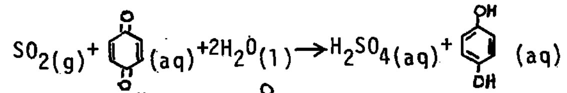
$$SO_{3(aq)}^{=} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)} + 2e^- \quad E=-0.17V^{12} \qquad (17)$$

$$UO_{2(aq)}^{2+} + 4H^+_{(aq)} + 2e^- \longrightarrow U^{4+}_{(aq)} + 2H_2O_{(l)} \quad E=0.32V^{12} \qquad (18)$$

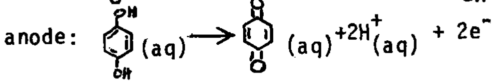
should proceed spontaneously to form sulfuric acid and U^{4+}. The reaction, however, occurs to slowly to be observed. Forutnately, the reaction can be assited photochemically. Irradiation with non-monochromatic light in a magnetically stirred, high pressure reaction vessel containing from 1M H_2SO_4 to 50% H_2SO_4 in the presence of 0.08 M UO_2^{2+} and liquid SO_2 resulted in the formation of U^{4+} as noted by the appearance of a visible absorption band at 650 nm ($\varepsilon \sim 500$). The absorbance of the solution changed from 0 to 0.05 after 1/2 hr. photolysis and to >2 after 2 days irradiation. Some precipitate was noted after prolonged photolysis. The precipitate was white and attributed to formation of elemental sulfur via a side reaction. The UO_2^{2+} photocatalyst can be regenerated from U^{4+} by reaction of U^{4+} with oxygen in the presence of Cu^{2+} as a catalyst.[13] The process can thus be cycled, $UO_2^{2+} \underset{O_2}{\overset{h\nu}{\rightleftharpoons}} U^{4+}$ and a potential solar method exists for reconcentrating sulfuric acid to concentrations >50%.

Catalyzed Elcetrolytic Formation of Hydrogen and Sulfuric Acid

It was recently reported[14] that polyquinones could catalyze the conversion of SO_2 to H_2SO_4. In a quest to find a better catalyst than I^- for the electrochemical production of hydrogen and sulfuric acid from sulfur dioxide, it seemed reasonable to substitute quinones (known to react with SO_2) for iodide ion in the anode compartment. Benzoquinone and benzhydroquinone exemplify the expected reactions:



(19)



(20)

$$\text{cathode:} \quad 2H^+_{(aq)} + 2e^- \longrightarrow H_2 \qquad (21)$$

The net reaction is:

$$SO_{2(g)} + 2H_2O_{(l)} \xrightarrow[\text{elec.}]{\text{quinone}} H_2SO_{4(aq)} + H_{2(g)} \qquad (22)$$

Two quinones synthesized special for this investigation were an organic polyquinone derived from naphthalene-1,7-diol and $\{Ru(bpy)_2(\text{phendione})\}^{2+}$ where phendione is 1,10 phenanthrolene-5,6-dione.

The ruthenuim complex appeared interesting to study since it had potential of being a photocatalytic center. The compound did have a visible absorption maximum at 440 nm as expected but did not have the luminescence properties of $Ru(bpy)_3^{2+}$. The hydroquinone derivative will have to be synthenzied to determine what its luminescence properties are before discounting the possible production of hydrogen via intramolecular electron transfer from the ruthenium excited state. The $\{Ru(bpy)_2(\text{phenedione})\}^{2+}$ species did have desirable electrochemical properties. The cyclic voltammogram of the compound showed irreversible waves centered at 0.84 and 1.14 volts vs SCE and a second reversible wave at 1.37V vs SCE. The former irreversible process is typical of quinone-hydroquinone electrochemisty, the second reversible wave is in the region normally found for $Ru^{3+/2+}$ couples of bipyridine complexes.

Two sets of experiments are planned pending fabrication of the desired equipment. The first set of experiments involves following the change in conductivity as the quinone reacts with SO_2 to give H_2SO_4 (eq. 22). The second set of experiments involves the use of an electrolytic cell with the quinone present in the anode compartment for catalyzing the conversion of SO_2 into sulfuric acid and hydrogen gas.

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PROGRESS REPORT ON THE DEVELOPMENT OF THE GENERAL ATOMIC THERMOCHEMICAL WATER-SPLITTING PROCESS

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Abstract

The major accomplishments of the DOE funded part of the GA thermochemical water-splitting program are reported. They include:

1. Completion of installation of all bench-scale equipment.
2. Operation and preliminary data acquisition for bench-scale subunits I and II.
3. Design, installation and operation of a system for iodine removal from the low phase.
4. Review and modification of section III of the engineering flowsheet resulting in an increase in process efficiency and decrease in capital cost.
5. Completion of the Funk panel review.

The results of the experimental work have demonstrated that flowsheet conditions can be achieved in all cases tested. Continued work on the flowsheet has increased our confidence in the economic viability of the sulfur-iodine process.

Introduction

Thermochemical water-splitting has been under investigation at GA since 1972. The U.S. Department of Energy (then ERDA) joined the program in 1976. At present, the total GA water-splitting project is cosponsored by the U.S. Department of Energy (Energy Storage Division and Solar Thermal Power Office), the Gas Research Institute, the Metal Properties Council, and General Atomic Company.

The process can be described by the following three chemical equations:

$$xI_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HI_x \qquad 370\text{ K} \quad (1)$$

$$2HI_x \rightarrow H_2 + xI_2 \qquad 390\text{ K} \quad (2)$$

$$H_2SO_4 \rightarrow SO_2 + 1/2\text{-}O_2 + H_2O \qquad 1144\text{ K} \quad (3)$$

The main advantages of the cycle are that it can be conducted as an all-liquid and gas-phase process and that its unit operations are simple, industry-developed processes like distillation, vaporization, and phase separation.

Bench Scale

A major part of the bench-scale effort was spent in the installation of bench-scale subunit III, (HI purification and decomposition). Figures 1 and 2 show photographs of the unit. The installation was completed on schedule and operational shakedown will be completed before the end of September.

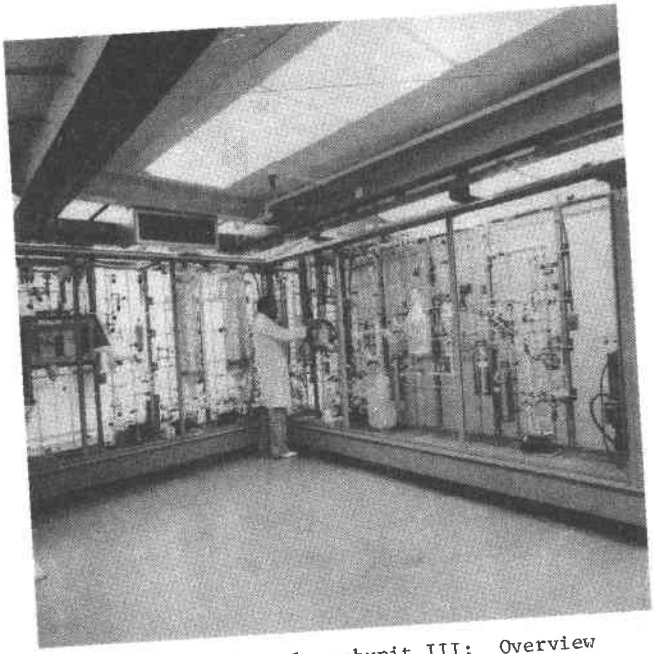

Fig. 1. Bench-scale subunit III: Overview

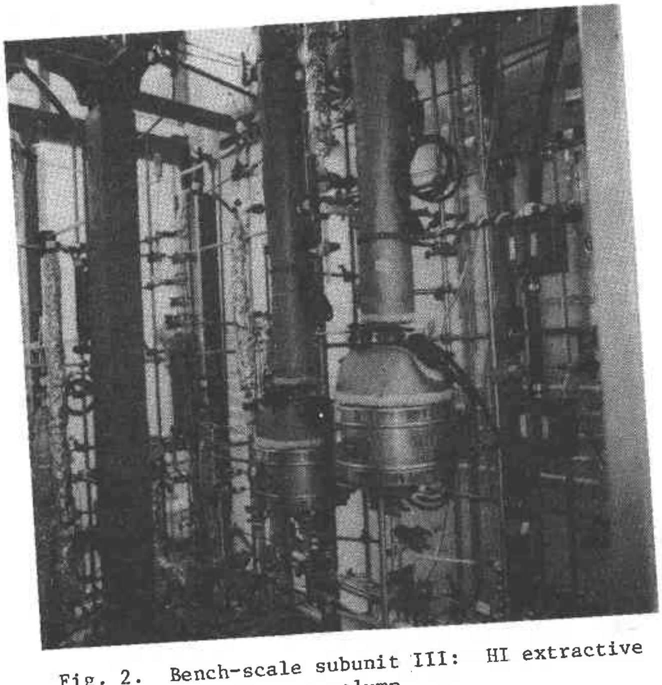

Fig. 2. Bench-scale subunit III: HI extractive distillation column

Data acquisition on bench-scale subunits I and II (main solution reaction and H_2SO_4 decomposition, respectively), was carried out and resulted in the verification of flowsheet conditions for all of the unit operations tested. Figures 3, 4, and 5 show photographs of subunits I and II. Early tests on subunit I resulted in H_2SO_4 concentrations in the upper phase of 42 -44 wt % while the design concentration is 50%. Recent tests have resulted in H_2SO_4 concentrations of 49 -52 wt %. This is well within the flowsheet design conditions. The experiments in subunit II were carried out to evaluate the performance of the iodine strippers and of the sulfuric acid decomposition system.

The iodine stripping column shown in Fig. 6 consists of a pyrex tube (60 cm long, 3 cm diam) filled with glass beads (3 mm diam). The column is externally heated and insulated. Sulfuric acid (~50 wt %) containing ~1.2% HI and 0.6% I_2 is fed to the top of the heated column. Iodine is removed from the liquid by steam stripping with the water evaporating from the liquid. This changes the HI/I_2 equilibrium, allowing the hydrogen iodide to react with the H_2SO_4 to form I_2, SO_2, and H_2O via Eq. 1. The I_2 and SO_2 so formed are further stripped from the liquid. The experiments were carried out at various temperatures and three different feed flow rates. The results plotted in Fig. 7 indicate that at flowrates of 10 and 17 cm^3 H_2SO_4/min very good stripping of the iodine can be achieved at relatively low temperatures. At a flowrate of 5 cm^3/min, bypass flow apparently occurs in the column, and the results are erratic.

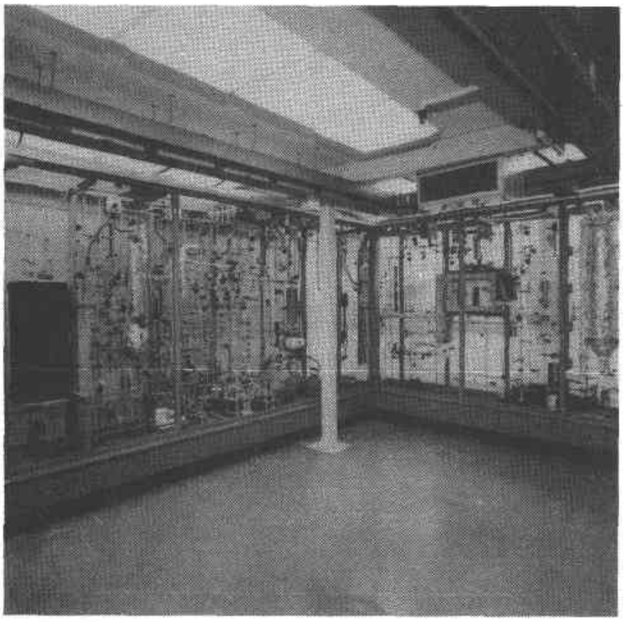

Fig. 3. Bench-scale subunit II: Overview

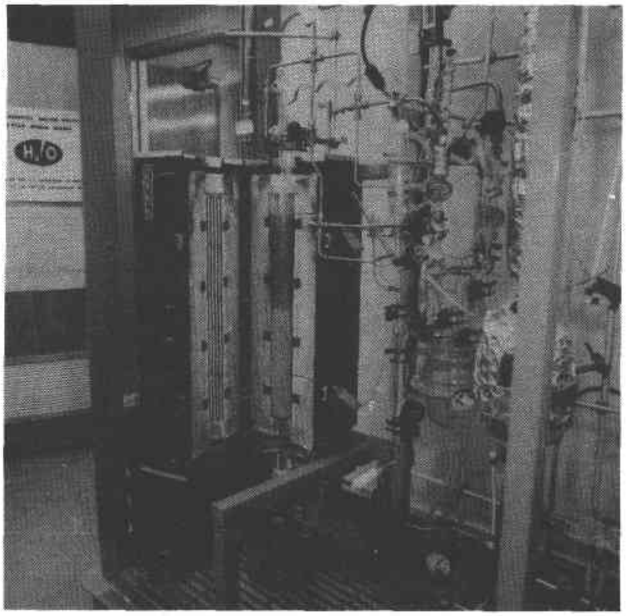

Fig. 4. Bench-scale subunit II: SO_3 decomposer with catalyst in place

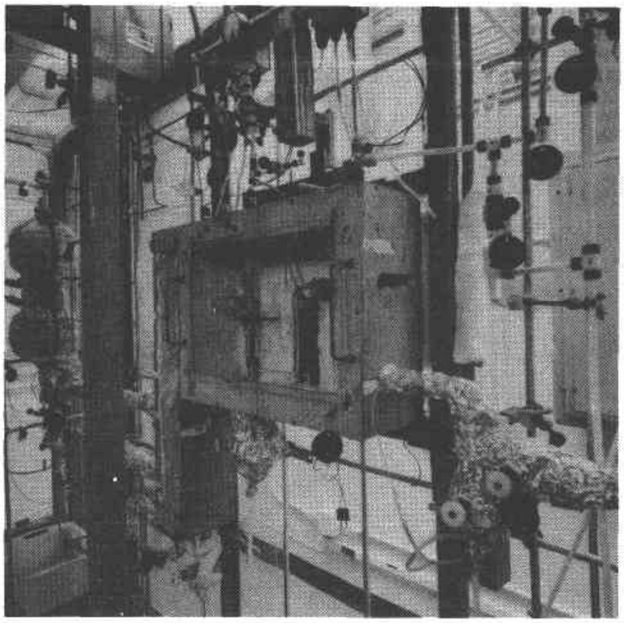

Fig. 5. Bench-scale subunit I: Main solution reactor and phase separator

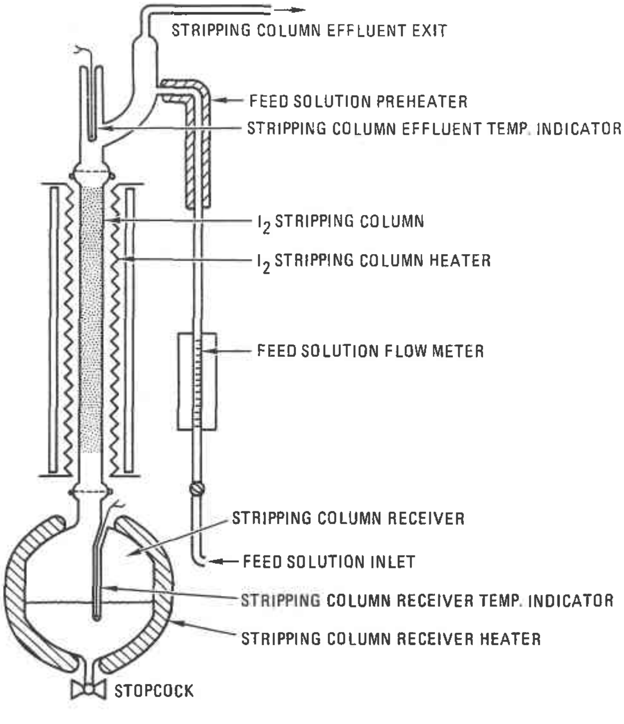

Fig. 6. Schematic of iodine stripping column in use in subunit II

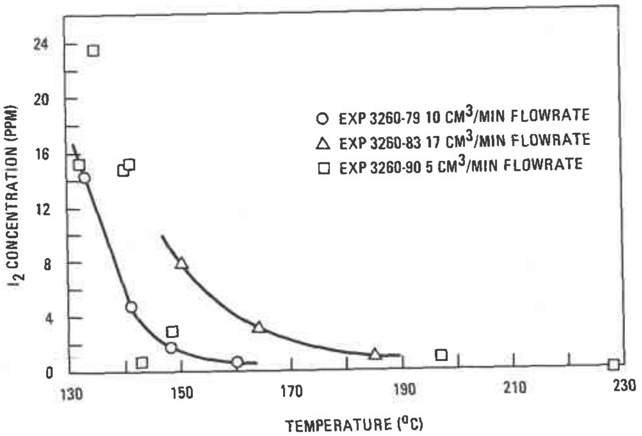

Fig. 7. I_2 concentration versus column temperature for subunit II for 5, 10, and 17 cm^3/min feed flowrates

It is believed that the I_2 concentration in the liquid effluent is controlled by the rate of reaction between HI, which is also present in the upper phase (~1%), and H_2SO_4 to generate free, volatile I_2. Also, probably, the average residence time of the fluid flowing through the column is an important parameter with respect to this reaction. Further experiments to test the foregoing hypothesis are planned.

In the sulfuric acid cracking experiments the decomposition of H_2SO_4 into SO_2, H_2O, and O_2 was evaluated. A platinum on zirconia catalyst, 0.3175 cm (1/8 in. diam) right cylinder pellets containing ~0.2 wt % platinum was used at temperatures between 800° to 900°C. The gas slugflow residence time in the reactor was between 0.3 to 1 s. Figure 8 shows the gas decomposition results for the experiments. The data points were calculated both by measuring the amount of unreacted H_2SO_4 which condensed in the decomposer effluent and the oxygen output flowrate after caustic absorption of the SO_2. The two methods agree to within ±5%, with the condensed H_2SO_4 analysis being preferred as the more accurate; this latter method is the basis for Fig. 8. Catalyst bed temperature is taken to be the maximum reading of an axial temperature traverse of the bed taken during steady-state operation.

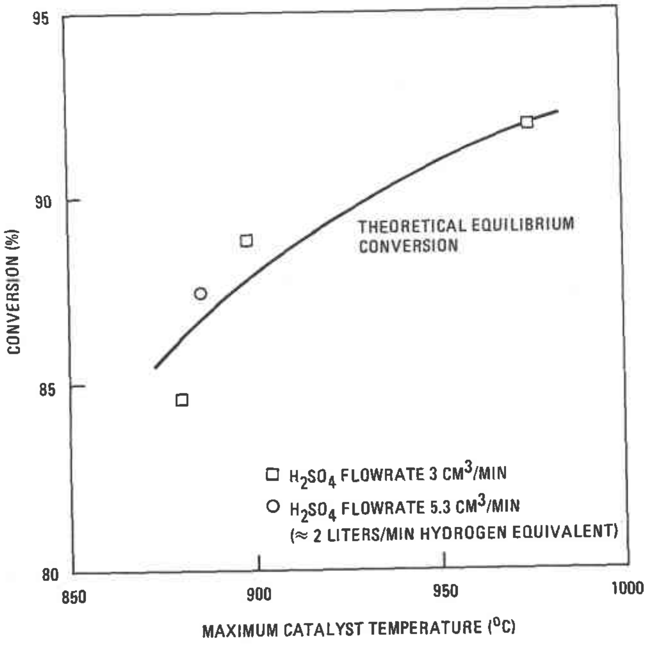

Fig. 8. Performance of bench-scale H_2SO_4 decomposition equipment

The experimental results are within ±2% of the theoretical prediction using the maximum catalyst temperature and the equilibrium composition calculated from the JANAF tables. The low point at ~875°C in Fig. 8 was obtained in a loading of the catalyst bed for which a significant portion of the bed was in the exit region where the temperature had substantially fallen off from the maximum near the axial center of the decomposer. This resulted in a significant back reaction of the decomposition products from the hotter region and thus a low conversion compared to theoretical. This problem was rectified by shortening the catalyst bed and using only the hottest region of the decomposer. The other data points in Fig. 8 were taken using such a configuration. The overall simultaneous operation of all subunit II components was demonstrated at a flowrate equivalent to 2 std liters/min H_2. All process steps functioned as designed.

Engineering

Redesign of section III of the engineering flowsheet was completed. The changes incorporated include the use of a medium pressure extractive distillation system for separation of HI from the $HI/H_2O/HI$ phase. The redesign resulted in an increase in thermal efficiency equivalent to 1.5%. The equipment requirements were also significantly reduced through elimination of two turbine expanders, two turbine compressors, and several heat exchangers. A conceptual flowsheet of the revised section III is shown in Fig. 9.

Conclusions

Installation and operation of the bench-scale system have shown that design conditions assumed in the engineering flowsheet are being verified in each of the subsystems tested, demonstrating the validity of the GA water-splitting flowsheet. Additionally, the flowsheet design effort continues to improve the efficiency of the process while at the same time reducing the capital equipment requirements. The significant progress made in the last year further increased our confidence that thermochemical water-splitting utilyzing the GA sulfur-iodine cycle is a viable, economic alternative for hydrogen production.

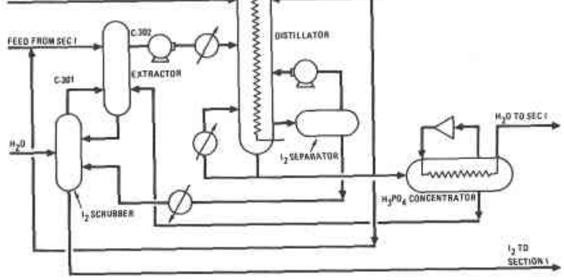

Fig. 9. Section III HI separation

THE LASL THERMOCHEMICAL HYDROGEN PROGRAM STATUS ON SEPTEMBER 30, 1980*

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Abstract

The work described here was accomplished during the period October 1, 1979--September 30, 1980. Highlights of the experimental program were:

- A solids decomposition facility was constructed and used to study the handling of bismuth oxysulfates and the kinetics of their decomposition.
- The results of our kiln experiments showed that a substantial amount of bismuth oxysulfate decomposition occurs with residence times under 2 min. at temperatures between 973 and 1143 K.

The LASL bismuth sulfate sub-cycle thus appears a candidate for hydrogen production utilizing a solar heat source. In the evaluation phase of our work, the technoeconomics of the hybrid sulfur cycle were determined and compared with several published results as well as compared to the technoeconomics for water electrolysis processes for hydrogen production.

We aided the efforts of the Department of Energy (DOE) Thermochemical Cycle Evaluation Panel in reviewing the Lawrence Livermore Laboratory (LLL) zinc selenide cycle as well as the General Atomic (GA) sulfur-iodine cycle.

M. G. Bowman, U. S. Technical Contact for the International Energy Agency (IEA) Annex I Agreement on Thermochemical Hydrogen Production, coordinated U. S. contributions to the 3rd Annual Workshop held at Tsukuba Science City, Japan, June 18-21, 1980. The successful workshop was attended by five delegates from the U. S. and also included international participation.

I. Solids Decomposition Facility

The metal sulfate sub-cycle currently being studied as part of our applied program under the Office of Advanced Conservation Technologies is a bismuth oxysulfate cycle. In a related program under the Office of Energy Research, more basic studies of alternative sulfates are being conducted to determine whether they offer advantages for the applied program.

The present version of the bismuth oxysulfate cycle may be described as follows.

$$2H_2O(l)+SO_2(g)=H_2SO_4(aq)+H_2(g) \quad \text{Electrolysis 350K}$$

$$Bi_2O_2SO_4(s)+H_2SO_4(aq)=Bi_2O(SO_4)_2(s)+H_2O(l) \quad \text{350K}$$

$$Bi_2O(SO_4)_2(s)=Bi_2O_2SO_4(s)+SO_3(g) \quad \text{1000-1150K}$$

$$SO_3(g)=SO_2(g)+0.5\ O_2(g) \quad \text{1200+K}$$

The bismuth oxysulfate system is desirable because it decomposed rapidly at moderately high temperatures, and the decomposed product reacts rapidly with dilute sulfuric acid solutions, giving an insoluble product. This is important in minimizing solution concentration steps.

Two disadvantages are the rather high cost of bismuth compounds, although this becomes a plant inventory rather than an operating cost, as nearly all of the bismuth is recovered and recyled. The other is the water-retention problem and the fact that the disulfate forms a trihydrate.

A laboratory-scale rotary kiln was constructed from a 25-mm o.d. quartz tube, so supported that it could rotate freely inside a 330-mm long, 25.4-mm tube furnace. This furnace was capable of temperatures to 1283 K. The quartz tube terminated in a standard taper female joint which rotated on a male counterpart machined from Teflon. This afforded a gas-tight rotary seal without need of lubrication. The Teflon joint extended to a Teflon body which supported a rectangular hopper constructed from Lexan polycarbonate sheet. A Teflon auger passed through the body and the tapered joint. The auger was rotated by a geared drive so that the feed rate could be varied in steps. Also, built into the body and out through the tapered joint was a gas passage, which could support a quartz tube protruding into the center of the quartz kiln, providing a leak-free exit for SO_3 and carrier gas. The kiln is shown in Fig. 1.

A matrix of kiln experiments using composite feed and the same kiln inclination were made. These explored the effect of four set temperatures and three rotational speeds. Temperatures of 993, 1023, 1073, and 1123 K were chosen.

The results of these experiments are presented in Fig. 2. Previous experiments of this type have shown that the maximum decomposition that will occur in a few minutes such as in a kiln experiment, never seems to go beyond a composition of approximately $Bi_2O_{2.28}(SO_4)_{0.72}$. Since the feed composition is $Bi_2O_{0.94}(SO_4)_{2.06}$, it is assumed that a maximum of 1.34 moles of SO_3 can be driven off in the laboratory-scale kiln with this feed.

The main conclusions to be drawn from this matrix of experiments is that a substantial amount of decomposition was obtained in short (less than 2 min.) reaction times at 973 K to 1143 K. In addition, by proper procedures, which appear to be industrially compatible, bismuth monoxydisulfate can be prepared with an altered morphology and particle size conducive to good solids handling characteristics.

Our latest work has been done with reconstituted feed with a composition, $Bi_2O_{0.6}(SO_4)_{2.4}\cdot H_2O$ made from five batches that had been run through the kiln and treated with 3 M sulfuric acid. This material decomposed to $Bi_2O_{2.25}(SO_4)_{0.75}$ at 1143 K however, the solid showed different handling characteristics than the earlier feed prepared from reagent grade Bi_2O_3. Further experimentation will

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*Work performed under the auspices of the US DOE.

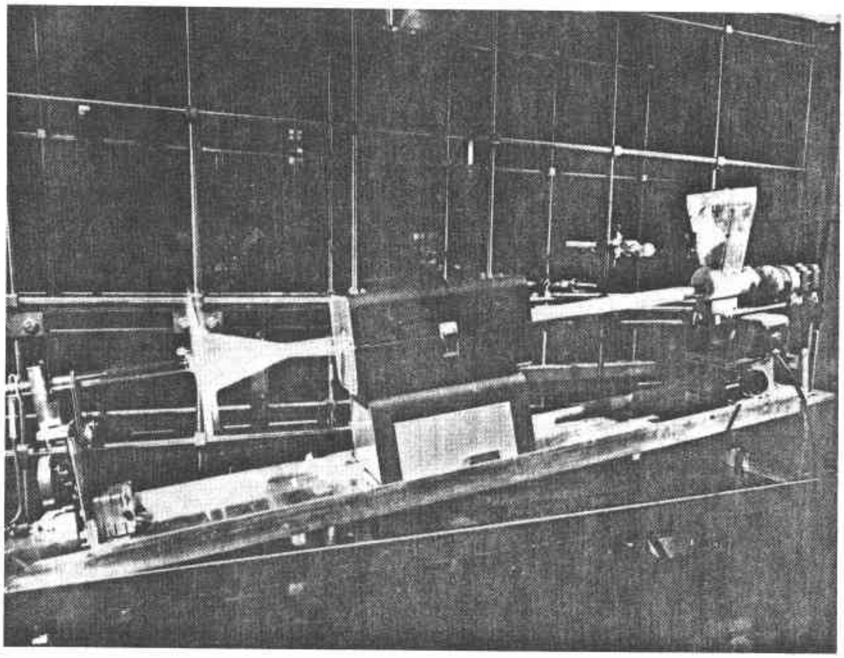

Figure 1. LASL Solids Decomposition Facility (Rotary Kiln)

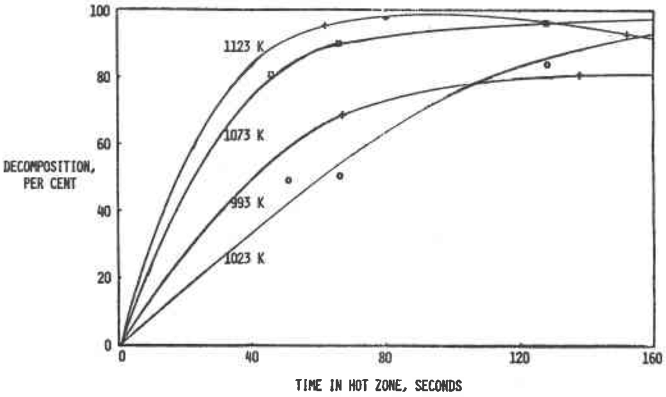

Figure 2. Decomposition Rate in Kiln.

relate these characteristics to practical operating conditions.

In summary, it appears that the LASL bismuth sulfate sub-cycle offers a practical means to minimize some of the difficulties in handling sulfuric acid that are associated with cycles such as the hybrid sulfur cycle and the sulfur-iodine cycle. If solids handling problems are not too severe, this cycle appears well adapted for hydrogen production from a solar thermal energy source.

II. Cycle Evaluation

A survey of capital cost estimates and process efficiencies for two different technologies for the production of hydrogen has been performed. Thermochemical cycles show costs ranging from \$600 - 1100/kW H_2 while advanced methods of water electrolysis were estimated in the range of \$700 - 1100/kW H_2. In general, efficiencies for thermochemical cycles were higher at 40 - 55%, than for water electrolysis systems at 30 - 40%.

In the techno-economic evaluation of thermochemical cycle technology, the hybrid sulfur cycle, known commonly as the "Westinghouse Sulfur Cycle" and the "JRC Mark 11 Cycle," has received the most attention. This cycle is characterized by the following reaction sequence:

$$2H_2O + SO_2 \xrightarrow{\text{electrolysis}} H_2SO_4 + H_2 \qquad 350k$$

$$H_2SO_4 \xrightarrow{\text{Thermal}} H_2O+SO_2+1/2O_2 \qquad 1100K$$

In both the Westinghouse and the JRC versions, the process operates off nuclear heat delivered as a high-temperature helium gas stream from a HTGR or a Very-High Temperature Reactor (VHTR). If instead solar heat is considered for a thermochemical cycle, an additional factor must be considered. This is the cost of solar heat at the temperature required for the process. Solar heat is intermittent both on a daily basis (night and day) as well as during cloudy periods during the day. The lower capacity factor for solar plants (as contrasted to nuclear plants will have a larger effect on capital cost as compared to a nuclear plant. Solar-thermochemical schemes are just now receiving attention and this potentially promising technology has in its favor the capability of delivering heat at a practically isothermal temperature to a thermochemical cycle allowing consideration of cycles involving solid oxide or sulfate decompositions.

Detailed summaries of the estimated investment costs and efficiencies derived for the different processes are presented in bar chart format in Figs. 3 and 4 on the basis of \$ Investment/KWH_2 (1979 \$) and (%) efficiency. The data were drawn from a number of original references in the literature.

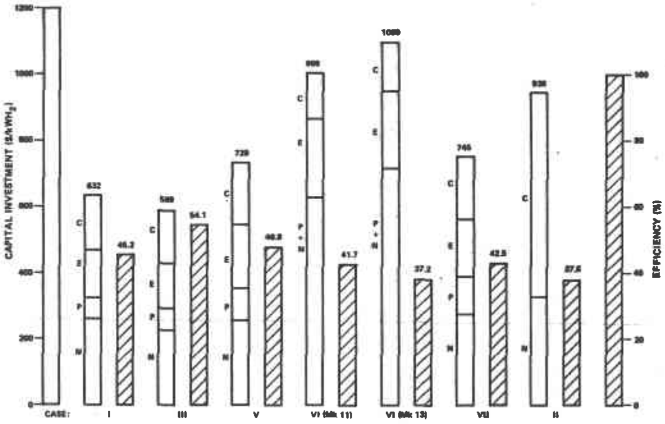

Figure 3. Investment and Efficiency Estimates for Thermochemical Cycles.

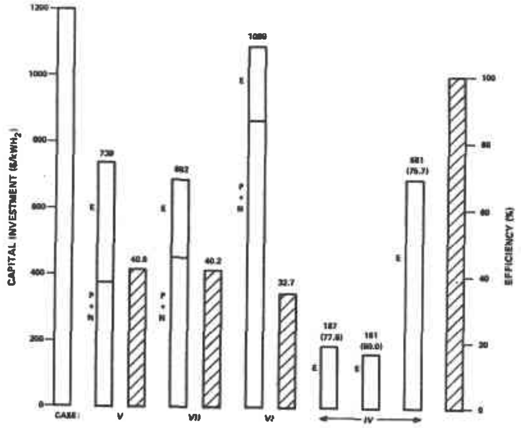

Figure 4. Investment and Efficiency Estimates for Water Electrolysis.

The cost data show slight differences in investment between two methods of hydrogen generation. All costs were in the range, \$589 - 1089/kW H_2. Efficiencies are in general, higher for thermochemical cycles than for water electrolysis. These range from 37.2% to 54.1% for thermochemical cycles and from 32.7 to 40.8% for water electrolysis.

The values of investment cost or efficiency derived are only as good as the assumptions. Values of the sulfur dioxide electrolyzer voltage assumed in early studies on the hybrid sulfur cycle were below 0.5 V at acid concentrations of the 75 - 80 wt%. These voltages are impossible to attain under the assumed conditions. In these cases, investment costs and efficiencies must be revised to reflect conditions that are more realistic.

There does not appear to be any simplistic method to determine investment costs or efficiencies for new technologies such as thermochemical cycles or advanced water electrolysis. Computer codes will speed the process of cost estimation but a flowsheet reflecting reliable operating conditions is still the prime requirement in techno-economic evaluation.

III. DOE Thermochemical Cycle Evaluation Panel.

LASL support is being provided to this panel that is chaired by Dr. J. E. Funk (University of Kentucky). Two cycles have undergone evaluation in this reporting period, the LLL zinc selenide cycle and the GA sulfur iodine cycle.

IV. IEA Annex I Workshop

The third annual IEA, Annex I Workshop on Thermochemical Hydrogen Production was held in Tsukuba Science City, Japan, 18-21 June, 1980.

Attendees from the United States were:

M. G. Bowman, Los Alamos Scientific Laboratory
C.F.V. Mason, Los Alamos Scientific Laboratory
G. Besenbruch, General Atomic Company
G. Parker, Westinghouse Electric Corporation
O. Krikorian, Lawrence Livermore Laboratory

M. G. Bowman, U. S. technical contact for Annex I coordinated U. S. participation at this Workshop.

DEVELOPMENT STATUS OF THE SULFUR CYCLE ELECTROLYSIS TECHNOLOGY

P. W. T. Lu, R. L. Ammon and G. H. Parker*

Abstract

Recent advances in electrode fabrication techniques and cell configuration have substantially improved both the cell voltage and the performance stability. While operating in 50 w/o sulfuric acid at 50°C and 1 atm, the measured cell voltage of an SO_2-depolarized electrolyzer was 736 mV (including ohmic loss) at 200 mA/cm^2. A one-week endurance test was successfully conducted at 100 mA/cm^2, and a stabilized cell voltage of 675 mV was achieved after 80 hours of continous operation. The resulting gas from the test cell contained 98.7 v/o hydrogen.

Experimental efforts also included kinetic studies on metal electrodes, measurements of temperature effects on electrode kinetics, investigations of electrocatalytic activities of metal electrodes, cyclic voltametric studies and evaluation of alternate catalysts. The RAI P-4010 membrane has been identified as a promising gas separator. The noble metal loading has been reduced to $\sim$2 mg/cm^2 at the anode and cathode, respectively, with no loss in cell performance.

I. Introduction

Westinghouse Electric Corporation is currently developing the Sulfur Cycle, a hybrid thermochemical process for the production of hydrogen and oxygen from water. The development work has been cofunded by the Conservation (STOR) and Solar Divisions of the Department of Energy; the work funded by STOR on research and development of the electrolytic subsystem was contracted via interagency-transfer through the Jet Propulsion Laboratory (JPL) during 1979. Technical work under the JPL contract was completed during February 1980 and a follow-on contract on the electrolyzer development was initiated through the Brookhaven Area Office (BHO) in May 1980. This status report highlights the progress under the JPL contract and preliminary results under the on-going BHO contract.

Under the JPL contract research and development activities, sulfur dioxide depolarized electrolysis technology focused on evaluation of electrode kinetics and electrode catalysis, development of electrode fabrication techniques, and investigation of separator materials. The major objectives were to increase the understanding of the electrochemistry of depolarized anode electrolysis in sulfuric/sulfurous acid solutions and provide a foundation for the long-term development of efficient, long-life and inexpensive electrolyzer systems. This long term development is being continued under the new BHO contract with a current emphasis on reducing the loadings of noble metal catalysts on the electrodes without compromising cell performance. The long range performance goal of this program is to obtain a stable cell voltage less than 600 mV at 200 mA/cm^2 while the electrolyzer is operated at $\sim$100°C and 5-20 atm, using 50-60 w/o sulfuric acid solutions.

II. Development of Electrode Fabrication Techniques

Novel manufacturing processes have been developed for preparing a platinum catalyzed carbon plate electrode and a carbon cloth backed electrode. The resulting electrodes exhibited high specific surface area and improved electric conductivity. To provide tangible evidence of progress in the development of electrodes, a series of tests was performed with experimental single cells. In the contract year 1979, major improvements in cell performance were attained as indicated by measured cell voltages. When operated at 200 mA/cm^2 using 50 w/o acid at 50°C and 1 atm, a reference cell (designated OC-1) which used briquetted carbon electrodes, required 1.22 volts and degraded at a rate of 16 mV/hr (see Table 1). After several improvements had been incorporated into electrodes and test cell configuration, one of the cells (designated LC-12) required only 0.77 volts under identical operating conditions. This cell exhibited stable operation with no measurable performance degradation. At a lower current density, 100 mA/cm^2, LC-12 required only 0.63 volts.

Some of the improvements incorporated into LC-12 included:

- The use of commerically available porous carbon substrates.
- A reduction in platinum catalyst loading in the anode from 10 to 7 mg/cm^2
- The incorporation of a carbon cloth backed anode with 2 mg/cm^2 of fine platinum particles deposited on carbon "black pearls" (designated MBI-303-8).
- An improved cell configuration test incorporating a cylindrical geometry with attendant O-ring sealing.

A one-week endurance test was conducted with one of the intermediate cells (designated LC-8). As seen from Table 1, this cell had all of the features of LC-12 except for the carbon supported platinum catalyst. Instead, LC-8 used a catalyst of platinum particle/carbon powder mixture (designated EC-9885). Operated at a 100 mA/cm^2 current density for 173 hours continously, the overall cell voltage, anodic overpotential, cathodic overpotential and ohmic loss were studied as a function of time. As shown in Figure 1, cell LC-8 demonstrated a stable voltage of 675 mV with no degradation after the first 80 hours. During the first 80 hours, the cell voltage had increased from 644 mV to 675 mV because of a slight performance degradation at the anode. As verified in mass spectroscopic studies, the resulting gas from the test cell contained 98.7 vol. % hydrogen.

Chemical compositions of the Pt-catalyzed carbon plate cathode tested in LC-8 were characterized using ESCA techniques. Sulfide ions were found to be present on the tested electrodes. However, no elemental sulfur or SO_2-containing species were observed.

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III. Evaluation of Electrode Kinetics and Catalysts

A number of metal and oxide electrodes were investigated for SO_2 oxidation in 50 w/o sulfuric acid solutions. A majority of experimental results have been reported previously.[1,2] These experiments provided verification of the potential attractiveness of palladium or palladium oxide catalyzed electrodes as an alternative to platinum provided that electrode fabrication can be optimized. The effect of temperature on kinetic parameters for this reaction was studied on preanodized palladium and platinum electrodes in the temperature range of 25-90°C. Significant improvements in exchange current densities and reductions in anodic overpotentials were achieved by increasing temperature. However, the measured Tafel slopes are approximately constant at various temperatures, indicating that the reaction mechanism is independent of temperature.

Voltammetric studies were conducted at various sweep rates in 50 w/o sulfuric acid solution. The electrochemical oxidation of SO_2 commences at an anodic potential where the formation of adsorbed oxygen-containing species is initiated. On the Pt, Ru, Ir and Rh anodes, the chemical transformation of the adsorbed species to metal oxides at higher potentials, creates passivated surface layers which partially cover the electrode surface and inhibits the SO_2 oxidation reaction.

IV. Investigation of Separator Materials

While cell tests have used a commerically available microporous rubber diaphragm that has proved to be adequate for experimental/developmental cells, it is desirable to find a gas separator that has improved qualities compared to rubber. For this reason, experiments were made on two key separator figures of merit: (1) diffusivity for sulfur dioxide-containing species, and (2) ionic resistivity. Both of the quantities should be as low as possible.

As seen in Table 2, several materials were identified that have diffusion coefficients substantially lower than microporous rubber. One of these materials, P-4010, a cation exchange membrane material, has an excellent diffusion coefficient, more than two orders of magnitude lower than that of microporous rubber diaphragm.

Measurements of diffusion coefficients as functions of temperature were made with three materials, microporous rubber, P-4010 and Nafion-120. As expected, the diffusion coefficients increased slightly with temperature.

Measurements of ionic resistivity; i.e., the resistivity to hydrodrium ions, were made in sulfur dioxide saturated solutions and in sulfur dioxide free solutions via an interruptor technique. Eight materials were tested in 50 w/o sulfuric acid at 23°C. As shown in Table 2, microporous rubber had the lowest resistivity, approximately 2 ohm-cm. The other materials ranged from 8 to 21 ohm-cm.

While P-4010 had the lowest diffusion coefficient for sulfur dioxide, it also had the highest resistivity among those tested. Since the thickness of P-4010 membranes is small in cell tests, it should offer an ionic resistance comparable to microporous rubber. This membrane was evaluated in the electrolyzer LC-18 that used electrodes similar to those in LC-12 (see Table 1). Figure 2 depicts the performance of the two electrolyzers. The incorporation of P-4010 membrane in the test cell resulted in improvements in the cell voltage. At 200 mA/cm^2, LC-18 exhibited a cell voltage of 730 mV as compared to 770 mV for LC-12.

V. Electrocatalyst Reduction Experiments

Noble metals or metal oxides as electrocatalysts in the electrolysis cells can represent a substantial portion of the capital cost of a hydrogen production plant. Initiated in FY80, experimental efforts are being made toward the reduction of noble metal loading with minimum or no loss in the cell performance. The ongoing program focuses on (1) procurement of highly dispersed electrocatalysts, (2) electrochemical evaluation of supported catalysts of various crystallite size, and (3) identification of catalyst support materials.

As shown in Table 3, the noble metal loadings at the anode and cathode of the reference electrolyzer LC-12 are relatively high, ∿7 and 10 mg-Pt/cm^2, respectively. The Pt-foil spacers in both anodic and cathodic compartments have been substituted by an inexpensive and conductive carbon paper. Catalyst loadings in LC-22 have been successfully reduced to ∿2 mg/cm^2 at both the anode and cathode, with no loss in the cell performance (see Table 3). In fact, the measured cell voltage at 200 mA/cm^2 was improved from ∿769 mV for LC-12 to ∿736 mV for LC-22. The performance improvement is essentially attributed to (1) the incorporation of sandwich type electrodes, (2) the advance in the electrode fabrication techniques, and (3) the optimization of the anode plate configuration. Figure 3 shows the performance characteristics of key electrolyzers OC-1, LC-8, LC-12, and LC-22. Although the catalyst loadings on both anode and cathode were substantially decreased, LC-22 exhibited the lowest cell voltages at various current densities. At 200 mA/cm^2, the measured cell voltage has been improved from 1.22 V in July, 1979 to 736 mV in July, 1980.

This task is aimed at a further decrease of noble metal loading to meet the interim goal of 1 mg/cm^2 on each electrode. At the end of FY80, the achievement of this goal will reduce the capital investment for the noble metal catalysts to a small fraction of the total capital costs of a large hybrid thermochemical/electrochemical hydrogen production plant.

VI. Improved Cell Configuration

Recent tests, including LC-22, have been performed with a new configuration constructed with sandwich type electrodes. The electrolyzer was designed for operation in a flow-by mode and was constructed of lucite with O-ring seals. A microporous rubber diaphragm was employed as the gas separator. On the back of each current collector, a pressure pad was placed to assure good electrical contact in the electrode/collector interface and to reduce the inter-electrode spacing.

Experimental efforts are being made to develop a square Teflon cell which will provide a better configuration for manifolding the electrolyte and hydrogen gas than the lucite cell described previously. This cell will be capable of operating at temperatures up to 90°C. Using the most promising catalyst loading identified, the performance characteristics

TABLE 1: CELL COMPONENTS AND PERFORMANCE CHARACTERISTICS OF KEY ELECTROLYZERS EVALUATED IN THE CONTRACT YEAR 1979(1)

ELECTROLYZER	ANODE	CATHODE	E_{cell} at 200 mA/cm^2 (mV)	IMPROVEMENT(2) (mV)	$\frac{dE_{cell}}{dt}$(3) (mV/hr)
OC-1	Pt/C-plate (P7620) 10 mg/cm^2	B.C.E.(4) 10 mg/cm^2	1,220	-	10
LC-1	Pt/C-plate (P7620) 10 mg/cm^2	B.C.E. 10 mg/cm^2	1,150	70	4
LC-2	Pt/C-plate (FC13) 10 mg/cm^2	B.C.E. 10 mg/cm^2	930	220	4
LC-5	Pt/C-plate (FC13) C.C.E. (EC-9885)(5) 12 mg/cm^2	Pt/C-plate (FC13) 10 mg/cm^2	840	90	<1
LC-8	Pt/C-plate (FC13) C.C.E. (EC-9885) 7 mg/cm^2	Pt/C-plate (FC13) 10 mg/cm^2	830	10	<1
LC-12	Pt/C-plate (FC13) C.C.E. (MBI-303-8) 7 mg/cm^2	Pt/C-plate (FC13) 10 mg/cm^2	770	60	<1

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(1) Testing Conditions: 50 w/o H_2SO_4 at 50°C and atmospheric pressure, anolyte flow rate 700 ml/min., microporous rubber diaphragm used as a separator.

(2) Achievable improvement in cell voltage in comparison with the previous electrolyzer.

(3) Performance degradation rate after operating at a constant current density 100 mA/cm^2 for 2 hours.

(4) B.C.E. = Briquetted carbon electrode.

(5) C.C.E. = Carbon cloth supported electrode.

TABLE 2: COMPARISON OF DIFFUSION COEFFICIENTS AND IONIC RESISTIVITIES IN CANDIDATE SEPARATOR MATERIALS*

MATERIALS	THICKNESS, CM	DIFFUSION COEFFICIENTS 10^{-6}, CM^2/SEC	PERMEABILITY 10^{-7}, CM^3(STP)/ SEC.CM.CM-HG	IONIC RESISTIVITY (Ω-CM) SO_2-FREE SOLUTION	SO_2-SATURATED SOLUTION
MICROPOROUS RUBBER	0.114	2.2	7.8	1.75	2.02
NAFION 110	0.028	0.8	2.8	10.4	10.4
NAFION 120	0.028	0.38	0.13	13.6	15.0
NAFION 135	0.040	2.4	8.5	19.2	19.2
NAFION 390	0.040	2.4	8.5	8.5	9.0
P-4010	0.013	0.005	0.017	20.2	20.8
P-5025	0.025	0.16	0.57	8.0	8.4
YUMICRON	0.020	0.19	0.67	9.0	9.5

*IN 50 W/O SULFURIC ACID SOLUTIONS AT 23°C AND ATMOSPHERIC PRESSURE.

TABLE 3: COMPARISON OF CELL COMPONENTS AND PERFORMANCE CHARACTERISTICS OF KEY ELECTROLYZERS*

ELECTROLYZER	ANODE LOADING (mg-Pt/cm^2)	CATHODE LOADING (mg-Pt/cm^2)	ANODE SPACER	CATHODE SPACER	E_{cell}‡ (mV)	η_a‡ (mV)	η_c‡ (mV)	IR‡ (mV)
LC-12	7	10	Pt-foil	Pt-foil	769	240	69	161
LC-17	7	2**	Pt-foil	C-paper	770	246	57	168
LC-21	7**	2**	C-paper	C-paper	738	238	32	168
LC-22	2**	2**	C-paper	C-paper	736	238	34	164

*Experiments conducted in 50 w/o H_2SO_4 at 50°C and atmospheric pressure, using microporous rubber diaphragm as separators.

**Sandwich type electrode.

‡Experimental data at 200 mA/cm^2.

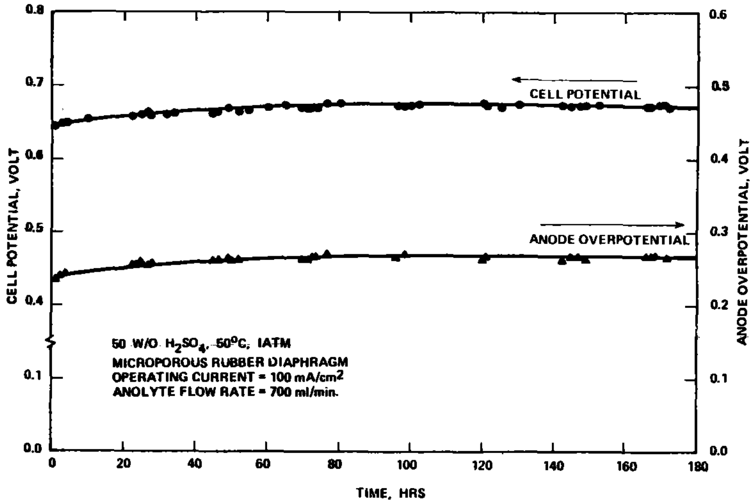

Figure 1. Variation of the Cell Potential and Anodic Overpotential in Electrolyzer LC-8 with Time During a Cell Endurance Test

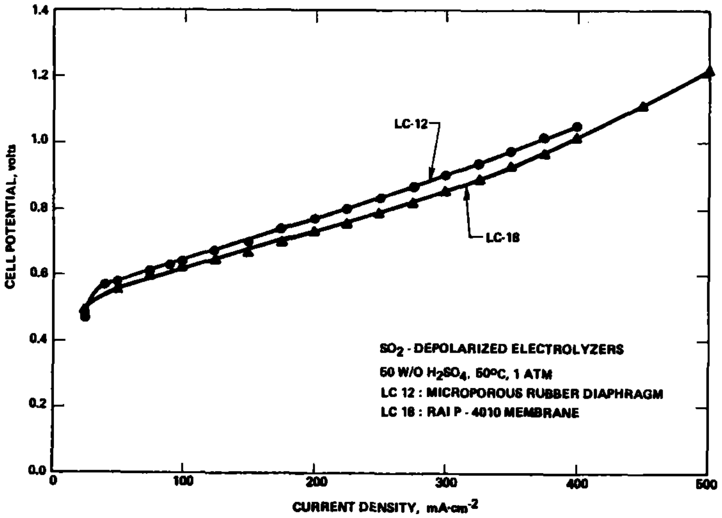

Figure 2. Cell Performance of the Electrolyzers LC-12 and LC-18

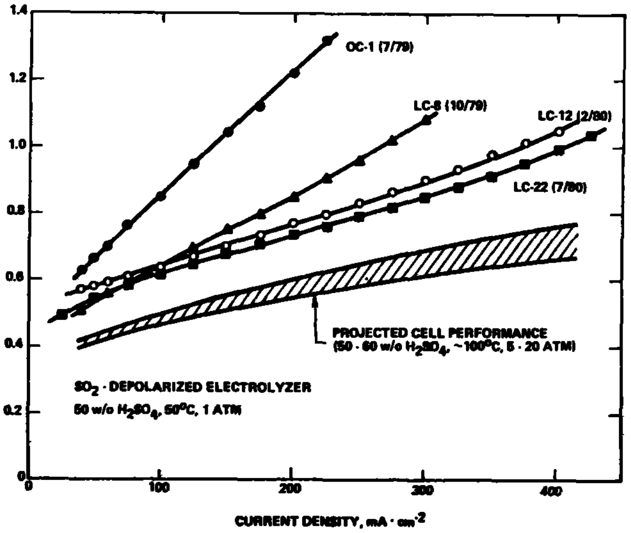

Figure 3. The Measured and Project Cell Performances of Sulfur Dioxide Depolarized Electrolyzers

of the improved cell configuration will be studied using 50 w/o sulfuric acid at 50°C and atmospheric pressure. It is expected that Teflon cell will have better performance than the lucite cell in which identical cell components (e.g., electrodes and separators) will have been used.

Acknowledgment

The authors are grateful to R. W. Buckman, Jr. and G. H. Farbman for their constant interest and encouragement. Special thanks are due to E. R. Garcia, D. R. Zamba and H. F. Ebner who performed the experimental work.

References

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2. P. W. T. Lu and R. L. Ammon, J. Electrochem. Soc. (in press).

STUDIES ON THERMOCHEMICAL WATER-SPLITTING CYCLES

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ABSTRACT

The purpose of this program was to assess the electrochemical oxidation of sulfur dioxide in relative dilute (less than 50 weight percent) sulfuric acid and to determine the preferred operating conditions (acid concentration, temperature, electrode materials) for such a cell to be mated with a metal oxide-metal sulfate water-splitting cycle. Our rough performance goals were 200 mA/cm² at 0.5 V. A sulfuric acid concentration of 33 weight percent was chosen for the experiments. As both anode and cathode performance increased with temperature in the range investigated (0° to 75°C), a temperature of 75°C or higher would appear to be optimal. Of the five materials examined, smooth or platinized platinum gave the best anode kinetics for a given potential. Nevertheless, these experiments fell short of the performance goals of 200 mA/cm² at 0.5 V or less. Altering the anode mechanism by means of a homogeneous catalyst such as iodine was, therefore, considered; experiments with potassium iodide yielded a current density of 100 mA/cm² at 450 mV on porous carbon electrodes at 25°C in 33 weight percent acid. Although such factors were not explored in this program, the authors suggest experimentation at even higher temperatures and sulfur dioxide pressures, along with more sophisticated anode fabrication. They believe that continued cell development with inexpensive electrode materials can, under those conditions, meet or exceed their initial performance goals.

Introduction

The higher temperatures and more nearly isothermal heat profiles of solar heat sources require that new thermochemical cycles be developed to realize the full potential of these newer heat-source technologies. The metal oxide-metal sulfate class of cycles under development at IGT appear well-suited for solar heat sources. This class of cycles may be represented by Reactions 1 through 3, where M indicates a metal or reduced metal oxide species.

$$MO_{(s)} + SO_{2(g)} + (x + 1)H_2O_{(\ell)} \overset{\varepsilon}{\rightarrow} MSO_4 \cdot xH_2O_{(s,aq)} + H_{2(g)} \quad (1)$$

$$MSO_4 \cdot xH_2O_{(s)} \rightarrow MSO_{4(s)} + xH_2O_{(g)} \quad (2)$$

$$MSO_{4(s)} \rightarrow MO_{(s)} + SO_{2(g)} + 1/2\ O_{2(g)} \quad (3)$$

Reaction 1 may be written as the sum of Reactions 1a and 1b, where Reaction 1a is the electrochemical oxidation of sulfur dioxide (SO_2) and Reaction 1b is a thermochemical reaction:

$$SO_{2(g)} + 2H_2O_{(\ell)} \overset{\varepsilon}{\rightarrow} H_2SO_{4(aq)} + H_{2(g)} \quad (1a)$$

$$MO_{(s)} + H_2SO_{4(aq)} \rightarrow MSO_4 \cdot H_2O_{(s,aq)} \quad (1b)$$

The cell voltage at workable current densities required for the oxidation of SO_2 (Reaction 1a) is critical to the efficient operation of any metal oxide-metal sulfate cycle. The key to making a practical sulfur dioxide depolarized electrolysis cell for the splitting of water is the optimization of the anode reaction.

Program Scope

The electrolytic oxidation of sulfur dioxide to produce sulfuric acid and hydrogen has been studied extensively in conjunction with the WAES sulfur cycle. These studies, however, have been limited to sulfuric acid concentrations of 50 weight percent or more because of the need to produce concentrated acid in that cycle. Metal oxide-metal sulfate cycles do not require the production of concentrated sulfuric acid. The purpose of this program is to examine the electrolytic oxidation of sulfur dioxide in dilute sulfuric acid solutions that are appropriate for metal oxide-metal sulfate cycles and to determine preferred cell operating conditions.

Equipment and Experimental Procedures

An H-cell constructed from 1-1/2-inch ID Pyrex process pipe was used as a containment vessel for all experiments. Separator materials were fitted across the center junction to create isolated anode and cathode reservoirs, which were electrochemically accessible to each other only through the separator material. For those experiments performed above and below ambient temperature, the cell was submerged to within 1 inch of the top in a well-regulated water bath.

Sulfur dioxide was introduced into the anode chamber of the cell via a porous glass sparging tube. The top of this chamber was sealed with a neoprene stopper containing a small vent hole to assure an atmosphere of sulfur dioxide above the liquid level. No cap was used above the cathode chamber.

A fresh mercury/mercurous sulfate reference electrode was prepared 24 hours prior to each experimental run using sulfuric acid of the same concentration as in the day's experiments. However, all electrode potentials reported in this work (except where otherwise noted) are relative to an RHE (reversible hydrogen electrode). RHE potentials were calculated using measurements taken against the mercury/mercurous sulfate electrode and formulas provided by Bode.[1]

Anode Passivation

One significant problem encountered in preliminary experiments concerned the passivation of smooth platinum anodes at moderate current densities. Clean platinum electrodes used as anodes for the oxidation of sulfur dioxide in dilute sulfuric acid exhibited excellent current densities for short periods of time. Over an extended period, however, their performance depreciated significantly. Figure 1 shows the results of experiments conducted on a 1 sq cm smooth platinum electrode in 33 weight percent sulfuric acid saturated with sulfur dioxide. The 250 ml of solution contained in the anode chamber was continuously stirred and sparged with sulfur dioxide at ~10 ℓ/hr to assure the maintenance of saturation.

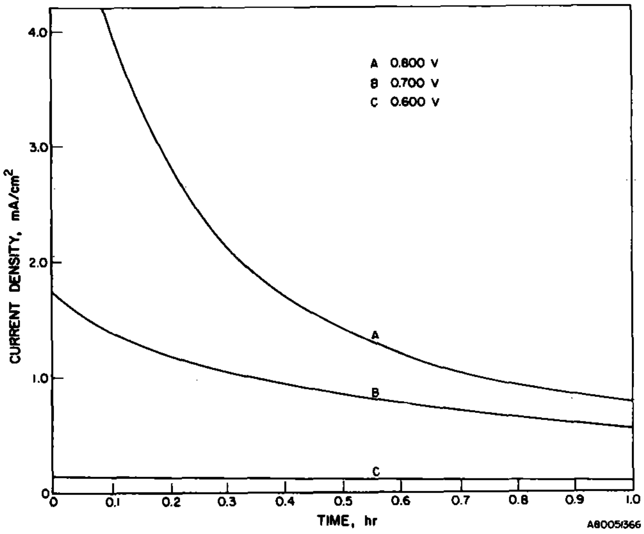

Figure 1. Decay in Anode Performance as a Function of Anode Potential (SO_2- Saturated 33 wt % H_2SO_4 at 1 atm and 22°C)

The platinum anode was first allowed to reach open circuit equilibrium with the solution and was then potentiostated to 600, 700, or 800 mV positive of reversible hydrogen in separate experiments. Changes in current density were monitored for 1 hour with a recorder.

As Figure 1 shows, passivation of the electrode at 600 mV is slight compared to that at 800 mV. Also, the rate at which the electrode passivates under these conditions is considerably faster than can be attributed to either the consumption of reactants or the buildup of soluble reaction products. On the other hand, the rate of passivation is several orders of magnitude too slow to be consistent with the rapid depletion of an adsorbed monolayer.

Although this passivation phenomenon does not present a problem in the potential region of most interest (400 to 600 mV positive of reversible hydrogen), it does demonstrate the weakness of using linear-scan cyclic voltammetry to estimate equilibrium current densities. Determination of true equilibrium current densities at a stationary voltage by monitoring the long term passivation of the electrode is impractical when a large number of measurements are to be made. As a result, a potential-step procedure was developed that takes into account both the passivation phenomenon and the need to complete an experiment within a reasonable time frame.

The purpose of these studies was to evaluate the catalytic behavior of a variety of materials used as anodes for the oxidation of sulfur dioxide. A 33 weight percent sulfuric acid solution saturated with sulfur dioxide was chosen as the preferred acid concentration and 27°C as the most convenient temperature. The potential-step technique was used in electrode experiments to arrive at equilibrium current densities. Results are summarized in Figure 2.

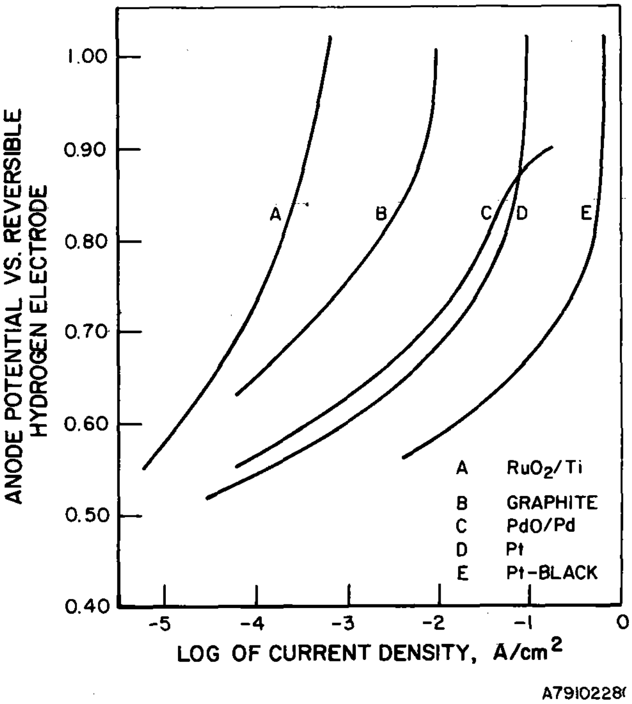

Figure 2. Tafel Plots for the Electrochemical Oxidation of SO_2 on Various Candidate Anode Materials

Discussion

At the conclusion of the initial phase of experiments, a serious discrepancy existed between our results and the results of others in the field. B. D. Strück[5] claims to have investigated 50 nonnoble materials as possible electrocatalysts for the SO_2 oxidation reaction and found none better than platinum. This conclusion is compatible with our results in light of the limited number of materials we have tested. Westinghouse,[4] however, claims that two proprietary materials show electrocatalytic performance superior to platinum. Material WAE 2 is reported to be 4 times better than platinum, and WAE 3 is 30 times better. The major discrepancies arise not with claims for the proprietary electrodes but with the published results for platinum. Parker reports a Tafel slope of 67 mV/decade, exchange current densities of 1.9×10^{-7} mA/cm^2, and limiting current densities of 1.2 mA/cm^2 at anode potentials of 770 mV RHE for the oxidation of SO_2 on platinum in 50 weight percent acid. We observed Tafel slopes of 55 mV/decade, exchange current densities of 3×10^{-7} mA/cm^2, and limiting current density of 11 mA/cm^2 at 940 mV RHE under the same conditions. In addition, we have observed limiting current densities of 100 mA/cm^2 in 33 weight percent acid on smooth platinum and 675 mA/cm^2 on platinum black electrodes.

These discrepancies can be resolved if we accept several as yet unproven assumptions concerning the origin of the passivating layer described in the preliminary experiments. Figure 3 is a current-voltage plot extended to potentials 2.0 V positive of RHE. Data were obtained using the 50 mV per five minutes potential-step technique previously discussed. Nevertheless, because a full 2.7 hours were required to reach the final voltage, Figure 3 also approximates a linear scan potentiograph with a scan rate of 10 mV/min. Peak current densities are reached at about 950 mV RHE, but unlike limiting current densities resulting from mass transfer limitations, the performance here decays at higher potentials. Because of the large volume of reactants available and the slow scan rate, this decrease in performance can only be attributed to a passivation phenomenon. It should also be noted that in the potential region from 1.5 to 1.75 V where strong oxygen evolution is observed in dilute SO_2-free sulfuric acid, the current density in the presence of SO_2 continues to decrease. This indicates that the phenomenon inhibiting the SO_2 oxidation reaction is also blocking the oxygen evolution reaction. The absence of oxygen evolution in an operating cell containing SO_2 in the anolyte was verified visually.

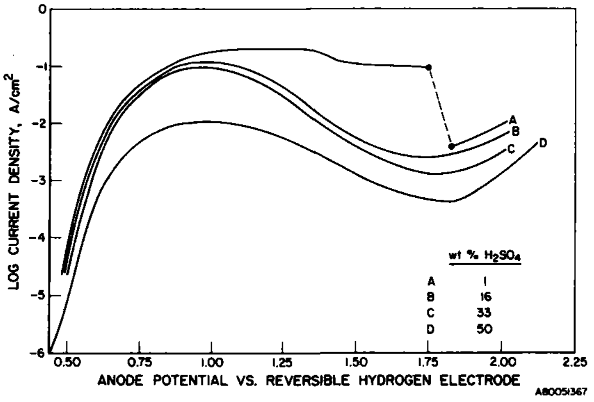

Figure 3. Electrode Performance at High Anodic Potentials (SO_2-Saturated H_2SO_4 Solution at 1 atm and 22°C)

Unusual performance is also exhibited by 1 weight percent sulfuric acid solutions saturated with SO_2. A metastable conditions appears to develop on smooth platinum in 1 weight percent acid in potential regions where the same electrode has already begun to passivate in solutions of higher concentration. This metastable condition fails suddenly, and yields a curve paralleling that observed in acid solutions of higher concentration. Although the phenomenon of sudden passivation could be reproduced in 1 weight percent acid, the potential at which the onset of failure occurred was between 1.25 and 1.8 V and was not reproducible.

Data presented in Figure 3 indicate an inverse relationship between the passivation phenomenon and acid concentration. Furthermore, the onset of the passivation phenomenon roughly corresponds with the point where adsorbed oxygen first appears in cyclic voltammograms of smooth platinum in SO_2-free sulfuric acid solutions. Coupled with the suppression of the oxygen evolution reaction at higher anode potentials, this suggests that surface oxides, which are known to catalyze this latter reaction, are intimately involved in the passivation phenomenon.

If this is true, then the practice followed by Westinghouse[2] and others of anodizing test electrodes prior to use could have an adverse effect upon their performance and lead to the report of low current densities. This is supported by the fact that the minimum in the 50 weight percent current density curve, which we observe at 1.8 volts, is below the limiting current density reported by Westinghouse, although our peak performance is an order of magnitude better. Westinghouse also reports open circuit anode potentials at 480 mV RHE after 4 hours in 50 weight percent sulfuric acid saturated with SO_2. We observed, however, potentials at 405 mV after 4 hours with annealed electrodes, suggesting that anodized electrodes may start out in a partially passivated state.

Because we have not observed passivation at anode potentials below 600 mV RHE, and a practical cell must for purposes of efficiency operate below this potential, we feel our data are more representative of the performance that can be expected from platinum electrodes in this system.

Homogeneous Catalysis Using Iodine

Midway through the program, information provided by B. D. Strück[3] indicated that small amounts of hydrogen iodide can be used as a homogeneous catalyst for the electrochemical oxidation of sulfur dioxide. A series of experiments were performed to assess this effect.

Experimental Results

Two series of experiments were conducted using potassium iodide as an additive to the anode chamber. In the first series, smooth platinum electrodes were placed in 33 weight percent sulfuric acid solutions saturated with SO_2 at 25°C and containing 0.01, 0.02, and 0.05 M potassium iodide, respectively. The current-voltage characteristics of the platinum anodes were determined using the potential-step techniques.

Two results were immediately obvious: 1) The open circuit anode potential was now about 240 mV versus RHE instead of 405 mV RHE, and 2) stable open circuit anode potentials were reached within minutes instead of hours. Figure 4 presents the results of this series of experiments as a plot of anode potential against current density. These coordinates were chosen in place of the standard Tafel plot to better illustrate the direct relationship between electrode performance and iodide concentration.

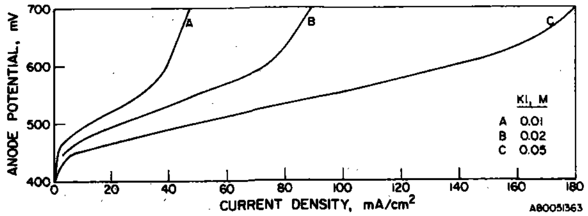

Figure 4. Effect of Iodide Concentration on Electrode Kinetics

The second series of experiments evaluated the performance of six candidate electrodes in an SO_2-saturated 33 weight percent sulfuric acid solution containing 0.05 M KI. Figure 5 presents the results of these experiments as Tafel plots.

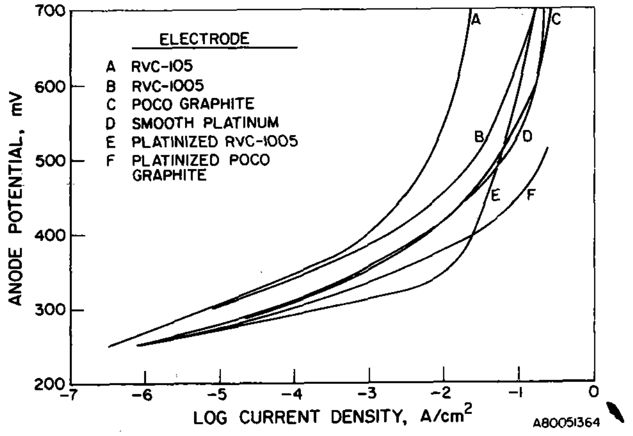

Figure 5. Performance of Various Candidate Electrodes in the Presence of 0.05 M KI

In order to minimize edge effects, electrodes of 5 sq cm frontal area were constructed. All electrodes were then mounted in wax so that only the front face was accessible to the electrolyte. The following candidate electrode materials were evaluated at 25°C:

- RVC-10-S (Reticulated Vitreous Carbon). RVC-10-S is a porous glass carbon which has a coarse pore structure with a large void space. Prior to use, this electrode was anodized at 100 mA/cm^2 for 10 minutes in 33 weight percent sulfuric acid to increase its effective surface area by etching the glassy carbon fibers.
- RVC-100-S. This glassy carbon material has a medium-coarse pore structure with about 10 times the actual surface area per unit frontal area as RVC-10-S. This electrode was also etched prior to use.
- POCO Graphite. This electrode was fabricated from an engineering sample of porous graphite provided by POCO, a division of Union-76. No information concerning the actual surface area was available, but examination with an optical microscope indicated a very fine pore structure. This electrode was not etched prior to use.
- Smooth Platinum. The electrode was anodized prior to use.
- Platinized RVC-100-S. This electrode was fabricated by electroplating platinum onto Electrode No. 2. The approximate loading of platinum was 2mg/sq cm of frontal area. Sectioning of the electrode after use and microscopic examination of a cleaned edge indicated that most of the platinum was deposited on the top few glassy fibers.
- Platinized POCO Graphite. This electrode was prepared by electroplating platinum onto Electrode No. 3. The approximate loading of platinum was 1 mg/sq cm of frontal area.

Discussion

It is apparent from Figure 4 that the current density on smooth platinum is related in an almost linear fashion to the concentration of iodide ion at any given potential. Figure 5 indicates there is at least a qualitative relationship between performance and surface area of the three carbon electrodes tested. Figure 5 also suggests that platinizing enhances the performance of carbon-based electrodes.

Although time did not permit the systematic investigation of electrode kinetics in the presence of both potassium iodide and metal sulfate, qualitative experiments indicated that KI is an effective homogeneous catalyst in the presence of either zinc sulfate or cadmium sulfate. Potassium iodide is incompatible with copper sulfate in the presence of sulfur dioxide, however, and a reaction occurs which results in a white precipitate of copper (I) salts.

One factor, as yet untested, which can be expected to improve anode performance in the presence of iodine is an increase in temperature. No problems are envisioned with respect to iodine volatility at high temperatures, because in the presence of excess SO_2 virtually all of the catalyst exists in solution as iodide ion. However, it is expected that a substantial increase in SO_2 pressure will be required to maintain this excess of SO_2 at high temperatures and high current densities.

Because it is a fully reduced species, iodide ion cannot undergo reaction at the cathode and will not present a problem should small amounts of iodide reach the cathode chamber. Iodine, on the other hand, can be reduced at the cathode. In the present system, however, substantial iodine concentrations exist only in the immediate vicinity of the anode.

The best performance observed to date on an unoptimized electrode with potassium iodide as a catalytic agent indicated a current density of 100 mA/cm^2 at a projected cell voltage of 600 mV. There is every reason to believe that with proper electrode development and the application of higher temperatures and pressures, the project goals of 200 mA/cm^2 at a cell voltage of 500 mV can be achieved.

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PROGRESS IN THERMOCHEMICAL HYDROGEN PRODUCTION

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ABSTRACT

Rapid progress in the technology of thermochemical hydrogen production coupled with rising energy prices brought this technology closer to parity with conventional energy conversion processes in 1979-1980. Progress in the major pure thermal cycle (sulfur-iodine) and the major hybrid cycle indicated that cost and efficiency goals set for these cycles could be met with continued process research and development.

Rising projections for synfuels costs place fuels from primary heat within range of fuels from fossil energy. Present projections indicate hydrogen may be produced by either major cycle for about \$12.00/GJ vs. about \$9.00 for gasified coal.

INTRODUCTION

Hydrogen produced from water by largely thermal reactions has progressed from a speculative topic of research to demonstration since the energy problem became visible in 1974. Initially, the thermodynamics of thermochemical cycles were poorly understood, leading to claims of very high efficiency and, correspondingly, very low costs. Recognition of second law requirements for heat rejection were soon applied, resulting in lesser claims but sounder chemical processes with which to work.

The thermodynamics of thermal processes show that the same restrictions apply to chemical processes as apply to heat engines. Thus, the advantage of thermochemical hydrogen production over electrical production followed by electrolysis must lie in a better utilization of heat.

It is generally (but not universally) conceded that electrolysis will be superior to thermochemical cycles when process temperatures do not exceed about 750°C. This is related to the thermodynamic properties of materials which translates to the need for processes with multiple high-temperature steps. It may be roughly estimated that each high-temperature step with related separations will cost from \$5 to \$8 in capital charges.

Above 800°C, processes with a single high-temperature process are possible. The decomposition of sulfuric acid or of metal sulfates is the most common high-temperature step proposed. The decomposition of sulfuric acid is especially attractive because it proceeds catalytically at about 850°C, does not require rapid quenching to prevent back reaction, and inputs the major share of the total energy requirement into the process.

Once accomplished, however, the resulting sulfur dioxide, separated from the co-product oxygen, must be combined with water to make hydrogen and reform the sulfuric acid. This may be considered as a process to recover the energy value of sulfur dioxide in the form of hydrogen. When reacted to form sulfuric acid, sulfur dioxide has about 80% of the energy required for water decomposition.

The sulfur-iodine and hybrid processes differ primarily in their approach to conversion of sulfur dioxide. Both have promise for commercial success. An analogous situation is seen in the production of hydrogen peroxide where both an electrolytic and a pure chemical process co-exist, the latter being the newer process.

SULFUR-IODINE CYCLE

Process improvements in this cycle were derived from applied research on the water-sulfuric acid-iodine hydrogen iodide system at General Atomic Co. (San Diego, CA). The process (described elsewhere in this Proceedings) must achieve good conversion of sulfur dioxide with a minimum of water and without excessively exothermic reactions whose energy would have to be resupplied at higher temperature. At present, the major technical problem appears to be the preparation of dry hydrogen iodide from the lower phase iodine-water-hydrogen iodide system. The problem is complicated by the necessity of breaking the hydrogen iodide-water azeotrope (57% HI) which boils at 127°C. Extraction of water by phosphoric acid followed by distillation is presently used. Other methods of removing water from HI are under investigation.

After identification of several process improvements in FY 1979, principally liquid-phase decomposition of hydrogen iodide and staged reaction of sulfur dioxide with iodine and water, demonstration of these improvements was achieved in FY 1980. Other work included continued development of a bench-scale continuous process. Construction of this apparatus has already led to some improvements in design and control of the process.

The major effort in FY 1981 should be in process chemistry, particularly in the preparation of dry hydrogen iodide. A simple and cheap solution to this problem could make this cycle competitive with coal-based synfuels as a source of clean fuel.

HYBRID CYCLE

Substantial advances in the electrochemical part of this cycle (described elsewhere in this Proceedings) were achieved at Westinghouse Advanced Energy Systems Division (WAESD) on heterogeneous electrocatalysis, and at the Institute of Gas

Technology (IGT) on homogeneous electrocatalysis of sulfur dioxide. Electrolysis of sulfur dioxide has turned out to be a difficult and subtle technology which must balance electrolyzer costs and electrical consumption in an electrochemical system sensitive to poisoning by sulfur dioxide. Several options are available.

In 1975, Westinghouse researchers achieved production of hydrogen and sulfuric acid from sulphur dioxide and water in a laboratory cell. The operating conditions were extremely promising (600 mV cell potential at 200 mA/cm^2). This performance, however, has turned out to be nearly an optimum in acid of 50% strength or greater, and actual cell performance has been substantially less favorable. The electrocatalyst, platinum, has risen in price five-fold since 1975. In addition, the relatively low concentration of sulfur dioxide which can be dissolved in sulfuric acid limits the current density achievable at acceptable voltages.

This year, Westinghouse began extensive tests on improved carbon electrodes with highly dispersed electrocatalysts. Preliminary results gave a good indication that an electrolyzer of reasonable cost could be manufactured. These results came after basic electrochemical experiments had shown how to prepare, age and maintain catalytic electrodes in the presence of sulfur dioxide. Further work is being conducted on reduced catalyst loading.

The Institute of Gas Technology conducted similar tests but at lower acid strengths. They found superior performance at acid concentrations near 30% due to the very low electrical resistance and viscosity. This is considered too low an acid strength for the hybrid cycle, but possibly acceptable for a cycle based on the decomposition of a metal sulfate.

Other work at IGT included a variation on German studies with an iodide homogeneous electrocatalyst for the sulfur dioxide electrode. These tests showed excellent prospects for eliminating platinum altogether on positive electrode (it is still required at the hydrogen electrode) while also bettering performance. Futher study may develop a breakthrough in this technology.

PROCESS ECONOMICS

There is still little definitive work on the costs of hydrogen by thermochemical cycles. Both hybrid and sulfur-iodine cycles, however, are relatively straightforward extensions of chemical process technology. Major costs uncertainties include the cost of nuclear, solar or fossil heat at 850°C, the cost of the sulfuric acid decomposer and the cost of the sulfuric acid vaporizer. The latter two can be estimated by costing similar critical high-temperature processes. For example, an ethylene plant which cracks ethane at high-temperature followed by a high-pressure distillation costs about $350/kW of ethylene (August, 1980 data), corresponding to about $6 to $8/GJ. Cracking of sulfuric acid should be at least comparable in cost since it is somewhat less complex.

Costs for the low-temperature steps will be at least comparable with the high-temperature step in both the hybrid and sulfur-iodine cycles. In the former case, the cost of the electrolyzer may be as low as $2000/$m^2$ or about $675/kW ($4 to $5/GJ) with electrical production accounting for another $300/kW ($1.70 to $2.20/GJ). The final cost will be dependent on heat costs. Estimated total cost may be about $16/GJ.

The sulfur-iodine system is somewhat less familiar, although the Kel-Chlor process is similar in that chlorine is obtained from hydrochloric acid by a thermal process, similar to the decomposition of hydrogen iodide. Costs in 1980 for Kel-Chlor processing would amount to about $3 - $6/GJ of hydrogen. It is expected that the sulfur-iodine process will have a somewhat higher process efficiency than the hybrid process (42 vs 38%), thus requiring slightly less heat. Estimated total cost for hydrogen may be about $13/GJ.

SUMMARY

Both the sulfur-iodine and hybrid thermochemical cycles appear promising as methods to produce hydrogen, especially in view of their technological advancement and the emerging high costs of other synfuels. Estimates of process costs are difficult and dangerous to make. It appears, however, that the pure thermochemical cycle will produce hydrogen in large, mature plants more cheaply than the hybrid plant. The reason is that eletrolytic processes do not acquire the economies of scale in sizes greater than a few megawatts as do chemical processes.

PROJECT SUMMARY

Project Title: Simulation and Evaluation of Latent Heat Thermal Energy Storage/Heat Pump Systems

Principal Investigator: T. W. Sigmon

Organization: Research Triangle Institute
P. O. Box 12194
Research Triangle Park, North Carolina 27709
Phone (919) 541-5878

Project Goals: To develop a simplified computer simulation of the performance of TES/Heat Pump systems and compute and compare system life cycle costs at various simulation sites.

Project Status: Technical tasks have been completed and final report is being prepared.

Contract Number: DE-AC-01-79ET-26707

Contract Period: 7/12/79 to 7/11/81

Funding Level: $78,000

Funding Source: Division of Energy Storage, Department of Energy

PROJECT SUMMARY

Project Title: Storage Assisted Air Conditioning

Principal Investigators:

1. Joseph E. Rizzuto
   New York State Energy Research
   and Development Authority
   Empire State Plaza
   Albany, New York 12223
   (518) 465-6251
2. Fred Avril
   Long Island Lighting Company
   250 Old Country Road
   Mineola, New York 11501
   (516) 228-2042
3. Maurice Lang
   Institute of Energy Conversion
   One Pike Creek Center
   Wilmington, Delaware 19808
   (302) 995-7155

Project Goals: The primary objectives of this program are to design and demonstrate a storage-assisted air conditioning system using CHUBS which will impose the minimum electric demand on the utility system. The CHUB storage system contains a Glauber's salt-based phase change material which will be evaluated under actual service conditions. Also to be evaluated under the program are: air conditioner system performance; energy storage sub-system performance; electrical demand and energy requirements; temperature and humidity control capability; and system cost.

Project Status: The tasks of this program include system design, parts procurement and fabrication, system and instrumentation installation, checkout, system test and monitoring, and analyses and reporting. The storage-assisted air conditioning system and instrumentation were installed in July of 1980. System checkout was completed during the first week of August. The system was operational as of August 8, however, system optimization and refinement of the data collection process will be on-going throughout the program.

Data will be taken throughout the remainder of this air conditioning season and during next season as required.

Contract Number: 194-31501V

Contract Period: August 1979 - December 1980

Funding Level: $50,000

Funding Source: $25,000 - Oak Ridge National Laboratory
$25,000 - New York State Energy Research and Development Authority

PROJECT SUMMARY

Project Title: Experimental Evaluation of Thermal Energy Storage

Principal Investigators: J.G. Asbury and H.N. Hersh

Organization: Special Projects Group, Energy and Environmental Systems Division
Argonne National Laboratory
Argonne, IL 60439

Project Goals:

- Experimentally determine the technical performance of commercially available TES residential heating units under severe U.S. weather conditions.
- Assess the benefits and costs of TES to the customer, the utility and society.
- Determine user acceptance of TES.
- Identify and define TES issues, R&D needs and barriers to commercialization.
- Establish optimal sizing procedures.
- Establish uniform TES testing standards.

Project Status:

- A data base has been developed based on two heating seasons and 45 test and 30 control homes in Maine and Vermont. Based on an analysis of monitored temperatures and electrical energy used for space heating, fuel bills and reports of users and utilities, the technical performance of TES ceramic and hydronic systems is deemed to be satisfactory.
- An assessment of the benefits and costs of customer-owned TES for residential and commercial applications indicates that the net returns to society of such investments exceed their costs by a substantial margin.
- A user survey by an independent organization indicates a high degree of customer acceptance and positive attitudes towards TES.
- At the end of the second heating season, the participating utility in Maine (Central Maine Power Co.) decided to promote TES in its service area in order to slow the growth of its peak capacity and to level the daily load.
- A calorimeter chamber has been built and standardized procedures for testing TES modular units are being developed as an aid to commercialization.

Contract Period - FY80
Contract Funding - $150K

PROJECT SUMMARY

Project Title: Development of Optimum Process for Electron Beam Crosslinking of High Density Polyethylene Thermal Energy Storage Pellets, Process Scale-Up and Production of Application Quantities of Material

Principal Investigator: Ival O. Salyer

Organization: University of Dayton
300 College Park
Dayton, OH 45469
(513) 229-4235

Project Goals: The objectives of this project are to determine the irradiation conditions for preparing thermally form stable polyethylene pellets for thermal energy storage applications and to process 15,000 pounds of pellets which are suitable for full scale application tests.

Project Status: The electron beam irradiation conditions for the preparation of thermally form stable high density polyethylene pellets have been determined. The values of the enthalpy of fusion have been measured on the polyethylene pellets as a function of the irradiation dose. A 225 pound pellet bed has been cycled through the melting temperature for more than 100 melt-freeze cycles. The pellet bed has remained porous to the free flow of the heat exchange fluid and the pellets have retained their initial physical form throughout the testing. A 15,000 pound quantity of the pellets is presently undergoing irradiation processing and is expected to be completed during the month of August 1980. The irradiated high density polyethylene pellets are to be delivered to DOE for full scale thermal energy storage tests.

Contract Number: 7641

Contract Period: 1 April 1980 - 31 October 1980

Funding Level: $42,000

Funding Source: Department of Energy
Division of Energy Storage
Oak Ridge National Laboratory

PROJECT SUMMARY

Project Title:	Operation of a Thermal Energy Storage Test Facility
Principal Investigator:	Mark P. Ternes
Organization:	Oak Ridge National Laboratory P.O. Box Y Oak Ridge, TN 37830 (615)-574-0749
Project Goals:	Design and build a thermal cycling facility for determining the behavior of full-scale TES units. The facility will have the capability for testing with both liquid (water, ethylene glycol solutions, and salt brines) and air transport at variable heat input/extraction rates over a temperature range from 0 to 140°C (32 to 284°F). Determine the thermal behavior of prototype and existing (commercial) PCM TES systems in both heating and cooling modes. Develop improved and advanced storage systems. Propose performance standards.
Project Status:	Construction of the liquid cycling loop has been completed. Thermal stratification tests for both hot and cold water are currently underway and will continue into November 1980. Testing and evaluation of four PCM TES units will immediately follow the stratification studies. Detailed design of the air cycling loop will be initiated by FY 1981.
Contract Number:	In-house
Contract Period:	Continuing
Funding Level:	$200,000
Funding Source:	Department of Energy Thermal and Mechanical Energy Storage Systems Division

PROJECT SUMMARY

Project Title: Technology Development of Earth Storage

Principal Investigator: M. P. Ternes

Organization: Oak Ridge National Laboratory
P.O. Box Y
Oak Ridge, TN 37830
(615)-574-0749

Project Goals: Develop technology and demonstrate systems for utilizing heat stored in undisturbed earth for improving the performance of heat pumps.

Carry out field experiments to determine storage characteristics of undisturbed earth under residential buildings (crawl space) and its effects on performance of heat pumps for both heating and cooling. Develop computer models of the crawl space and heat pump to investigate system performance and economics in different climatic regions throughout the nation. Demonstrate crawl space heat pump systems.

Project Status: Winter operating data from three field experiments has been collected and is currently being digitized, with data reduction and analysis to follow. Collection of summer operating data from three field experiments is underway. The computer model of the crawl space is complete and will be checked against the actual data now being digitized. Crawl space simulations will begin following this comparison. Heat pump models are currently under development. Planning for a definitive test addressing concept performance and economics has begun.

Contract Number: In-house

Contract Period: Continuing

Funding Level: $85,000

Funding Source: U.S. Department of Energy
Thermal and Mechanical Energy
Storage Systems Division

PROJECT SUMMARY

Project Title: Mathematical and Physical Modeling for TES Subsystems

Principal Investigator: A. D. Solomon

Organization:
Oak Ridge National Laboratory
Building 9704-1
P.O. Box Y
Oak Ridge, TN 37830
Telephone: (615) 574-8696

Project Goals: Develop capability for predicting the performance of TES subsystems and components using PCM's based on mathematical and physical models. Similarly, perform simulations of processes relevant to TES subsystem performance, and develop mathematical tools and techniques for predicting the behavior of PCM's undergoing changes of phase.

Project Status: A number of computer simulation programs have been prepared, of varying flexibility and applicability. The first, TES, permits us to simulate a simple body undergoing a phase change process due to forcing conditions at its surface of Dirichlet, flux or convective type. This has been specialized to a model of the behavior of a system of PCM containers and used to perform simulations of arrays of University of Delaware Chubs with the inclusion of dehumidification effects for the air transfer fluid. The latter includes the possibility of transfer fluid flow reversal at specified times. A second simulation model prepared is that of heat conduction with phase change in a block of earth beneath the crawl space of a house, interacting with air flowing through the crawl space. The model has thusfar been compared favorably with data obtained from a test house. Comparisons of computer simulation predictions with experimental results obtained for melting and solidification experiments with N-Octadecane Paraffin wax have been completed. In the past year closed form, easily computable expressions have been obtained for the melting time of a rectangular body and for a simple body with a convective heat transfer at its surface. These relations are extensions of the work of earlier years, aimed at obviating the necessity of performing lengthly computations in the search for answers to specific problems arising in sizing systems and estimating system performance.

The tasks for FY 80 will be: 1) Completion of simulation programs for phase change with natural convection in the melt, which are currently being developed; 2) Derivation of a closed form expression for the melting time and heat flux behavior in a body subject to a radiation (fourth power) boundary condition; 3) Development and study of simulation models for more advanced systems, and the development of techniques for deriving the maximum information from them with the least computational effort.

Contract Number: W-7405-eng-26

Funding Source: U.S. Department of Energy

PROJECT SUMMARY

Project Title: Thermal Energy Storage Testing Facility

Principal Investigator: Robert J. Schoenhals

Organization: Ray W. Herrick Laboratories
School of Mechanical Engineering
Purdue University
West Lafayette, Indiana 47907
Telephone: (317) 749-6321

Project Goals: Develop a prototype thermal energy storage (TES) testing facility for electrically heated TES units that can be duplicated at established commercial or government laboratories, or at TES manufacturers' R & D laboratories. Provide technical information to assist ASHRAE in its effort to establish a standard for performance evaluation of electrically heated TES units.

Project Status: A calorimeter chamber has been fabricated and instrumented for testing of room-size TES units. Apparatus has also been assembled for testing of central TES units. One central unit and several room-size units have been tested. Variations in test procedure and apparatus configuration have been investigated both analytical and experimentally, and information based upon the results has been provided to ASHRAE.

Contract Number: ANL 31-109-38-4666

Contract Period: January 2, 1979 - September 30, 1980

Funding Level: $98,170

Funding Source: Argonne National Laboratory
Energy & Environmental Systems Division
Special Projects Group

PROJECT SUMMARY

Project Title: Survey of Thermal Storage Installations in the United States and Canada

Principal Investigator: Harold G. Lorsch

Organization:
Franklin Research Center
20th and the Parkway
Philadelphia, PA 19103
(215) 448-1591

Project Goals: Create an inventory of thermal storage installations, for either hot or cold storage or both, in commercial and industrial use in the United States and Canada. This inventory will then be published in a special brochure by ASHRAE in order to obtain the broadest dissemination among designers and potential users.

Project Status: A team of mail and telephone inquirers has been organized at the Franklin Research Center. A Technical Evaluating Committee (TEC) has been created by ASHRAE (American Society of Heating, Refrigerating and Air Conditioning Engineers). This TEC is to oversee the progress of the project and to ensure that the results are valid and that the ensuing publication meets the publication standards of ASHRAE.

A questionnaire has been designed and approved by the ASHRAE TEC. In excess of 100 letters have been mailed out. Major source publications have been obtained.

Contract Number: BOA 41B-28915C

Contract Period: July 2, 1980 to September 30, 1980
(to be extended)

Funding Level: $24,000

Funding Source: Department of Energy/ UCC Subcontract

Project Title: Evaluation of Olivine Ceramic Refractories for Thermal Energy Storage Applications

Principal Investigators: Hayne Palmour III, Billy M. Gay and R. L. Cochrane

Organization:
North Carolina State University
Engineering Research Services Division
P. O. Box 5995
Raleigh, NC 27650
(919) 737-2351 (or 2347)

Project Goals: The principal objectives of this program are to (1) experimentally determine the degree of improvement in thermal and mechanical performance that can be obtained with an olivine thermal storage brick made of domestic materials using advanced processing techniques compared with state-of-the-art as represented by commercial European bricks, (2) conduct an assessment of existing German ceramic process technology and determine its adaptability to domestic raw materials and manufacturing practices, and (3) investigate, on a limited basis, methods for further improvement of domestic olivine brick.

Project Status: New Contract (since August 18, 1980), continuing previous work initiated January, 1978 by the University and supported in part by the North Carolina Energy Institute from June, 1978 through March, 1980. Prior accomplishments of that program have been reported in two prior papers and a Technical Report, and are briefly summarized in the attached paper.

Tasks under the present program include (1) installation and use of improved, computer-based instrumentation for performance evaluations of heat storage refractories under cyclic use conditions, (2) acquisition of the services of a European consultant knowledgeable about West German materials and processes for ceramic heat storage applications, and (3) continuing lab-scale process/property optimization studies. At this early stage, equipment orders have been placed, program planning and software development are underway, and arrangements are being made to bring the chosen consultant to the U.S. for analysis and discussions of established European technology.

Contract Number: US DOE Contract No. W-7405-eng-26, Union Carbide Corporation, Nuclear Division Subcontract No. 7959

Contract Period: August 18, 1980 - November 30, 1981

Funding Level: $73,013.00

Funding Source: Department of Energy through Union Carbide Corporation, Nuclear Division (ORNL).

PROJECT SUMMARY

Project Title: Evaluation of Stratified Thermal Storage System for Oliver Springs Elementary School

Principal Investigators: R.L. Reid and A.F.G. Bedinger

Organization:
The University of Tennessee
Energy, Environment, and Resources Center
329 South Stadium Hall
Knoxville, Tennessee 37916
615-974-4251

Project Goals: A combination refrigeration heat recovery system and stratified thermal storage system using a flexible membrane to resist temperature blending will be evaluated. The evaluation will consist of two related parts: 1) evaluation of overall HVAC system thermal performance and comparison with alternate systems and 2) evaluation of the flexible membranes ability to resist temperature blending.

Project Status: The Oliver Springs Elementary School is under construction with an expected completion date of January 1981. Installation of the data acquisition system is underway with data gathering expected to begin in January 1981.

Contract Number: 7685 (Project Authorization X60)

Contract Period: June 1, 1980 through November 30, 1980

Funding Level: $64,888

Funding Source:
Union Carbide Corporation
Nuclear Division

PROJECT SUMMARY

Project Title: The SERI Solar Energy Storage Program

Principal Investigator: Charles E. Wyman

Organization: Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401
(303) 231-1753

Project Goals: The overall objective of this program is to gain a better understanding of advanced thermal energy storage technologies for specified applications and obtain the data and information that will allow developers to select the most promising thermal energy storage technologies for identified applications. Research is performed on direct contact heat exchange and thermochemical storage and transport to provide a basis from which to asses these promising technologies. Research is subcontracted to define new thermal energy storage and transport concepts. Analyses, research, and development are supported to improve the cost and performance of thermal energy transport concepts. Systems analyses identify thermal energy storage concepts for solar thermal applications. Finally, efforts are directed to help coordinate thermal energy storage programs.

Project Status: Preliminary analyses and experiments have been completed for direct contact heat exchange and equipment has been assembled to test the concept further. An analysis has been made of thermochemical storage and transport. Cost goals based on value have been derived for thermal energy storage in solar thermal electric applications and preliminary rankings have been completed of thermal storage for water/steam and organic fluid receiver systems. A workshop has been conducted to review progress on the Thermal Energy Storage for Solar Thermal Applications Program, and a basis has been developed for coordination of thermal energy storage R & D for solar heating and cooling of buildings.

Contract Number: EG-77-C-01-4042

Contract Period: October 1979-September 1980

Funding Level: $1,505,000

Funding Source: Department of Energy Division of Thermal and Mechanical Energy Storage Systems.

PROJECT SUMMARY

Project Title: Latent Heat Storage Research

Principle Investigator: John D. Wright

Organization: Solar Energy Research Institute
Solar Thermal Research Branch
1617 Cole Blvd.
Golden, Colorado 80401
(303) 231-1765

Project Goals: The goals of the latent heat storage research project are to understand the basic mechanisms which govern direct contact heat transfer, assess the operational characteristics of direct contact salt hydrate/oil latent heat storage systems, and provide a basis for selecting, assessing, and designing advanced storage concepts.

Project Status: A model of direct contact heat transfer in salt hydrate/oil systems has been developed which shows reasonable agreement with the limited experimental data available, and identifies controlling mechanisms for direct contact heat transfer. Experiments have been carried out to test methods of predicting drop size and to determine the heat transfer characteristics of droplets. An experiment has been constructed to test holdup predictions and to assess operational characteristics.

Contract Number: EG-77-C-01-4042

Contract Period: October 1979-September 1980

Funding Level: $170,000

Funding Source: Department of Energy Division of Thermal and Mechanical Energy Storage Systems.

PROJECT SUMARY

PROJECT TITLE: Systems Analysis of Thermal Storage

PRINCIPAL INVESTIGATOR: R.J. Copeland

ORGANIZATION: Solar Energy Research Institute
1617 Cole Blvd.
Golden, CO 80401
(303) 231-1012 (FTS-327-1012)

PROJECT GOALS: The objective of this project is to identify promising thermal storage concepts for research and development. The value of thermal storage concepts in solar thermal applications is analyzed to establish cost goals. Thermal Storage concepts are compared to each other using a consistent costing approach and accounting for the performance differences between the concepts. The best concept for specific applications are recommended for continued development. Analyses of new concepts and applications are also conducted to identify promising areas for research.

PROJECT STATUS: During FY80 a preliminary screening of thermal storage concepts was conducted. Solar thermal electric power production with a water/steam receiver (Barstow Technology) and a solar thermal total energy system with an organic fluid receiver (Shenandoah Technology) were the applications. Promising concepts for each were identified. The analysis is being extended to more applications (electric power, process heat and total energy) with water/steam, organic fluid, and air/Brayton solar thermal systems. A SERI subcontractor, Stearns-Rogers, is providing consistently calculated cost and performance data of the thermal storage concepts. Based on that data, SERI will analyzed the impacts on delivered energy cost and recommend concepts for continued development.

A ranking of thermal storage technologies based upon value for solar thermal electric power systems was performed. For diurnal applications, second generation thermal storage technologies must be improved 30% to 70% over first generation thermal storage technologies to meet the value derived cost goals. Potential long duration storage technologies were identified.

The value of thermal storage in solar thermal process heat systems is currently being studied. In addition ground mounted thermal storage concepts for a dish/stirling system are being evaluated.

CONTRACT NUMBER: EG-77-C-01-4042

CONTRACT PERIOD: October 1979 - Septmeber 1980

FUNDING LEVEL: $310,000

FUNDING SOURCE: Department of Energy, Division of Energy Storage

PROJECT SUMMARY

Project Title: Cost and Performance of Thermal Storage Concepts in Solar Thermal Systems

Principal Investigator: A. W. McKenzie

Organization: Stearns-Roger Services Inc., P.O. Box 5888, Denver, Colorado 80217

Project Goals: The objectives of this study are as follows:

°To provide consistently calculated cost data for several thermal storage concepts in several solar thermal systems.

°To provide consistent and realistic performance data for thermal storage concepts integrated into solar thermal systems.

°To provide the above data as projected for a mature technology based upon the state-of-the-art and anticipated improvements in the storage technolgies.

Project Status: The following has been accomplished in the course of the study to this point:

°Available thermal concepts have been reviewed through a literature search, and contacts with the Solar Energy Research Institute, national laboratories, and other contractors.

°Reference systems were established in which the storage systems were compared.

°The systems selected for further study were established on the basis of a developed set of screening criteria.

°Schematics were developed for the remaining forty systems.

°Quantities were established for the above and rough-order-of-magnitude (ROM) costs computed.

°Based on the ROM costs and the screening criteria, candidates for further study were selected.

°Schematics will be more fully developed and costing will be further refined for these twenty remaining systems.

°A technical review will be held in September, 1980 of these systems.

°The results of the technical review will be incorporated into the systems. Their storage range will be expanded, and further costing refinements applied.

°The results of the thermal storage analysis will be documented in a final report.

Subcontract Number: XP-0-9001-1

Contract Period: March 1980 - March 1981

Funding Source: Solar Energy Research Institute

PROJECT SUMMARY

Project Title: High Temperature Molten Salt Thermal Energy Storage

Principal Investigator: T. D. Claar, R. J. Petri

Organization: Institute of Gas Technology
3424 South State Street
Chicago, Illinois 60616
(312) 567-3650

Project Goals: The main objective of this program is to select and screen in 1000 and 3000 hour compatibility tests latent-heat alkali and alkaline earth carbonate storage salts, containment materials, and thermal conductivity enhancement (TCE) materials to satisfy the high temperature (704° to 871°, 1300° to 1600°F) thermal energy storage requirements of advanced solar-thermal power generation concepts. The results of these compatibility tests will lead to selection of the materials combinations that best meet the anticipated solar power system requirements.

Project Status: The tasks in this program include: 1) Materials Compatibility Testing — Materials Selection (Salt, Containment, and Thermal Conductivity Enhancement Materials Selection), 1000 Hours Compatibility Testing, and 3000 Hour Compatibility Testing; and 2) Salt Property Measurements. Accomplishments to date include completion of materials investigation and selection; assembly of capsules for total testing matrix; completion of 1000 hour compatibility testing; initiation of post-test examination and preliminary evaluations.

The tasks for FY 80 include: 1) completion of 3000 hour matrix selection and testing 2) completion of thermophysical and transport property measurements on two most promising salts.

Contract Number: DEN3-156

Contract Period: September 1979 - September 1980

Funding Level: $136,000

Funding Source: NASA-Lewis Research Center for U.S. Department of Energy

PROJECT SUMMARY

Project Title: Active Heat Exchanger System Development for Latent Heat Thermal Energy Storage System

Principal Investigator: J. Alario, R. Haslett

Organization: Grumman Aerospace Corporation
Bethpage, N.Y. 11714
Telephone: (516) 575-2433/3924

Project Objectives: Develop an active method of heat exchange in a latent heat (salt) thermal storage system that prevents a low thermal conductivity solid salt layer from forming on heat exchanger surfaces.

Project Status: A modular test unit of 10KW heat transfer rate and 10KW-Hr storage was designed and fabricated. Two interchangeable heat exchanger modules can be used to investigate heat transfer by 1) direct contact between salt and a liquid metal eutectic and 2) scraping the solidifying layer off a rotating drum. The concept selection, evaluation and design phases of the program have been published in Topical Report No. NASA CR 159726 (January 1980).

The test evaluation phase for the direct contact heat exchanger concept was started mid-February 1980, but was interrupted in June due to funding limitations. Various problems with the pumps, plumbing leaks and corrosion failure of electrical heaters contributed to delays. At the time of interruption, due to extensive heater failures, the media transfer technique had been verified, liquid metal was circulated through the heat exchanger, all system components were preheated and the salt system was about to be activated.

The program is in a hold status awaiting hardware refurbishment and heater replacement.

Contract Number: DEN 3-39

Contract Period: 6/13/78 to 8/13/80

Funding Level: $225,000

Funding Source: NASA-Lewis Research Center

PROJECT SUMMARY

Project Title: Heat-of-Fusion Energy Storage-Boiler Tank

Principal Investigator: Dr. Talbot A. Chubb

Organization: Naval Research Laboratory
Code 4120
Washington, DC 20375
Telephone: (202)767-3580

Project Goals: Demonstrate feasibility of heat-of-fusion energy storage-boiler tank.

Evaluate media and heat transfer fluid properties and cycle life characteristics.

Perform storage media-containment materials compatibility studies.

Design, build, and operate a 2 MWh storage-boiler tank.

Project Status: Completed site preparation. Completed detailed design of such items as pressure containment vessel, boiler, terphenyl circulation system, basket to hold salt cans, etc.

Published Progress Report which includes further study of Heat-of-Fusion Energy Storage Systems using containerized salts.

Procured major components such as terphenyl pump, feedwater pump, insulation, heaters, control parts, etc.

Fabricated 80% of pressure containment vessel and fabricated prototype of baskets required to hold salt cans.

Contract Number: EC-77-A-31-1024

Contract Period: July 1976 to January 1981

Funding Level: DOE - $460,000; NRL - $360,000

Funding Source: DOE-Division of Energy Storage Systems and NRL

PROJECT SUMMARY

Project Title: Heat Storage in Alloy Transformations

Principal Investigator: C. E. Birchenall

Organization: University of Delaware
Materials/Metallurgy Faculty
College of Engineering
Newark, DE 19711
(302) 738-2194

Project Goals: The primary purpose was to show that congruent solid to liquid transformations of metals and alloys provided energy storage densities that are high enough to compete with other storage materials, mainly inorganic salts. In addition to measuring transformation energies for melting of pure metals and alloy eutectics, expansion coefficients of solids and melts and volume changes during transformation were sought. Preliminary information on chemical stabilities of container materials has been obtained.

Project Status: Calorimetric measurements have been done on the transformation of aluminum and a wide selection of its alloys containing copper, magnesium, silicon, zinc, calcium and phosphorus. These data, combined with those obtained in earlier studies, appear to be sufficiently precise and to cover a sufficient number of cases to give a representative picture of the thermal performance that can be expected of eutectic alloys in the 600 to 1200 K range. Numerous alloys, having heats of transformation from 210 to 545 kJ/kg, cover this range so that few large temperature gaps exist. Measurements of representative alloys show that volume changes during transformation are on the order of 5 pct. Some salts show volume changes up to 5 times greater. The alloys have been handled successfully in the laboratory in graphite containers. SiC and other carbides probably would not be attacked by these alloys.

The major goals of this project have been met, and evaluation of alloys relative to other storage materials is going forward. It is anticipated that new support will be sought for the design and construction of container vessels and channels that are iron-based alloys protected by carbide coatings. The central issue will be whether a system can be fabricated then coated or whether the alloy pieces must be coated prior to final shaping, joining and finishing.

Contract Number: NSG-3184

Contract Period: July 1, 1978 - November 30, 1980

Funding Level: $183,783

Funding Source: NASA Grant with funds from U. S. Department of Energy, Division of Energy Storage Systems

Project Summary

Project Title: Thermal Energy Storage for Residential Energy Conservation

Principal Investigator: David Goldenberg

Organization:
TRW Inc.
Energy Systems Group
P. O. Box 3007
Oak Ridge, Tennessee 37830
Telephone: 615/482-9054

Project Goals: Evaluate the potential of thermal energy storage applications involving passive solar systems and waste heat recovery from fossil-fueled furnaces for gas and oil conservation in the residential sector.

A pebble bed device was analyzed for improvements in furnace seasonal efficiency. Passive solar systems were analyzed for fossil energy conservation benefits.

Project Status: Final report was submitted to Oak Ridge National Laboratory on July 31, 1980, in draft form for review.

Contract Number: 62B-13817C, Letter Release 62X-11

Contract Period: December 1979 - July 1980

Funding Level: $60,000

Funding Source: Oak Ridge National Laboratory

PROJECT SUMMARY

Project Title: Thermal Energy Storage for Solar Thermal Applications (TESSTA)

Principal Investigator: L. G. Radosevich

Organization: Sandia National Laboratories
Organization 8453
P. O. Box 969
Livermore, CA 94550

Project Goals: The overall objective of this storage development program is to develop general solar thermal energy storage technologies that provide:

- Second-generation storage subsystems offering cost/performance improvements over the first-generation storage subsystems currently being developed for solar thermal power applications.
- First-generation storage subsystems for those solar thermal applications that presently have no storage subsystems under development.
- A technology base to support storage subsystem development for future solar thermal power applications.

Implementation of the first two program elements, which are application oriented, is the responsibility of Sandia National Laboratories. Implementation of the technology base goal is the responsibility of the Solar Energy Research Institute (SERI). The program is organized through a work breakdown structure which includes the development of thermal storage technologies matched to solar thermal power system requirements for several near-term applications. Solar thermal power systems include troughs, dishes, and central receivers with working fluids at various operating conditions.

Project Status: The TESSTA program was initiated in FY80. Contracts have been awarded and in-house studies are underway in support of three high priority applications: 1) repowering/industrial retrofit; 2) total energy; 3) small community experiments.

Contract Number: AN-35, PACE 35-AL-10

Contract Period: October 1979-September 1980

Funding Level: $3,000.00

Funding Source: Department of Energy

PROJECT SUMMARY

Project Title: Molten Nitrate Salt Technology Development

Principal Investigator: R. W. Carling

Organization: Sandia National Laboratories
Division 8453
Livermore, CA 94550

Project Goals: The overall objective of this project is to develop a technology base for the use of molten nitrate salts as a heat transfer and energy storage medium in central receiver applications.

Project Status: Contracts have been awarded and in-house experimental studies are underway.

Contract Number: AN-35, PACE 35-AL-10

Contract Period: October 1979 - September 1980

Funding Source: Department of Energy

PROJECT SUMMARY

Project Title: Molten Nitrate Salt Chemistry Studies

Principal Investigator: S. H. White

Organization: EIC Laboratories, Inc.
55 Chapel Street
Newton, MA 02158
(617) 965-2710

Project Goals: The objective of this program is to provide a thorough understanding of the interactions of molten potassium nitrate, sodium nitrate, and their binary mixtures with water and carbon dioxide in the air. These studies will complement ongoing work at Sandia into the development of molten nitrate mixtures for application as heat transfer and sensible heat storage media in large solar energy power systems. The results of these studies will help to determine whether an open, closed or breathing system is needed in salt storage.

Project Status: To accomplish these goals, electroanalytical techniques are being applied to identify the interactions of water, carbon dioxide and air with the melts as a function of temperature. The rates of change of reactants and the rates of formation of products will be measured by electroanalysis. A combination of the rotating disc method and cyclic voltammetry or chronopotentiometry or chronoamperometry will enable the solution concentrations and the mass transfer rates to be uniquely determined. A literature survey to review the known chemistry and electroanalytical chemistry of nitrates has been carried out. Preliminary experiments to explore the behavior of water, carbon dioxide, and air in contact with the molten nitrate salts together with a supplementary investigation of the response of potential degradation products such as hydroxide, carbonate, and nitrite ions has been accomplished.

Contract Number: Sandia 20-2991

Contract Period: July 1980 - July 1981

Funding Level: $76,200

Funding Source: Sandia National Laboratories

PROJECT SUMMARY

Project Title: Mass-Transfer Characteristics of Nitrate-Based Salt Mixtures

Principal Investigator: J. H. DeVan

Organization:
Oak Ridge National Laboratory
Metals and Ceramics Division
P. O. Box X
Oak Ridge, TN 37830
(615) 574-4451

Project Goals: The objective of this program is to determine the corrosion kinetics of Fe-Cr-Ni alloys in flowing eutectic KNO_3-$NaNO_3$ salt as a function of temperature change along the salt flow path.

Project Status: Eutectic KNO_3-$NaNO_3$ is being circulated in thermal convection loops constructed of 304 SS, 316 SS, and Alloy 800, respectively. The loops are operating at a maximum salt temperature of 595°C and a salt temperature gradient of 235°C. Insert specimens are contained within each loop for determination of weight changes, corrosion product scales, and microstructural changes and will be examined after 500, 1500, and 4500 h, respectively. Voltammetry techniques developed for fluoride salt studies at ORNL are being used to monitor the oxidation potential of the nitrate salt as a function of corrosion reactions occurring in the loop system.

Contract Number: Sandia Lab P.O. # 92-85-68

Contract Period: March 1980 to April 1981

Funding Level: $65,500

Funding Source: Department of Energy

PROJECT SUMMARY

Project Title: Corrosion Behavior of Alloys

Principal Investigator: R. A. Osteryoung

Organization:
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214
(716) 831-3820

Project Goals: The objective of this work is to study the chemistry of solutes in molten nitrates at temperatures in the 450-500°C range to obtain information which will permit an understanding of the corrosion behavior of structural alloys, such as Incoloy 800, that will be employed in thermal loops in solar power systems. Solutes of interest are those which may be expected to result from the corrosion of these structural alloys, i.e., iron, nickel, chromium in particular. Ultimately, studies related to the formation of passivating films on appropriate alloys will be performed, and the effect of impurities, such as nitrite, hydroxide and chloride, will be investigated.

Project Status: This work has just recently been initiated; equipment for electrochemical studies has been ordered, cell design and construction is underway; familiarization with literature pertaining to prior studies in molten nitrates has been undertaken. Discussion with Sandia representatives has indicated that the heretofore unknown corrosion behavior of molten nitrates at these elevated temperatures is perhaps more severe than we originally anticipated, based on prior, but lower temperature, work. As a result, initial experiments will be performed in platinum or gold containers in quartz containment vessels.

Contract Number: 20-4478

Contract Period: May 5, 1980 - June 30, 1981

Funding Level: $85,100

Funding Source:
Sandia Laboratories
Livermore, CA 94550

PROJECT SUMMARY

Project Title: Experimental and Theoretical Investigation of Thermocline Degradation

Principal Investigator: J. A. C. Humphrey

Organization:
Department of Mechanical Engineering
University of California, Berkeley
Berkeley, California 94720
(415) 642-6460

Project Goals: There are four:

1) To obtain flow visualization and temperature measurements in a laboratory-scale experiment which simulates the basic characteristics of a thermocline storage system under a variety of operating conditions.

2) To provide a one-dimensional model describing the behavior of the laboratory thermocline storage system based on closed form solution of the energy transport equation and known boundary conditions.

3) To predict numerically the fluid-mechanical and heat transport aspects of the laboratory thermocline storage system, especially those features related to buoyant effects and diffuser performance.

4) To provide a comparative evaluation between experiment, theoretical and numerical analyses.

Project Status:

1) The experimental system is presently being completed and will be ready for operation by mid-August. It consists of a large plexiglass tank of rectangular cross-section and includes conducting and non-conducting side walls, variable aspect ratio and diffuser controlled constant temperature flow into and out of the tank.

2) The transient theoretical analysis has been completed. It is now being written into the form of a FORTRAN program. The next steps include testing, debugging and applying the code to the lab-scale system.

3) Transient, 2-D, laminar flow, numerical calculations of thermocline degradation including buoyant effects are presently being made for test cases corresponding to the experiment. They will be evaluated during the months of August and September.

Contract Number: 482447-26966

Contract Period: October 1979 - September 1980

Funding Level: $35,542

Funding Source: DOE, through Sandia Laboratories
Livermore, California

PROJECT SUMMARY

Project Title: Dish Mounted Latent Heat Buffer Storage
Principal Investigator: R. Manvi
Organization: Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103
(213) 577-9349

Project Goals: The development of parabolic dish mounted latent heat storage subsystems for three small community system applications. Power conversion cycles under consideration include Rankine, Brayton, and Stirling Operating at temperatures of 427°C (800°F), 816°C (1500°F), and 816°C (1500°F), respectively. The task provides for storage requirements definition, conceptual design, media stability and compatibility tests, thermal performance analyses, cost estimates, and subsystem research experiments (SRE).

Project Status: Three seperate industrial contracts awarded to identify and define buffer storage requirements for the dish mounted Rankine, Brayton, and Stirling engines, respectively.

Review of phase change material candidates and their containment completed, and selections made.

Review of Receiver integrated latent heat buffer storage concepts completed, and recommendations made.

High temperature (1500°F) material corrosion experiments initiated with NaCl, Na-NaCl, NaF-MgF$_2$ contained in SS316, SS321, SS430, 9Cr-1 Mo alloy steel. The experiments include natural convection loops and capsules.

Computer code developed for the transient analyses of a receiver integrated with latent heat storage.

An industrial contract awarded for the study of solidification control of PCM on heat transfer surfaces.

Contract Number: SLL Purchase Order 92-8545
Contract Period: FY 1980
Funding Level: $ 550K
Funding Source: Sandia Laboratories, Livermore, California

PROJECT SUMMARY

Project Title: Storage Requirements Definition and SRE Design for Dish Stirling Systems

Principal Investigator: W.F. Zimmerman

Organization:
General Electric Company
Advanced Energy Programs Department
P.O. Box 15132
Cincinnati, OH 45215
(513) 243-5294

Project Goals: The objective of the program is to assess the performance and economic merits of the use of latent heat thermal energy storage in point focussing solar Stirling power conversion systems. Comparisions are to be made between two types of solar receivers with and without the presence of a fossil fuel combustor and with amounts of storage time appropriate to the system design. Additional concepts for TES are to be identified, the developments required to promote the economic and performance acceptability of the TES concepts are to be specified and the nature of worthwhile subscale research experiments to demonstrate the technical and cost feasibility of TES concepts are to be defined.

Project Status: Both receiver systems have been modeled for finite element thermal performance analysis. Solar insolation and other weather data in one minute increments over a one year period at the test site have been received in tape form and processed into a mass data file suitable for data acquisition in the computer analysis program. The economic factors and the capital costs and operating and maintenance costs effecting the cost of electricity have been established. The system models have been checked out using brief spans of solar data and the basic comparison cases are ready to run.

Contract No.: JPL 955388

Contract Period: April 3, 1980 - December 15, 1980

Funding Level: $85,212

Funding Source: JPL/DOE

PROJECT SUMMARY

Project Title: Thermal Storage Requirement Definition Studies for Task 10 of The Small Community Solar Thermal Power Experiment

Principal Investigator: R. E. Polzien

Organization: Ford Aerospace & Communications Corporation
Aeronutronic Division
Ford Road
Newport Beach, California 92660
(714) 759-5925

Project Goals: The objective of this program is to study the application of a latent heat thermal energy buffer storage (TEBS) to the Small Community Solar Thermal Power Experiment (SCSE). The SCSE is a 1-MW_e electrical power generation system using multiple point focusing distributed receiver power modules equipped with organic Rankine Cycle power conversion units. The TEBS study goals are: 1) to establish the need and size of a latent heat TEBS, 2) to identify design concepts which are generally compatible with the SCSE power module design and cost and weight goals, 3) to identify and recommend component and subsystem development needs, and 4) to define subscale experiments for hardware demonstration of a selected concept.

Project Status: The tasks in this program include requirement studies, parametric evaluation of alternate TEBS design concepts, identification of development requirements, and definition of subscale hardware demonstration requirements. Accomplishments to date include performance and economic evaluation of the SCSE plant with and without a TEBS under time varying insolation conditions for an entire year using an FACC developed computer program.

The studies have identified the TEBS capacities and charge/discharge rate capabilities required to produce efficient and stable plant operation under conditions of intermittent insolation dropout. Preliminary design analyses have also been performed which define the performance, size, and mechanization requirements of alternate TEBS concepts.

The remaining tasks, for FY80 include completion of concept evaluation design studies, 2) selection of a best design concept, 3) detailed design analyses and study of development requirements for the selected design, and 4) design of a subscale experiment to demonstrate hardware.

Contract Number: 955637 - Modification No. 3

Contract Period: May 1980 - November 1980

Funding Level: $73,750

Funding Source: Jet Propulsion Laboratory

PROJECT SUMMARY

Project Title: Aluminum Waste Heat for Bellingham District Heating

Principal Investigator: Lincoln B. Katter

Organization:
Rocket Research Company
York Center
Redmond, WA 98052
Telephone: (206) 885-5000

Project Goals:

Assess the economic viability and public acceptance of a district heating system in Bellingham, Washington.

Conduct a review of the technological impact on the Intalco aluminum plant.

Evaluate other thermal energy sources for backup.

Evaluate institutional considerations.

Perform a detailed system cost analysis.

Project Status: All tasks are proceeding on schedule.

Contract Number: 86Y-4253C

Contract Period: April 1979 to November 1980

Funding Level: $1,000,000

Funcing Source: ORNL

PROJECT SUMMARY

Project Title: Collection and Dissemination of Thermal Energy Storage System Information for the Pulp and Paper Industry

Principal Investigator: Howard Edde, Ph.D., P.E.

Organization:
Howard Edde, Inc. Consulting Engineers
Rockwood Office Park
1402 140th Place N.E.
Bellevue, Washington 98007
(206) 643-0900

Project Goals: Recent studies have indicated that substantial reductions in a pulp and paper mill's net energy requirements can be realized by application of thermal energy storage (TES) system technology. This concept is not as widely applied today in the U.S. pulp and paper industry as it is in some international mills, especially within Scandinavia. The main objectives of this project are the collection and dissemination of TES system technology for the U.S. pulp and paper industry with the intent of reducing fossil fuel usage.

Project Status: The tasks of this project include: (1) a survey of the U.S. and international industries to identify TES systems and define their operational characteristics; (2) a benefit analysis which includes an energy conservation assessment, an economic analysis and an environmental impact assessment; and (3) information dissemination which includes a brochure, a display and presentation of papers at conferences.

A survey of North American and international pulp and paper mills was conducted to identify the existing applications of TES systems, to obtain and analyze the operating data from a representative number of these mills and to transfer this information to the U.S. pulp and paper industry. The survey was recently completed and the results are presently being analyzed and the benefit analysis being made. Sufficient results are available to indicate that a number of typical TES case example situations exist which are believed to have a high potention for application within the U.S. industry. Table 1 presents some of these mills' conditions selected for detailed investigation. The results of the overall study will be completed by early 1981.

(Continued)

Project Status:

Table 1

TES System Applications Studies

Production Type ton/year (metric)		Application
Dissolving Newsprint	140,000 245,000	Steam accumulator TES system to store steam during paper machine breaks
Sulfate (sack) Sulfite (Unbleached)	170,000 160,000	Mill owned boiler to provide district heating for adjacent community. TES system is hot water accumulator for mill transient hot water energy demands. Start-up scheduled September 1980, permitting before/after evaluation of energy demands.
Newsprint	170,000	Steam accumulator TES system to store steam during paper machine breaks and utilize steam when paper sheet is brought to full width.
Dissolving Sulfite	150,000	Boiler feedwater modulation.
Sulfate	218,000 (pulp) 286,000 (paper)	Steam accumulator for balancing steam production from recovery boiler in relation to batch digesters and board machine.

Contract Number: DEN3-190

Contract Period: February 1980 - May, 1981

Funding Level: $114,000

Funding Source: Department of Energy

PROJECT SUMMARY

Project Title:	Applications of Thermal Energy Storage to Waste Heat Recovery in the Food Processing Industry
Principal Investigator:	Wayne L. Lundberg
Organization:	Westinghouse Electric Corporation Advanced Energy Systems Division P. O. Box 10864 Pittsburgh, PA 15236 (412) 892-5600
Project Goal:	To assess the technical and economic feasibility of waste heat recovery in the food processing industry using systems employing thermal energy storage.
Project Status:	The completed project resulted in a proposal for a demonstration project to be undertaken at the H. J. Heinz Company Pittsburgh Factory. The proposal was submitted by the Heinz USA Division in November, 1979. Contract negotiations on the proposed project are currently incomplete.
Contract Number:	EC-77-C-01-5002
Contract Period:	September 1977 - September 1978
Funding Level:	$96,195
Funding Source:	Department of Energy

PROJECT SUMMARY

Project Title: Bellingham Project, Preliminary Assessment of the Once-Through District Heating System

Principal Investigator: Dr. I. Oliker

Organization:
Burns and Roe, Inc.
Power Technology Division
800 Kinderkamack Road
Oradell, NJ 07649
(201) 265-2000

Project Goals: The main objective of this project is to develop, in a conceptual form, the once-through heat supply arrangement and compare with two-pipe heat transport design.

Project Status: The tasks in this project include (1) assessment of the heat load data, (2) development of the conceptual design of the once-through heat supply system, (3) cost estimates of the transmission and distribution piping system, thermal storage facility, and water makeup system.

Accomplishments to date include tasks (1) and (2).

Contract Number: Supplemental Agreement No. 2 to Subcontract No. 7672 to Union Carbide Corporation.

Contract Period: August 1980 - October 1980.

Funding Level: $37,893.

Funding Source: Department of Energy.

PROJECT SUMMARY

Project Title: International Energy Agency Program on Hydrogen Production

Principal Investigator: James H. Swisher (for DOE)

Organization: Divison of Thermal and Mechanical Energy Storage Systems,
U.S. Department of Energy, 600 E Street, N.W.,
Washington, D.C. 20585
(202) 376-4919

Project Goals: Accelerate technology development in the production of hydrogen from water through international cooperation.

Project Status: Information and personnel exchange is now in progress in five project areas: thermochemical production, low temperature electrolysis, high temperature electrolysis, photocatalytic processes, and market projections. A final report on hydrogen market projections will be published shortly. Experimental work on the various production processes is proceeding at a steady pace, although no significant new discoveries have been made. Bench-scale facilities for thermochemical hydrogen production have been built and operated both in the U.S. and in Europe. One U.S. scientist has worked at a Commission of European Communities laboratory for six months under the Agreement and several European scientists have worked at U.S. labs for shorter periods. At least one workshop has been held each year for each activity to accomplish exchange of results and ideas. Some task sharing of projects has evolved since the Agreement was signed.

Contract Number: None

Contract Period: October, 1977, to October, 1980. Continuation likely.

Funding Level: U.S. Dept. of Energy - $6 million; IEA total-
$20 million in FY 1980.

PROJECT SUMMARY

Project Title: Sulfuric Acid/Water Chemical Heat Pump

Principal Investigator: E. C. Clark

Organization: Rocket Research Company
Redmond, Washington
(206) 885-5000

Project Goals: The project is structured to verify the capability of the sulfuric acid-water system and to enhance near-term commercialization. The primary objective is to design, construct and test a sulfuric acid CHP/CES verification test unit (VTU) which incorporates as many commercial, mass producible design features as necessary to demonstrate system economic and technical feasibility. The VTU will be designed to function both as a storage HVAC unit and a temperature enhancement industrial heat pump. For purposes of gaining scaling criteria, the nominal storage design capacity shall be 10^6 Btu with a nominal delivered heat rate of 150,000 Btu/hr.

Project Status: Rocket Research is currently under contract to Brookhaven National Laboratory to conduct a four-phase program. Phases 1 and 2 are completed and consisted of a requirement analysis and detailed design of the VTU. Generic applications have been identified which include industrial waste heat pumping, space conditioning, air or gas moisture removal, steam accumulation, cogeneration and energy storage. The VTU design incorporates two of the above designs: waste heat pumping and space conditioning. The design incorporates combined generator/condenser and absorber/evaporator reaction components made of steel shells coated with acid resistent porcelain. Teflon-lined acid plumbing and valves will be used and the acid storage tank will be fabricated from steel lined with porcelain and capable of vacuum operation.

The remaining Phases 3 and 4 consisting of VTU fabrication and testing, respectively, will be conducted in FY 81.

Contract No.: 494588-S

Contract Period: 1 October 1979 through September 1981

Funding Level: $699,740

Funding Source: Brookhaven National Laboratory.

PROJECT SUMMARY

Project Title: Methanol-Based Heat Pump for Storage of Solar Thermal Energy

Principal Investigator: Dr. Peter O'D. Offenhartz

Organization: EIC Laboratories, Inc
55 Chapel Street
Newton, MA 02158
(617) 965-2710

Project Goals: The purpose of this system was to test a 100,000 BTU thermal storage capacity $CaCl_2$-CH_3OH chemical heat pump and to evaluate the data obtained. Specific objectives were to 1) test the $CaCl_2$ reactor-heat exchanger design at a scale close to that which would be used in the field; 2) carry out off-design cycle tests, including simulated process upsets and control failure; 3) initiate and complete long-term (>100 cycles) testing; 4) evaluate salt bed heat exchanger performance; 5) calculate the system COPs for heating and cooling, including all parasitics; 6) evaluate overall performance and issue performance claims and specifications; and 7) issue a final report including a revised development plan.

Project Status: All tasks have now been completed. Cycling performance was excellent, although the heat exchangers showed some warpage due to plastic flow of the salt. The system appears impervious to process upset. The rate of reaction was a strong function of the temperature difference ΔT between the absorber heat transfer fluid and the evaporator, ranging from over 1.1 moles CH_3OH per mole $CaCl_2$ per hour at $\Delta T = 40°C$ to 0.094 M/M/hr at $\Delta T = 55°C$. The latter rate is still more than adequate for solar heat pumping. Performance degradation after 100 cycles, expressed as a contact resistance, was less than 2°C, and it appears that further cycling will not increase this resistance. The experimental COP for cooling was 0.52, close to the value expected theoretically (0.56). All performance objectives have been met, and our economic analysis indicates the system should prove cost effective.

Contract Number: BNL 490105-S

Contract Period: August 1979 - September 1980

Funding Level: $193,398

Funding Source: Brookhaven National Laboratory

PROJECT SUMMARY

Project Title: A Cost-Effectiveness Evaluation of Several Chemical Heat Pump Systems

Principal Investigator: W. Standley, R. Gorman, P. Moritz, and T. O'Gorman

Organization:
TRW Energy Systems Planning Division
8301 Greensboro Drive
McLean, Virginia 22102
(703) 734-6530

Project Goals: The objective of this project is to conduct an independent assessment of several chemical heat pump (CHP) systems providing HVAC services to both a residential and a commercial building, as well as one application in providing industrial process heat. The levelized annual cost of operation and ownership for the CHP systems will be compared to baseline systems and a set of emerging technologies. The baseline systems include conventional fossil fuel-fired heating systems, vapor-compression air conditioning, and electrically-driven heat pump HVAC. The emerging systems include solar-thermal (hydronic) heating, solar-driven absorption air conditioning, and vapor-compression heat pumps operating in the solar-assisted, ground-coupled, and aquifer-coupled modes.

Project Status: The tasks in this project involve collection and evaluation of existing cost and performance data for the baseline systems; adaptation of available data for the emerging systems; and detailed verification of cost and technical performance projections for the CHP systems of interest. The "standard" buildings in residential and commercial applications have been defined for two locations, Boston and Albuquerque. Each building in each location has been characterized with respect to HVAC requirements; HVAC system characteristics have been established; and the baseline and emerging HVAC systems have been run through the levelized-cost methodology.

The work for FY 81 will include completing the CHP system characterizations and working through the cost-effectiveness evaluation. A final report will summarize the results of the project, with the numerical results of the evaluation presented in sufficient detail to enable the reader to discern the impact of each component of levelized cost (i.e., the evaluation will be transparent.)

Contract Number: BNL 519403-S

Contract Period: June 9, 1980 through January 15, 1981

Funding Level: $98,346

Funding Source: Brookhaven National Laboratory

PROJECT SUMMARY

Project Title: HYCSOS Chemical Heat Pump and Energy Conversion System based on Metal Hydrides

Principal Investigators: J. M. Clinch and J. S. Horowitz

Organization: Argonne National Laboratory
Chemical and Electrical Systems Programs
9700 S. Cass Avenue , Argonne, Illinois 60439
(312) 972-7693

Project Goals: The major objective of this program is to develop a metal hydride heat pump for residential, commercial, and industrial applications.

Project Status: In FY 1980, both experimental and analytical work has been performed. Both of these tasks focus on a tubular metal hydride heat pump design. The experimental work consists of testing and evaluating a tubular design heat exchanger manufactured by INCO. The test results will assist in providing information on the heat pump performance of realistic hydrides beds. The analytical work centers on developing an approach for predicting the Coefficient of Performance (COP) of a tubular heat pump. Thermodynamic and heat transfer models have been formulated to account for thermal regeneration modes. Calculations indicate that a COP of 1.55 for heating is obtainable with the tubular heat pump design. However, this result requires verification by experiment.

In addition to the above work, a request for a proposal (RFP) has been prepared by ANL and issued through Brookhaven National Laboratory (BNL) to select an industrial contractor for the design and engineering development of a prototype metal hydride heat pump. Proposals have been evaluated and recommendations are being made through BNL's office for a contract award.

Contract Number: AL-10-05-15/49405

Contract Period: October 1979 - September 1980

Funding Level: $220,000

Funding Source: Department of Energy

PROJECT SUMMARY

Title: Hydrogen Chemical Compressor

Principal Investigator: P.P. Turillon

Organization:
Ergenics Division
MPD Technology Corporation
681 Lawlins Road
Wyckoff, NJ 07481
(201) 891-9103

Project Goals: Phase I: To build a bench scale metal hydride compressor prototype and evaluate its performance over several hundred cycles of operation. Phase II: To design and construct a scaled up hydride compressor coupled to an industrial water electrolyzer, and compare its performance and cost effectiveness in relation to a conventional compressor.

Project Status: The first phase was completed on July 15,1980. The prototype HCC was successfully operated continuously, delivering 20.3 Std. liters per minute (43SCFH) of hydrogen at a pressure of 42.2 Atma (650 psia). After 700 cycles of operation a slight decrease in absorption capacity of hydride was observed. A capsule containing a sample of the hydrided material was removed from the compressor and analyzed. A decrease in plateau pressure was measured. The measured efficiency of the compressor (4.5%) was lower than the predicted practical efficiency (12%). The decrease in efficiency can be readily explained by the large amount of copper inherent in the design of the electrically heated bench scale prototype.

Contract No.484822-S

Contract Period: Phase I, September 15, 1979 to July 15, 1980
Phase II duration 12 months in FY 1981 (if authorized)

Funding Level:

Phase I DOE/BNL:	$46,436.00	
Ergenics Cost Share	3,495.00	(7%)
	$49,931.00	

Phase II (estimated) $150K

Funding Source: DOE Chemical/Hydrogen Energy Storage Systems
Ergenics cost share 7% of Phase I.

PROJECT SUMMARY

Project Title: Development of a Commercial Metal Hydride Process for Hydrogen Recovery

Principal Investigator: Dr. E.L. Huston

Organization:
Ergenics Division
MPD Technology Corporation
681 Lawlins Road
Wyckoff, NJ 07481
(201) 891-9103

Note: Air Products and Chemicals, Inc. and INCO Research and Development Center, Inc. are subcontractors.

Project Goals: The primary objective of this project is the development and commercialization of a process for recovering hydrogen from waste gas streams based on metal hydride technology. The waste gas streams exist in chemical plants and refineries with a total hydrogen content of 3,200 million SCF per day and a potential resource recovery of 0.1 Quad.

Project Status: Phase I - Process Identification was initiated 7/14/80. Initial Tasks include a survey of chemical and petroleum refineries to document waste gas streams and determine future H_2 demand. Experiments seek to quantify the poison resistance of AB, AB_5, and Mg hydride formers to the gaseous contaminents of these streams. Subsequent tasks include: evaluation of stream pretreatment/hydride regeneration options; process integration; assessment of process economics and preparation of a commercialization plan. A go/no-go decision will be made at the end of Phase I regarding follow-on phases.

Contract No.: BNL-509926-S

Contract Period: August 14, 1980 - October 31, 1981

Funding Level:
Phase I - $316,727
Subsequent phase(s) total about $900,000
For a three-year program total of $1,200,000.

Funding Source:
DOE CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS
Cost Sharing 14.75% or $54,800 additional for Phase I.

PROJECT SUMMARY

PROJECT TITLE: SOLID POLYMER ELECTROLYTE WATER ELECTROLYZER TECHNOLOGY DEVELOPMENT

PRINCIPAL INVESTIGATOR: J. H. RUSSELL

ORGANIZATION:
GENERAL ELECTRIC COMPANY
DIRECT ENERGY CONVERSION PROGRAMS
50 FORDHAM ROAD
WILMINGTON, MA 01887
(617) 657-5277

PROJECT GOALS: THE MAIN OBJECTIVE OF THIS PROGRAM IS TO DEVELOP A LOW-COST ($<$$150/kW) HYDROGEN GENERATION PLANT (200kW -5MW) FOR ELECTRIC UTILITY/INDUSTRIAL CHEMICAL APPLICATIONS, USING THE SOLID POLYMER ELECTROLYTE TECHNOLOGY. TO MINIMIZE CAPITAL AND OPERATING COSTS, THE GOAL IS TO GENERATE HYDROGEN AT HIGH CURRENT DENSITIES ($\geq$1000 ASF) AT PRESSURES IN THE RANGE OF 100 TO 300 psig, WITH AN OVERALL SYSTEM EFFICIENCY OF 85-90%.

PROJECT STATUS: THE TASKS IN THIS PROGRAM INCLUDE THE ANALYTICAL DESIGN, MATERIALS EVALUATION, MECHANICAL SCALE-UP AND MANUFACTURING PROCESS DEVELOPMENT NECESSARY TO FABRICATE AND OPERATIONALLY TEST LARGE-SIZE CELLS. ACCOMPLISHMENTS TO DATE INCLUDE ASSEMBLY AND OPERATION OF 2.5 FT^2 CELLS IN 50kW (12 CELL), 100kW (30-CELL), and 200kW (60-CELL) MODULES AT UP TO 100 psi WITH AVERAGE CELL VOLTAGES OF 1.85-1.89 VDC AT 1000 ASF. DESIGN OF A SCALED-UP 10 FT^2 CELL AND MODULE HAS BEEN COMPLETED, AND FABRICATION DEVELOPMENT HAS STARTED.

CONTRACT NO: DE-AC02-78ET26202

CONTRACT PERIOD: GFY 80 - GFY 81

DOE FUNDING LEVEL: $1,200,000 TBD

FUNDING SOURCE: DEPARTMENT OF ENERGY AND CO-SPONSORS

PROJECT SUMMARY

Project Title: Advanced Alkaline Water Electrolysis

Principal Investigator: J. N. Murray

Organization:
Teledyne Energy Systems
110 West Timonium Road
Timonium, MD 21093
(301) 252-8220

Project Goals: This project is directed toward identification of improved electrolysis module components which exhibit stable operation at operating temperatures at 100 to 150°C, operating current densities of approximately 500 ma/cm^2 and allow process efficiencies to approach 100%

Project Status: In GFY 1980, a fourth generation computer program was completed and tested which allows the determination of the optimal hydrogen economics via alkaline water electrolysis. The relative merits of improved electrodes, the effects of electrode operating temperature(s) and the optimal design current densities are among the features tested to date. The experimental verification of the stability of improved anodes was continued using the TES-C-AN cathode structure. Samples of two new potassium titanate electrode separators have been obtained for testing. An optimum component five-cell module will be assembled for extended testing in the Applied Research Industrial Electrolysis System (ARIES) in GFY 1981.

Contract Number:	BNL 480421-S	BNL 507416-S
Contract Period:	April 1979 - January 1980	February 1980 - February 1981
Funding Level:	$79,727	$154,542
Funding Source:	Brookhaven National Laboratory	Brookhaven National Laboratory

PROJECT SUMMARY

Project Title: Static Feed Water Electrolysis for Large Scale Hydrogen Generation

Principal Investigator: F. H. Schubert

Organization: Life Systems, Inc.
24755 Highpoint Road
Cleveland, OH 44122
(216) 464-3291

Project Goals: The primary objective of this program is to demonstrate the inherent capability of the alkaline electrolyte, Static Feed Water Electrolysis System (SFWES) to generate low cost hydrogen for chemical storage/industrial chemical applications.

Reductions in capital and operating costs will be addressed through cell area scale-up demonstrations and studies (5 ft^2); operation at high current density (1 amp/cm^2); demonstration of low cell voltage operation; and testing with contaminated feed water, e.g., simulated sea water, to eliminate water treatment expendables and equipment.

Project Status: Negotiations between Brookhaven National Laboratory and Life Systems, Inc. have been completed and a four task project is scheduled to start August 15, 1980. These tasks will address (1) elevated current density (1 A/cm^2) investigations, (2) contaminated water operation, (3) cell area scale-up and (4) future scale-up sequence for the total system. Accomplishments to date include project organization and layout and readying of the Contractor furnished test facilities and test cell hardware for task one.

All tasks will be completed during FY81 (by April, 1981), including printing and submittal of the Final Report.

Contract Number: 522723-S

Contract Period: August 1980 - April 1981

Funding Level: $108,485

Funding Source: Department of Energy

PROJECT SUMMARY

Project Title: Selection and Evaluation of Materials for Advanced Water Electrolyzers

Principal Investigator: Glenn E. Stoner

Organization:
University of Virginia
Applied Electrochemistry Laboratory
Materials Science Department
University of Virginia
Charlottesville, VA 22901
(804) 924-3277

Project Goals: The main objectives are to examine the potential-time behavior in alkaline electrolyzers; develop an understanding of these effects and report the causes and suggest possible solutions to the sponsor. Another goal is to initiate an examination of the electrocatalytic effects of high surface area polycrystaline nickel whiskers.

Project Status: Most of the voltage-time effects were reported to be at the cathode and were found, by electrochemical experiments and theoretical calculations to be consistent with the formation of a nickel hydride. Polycrystalline whiskers were encouraging on a per weight basis but more studies are required with regard to their properties as electrocatalysts. A Ph.D. dissertation by P. J. Moran was successfully prepared and defended.

Contract Number: BNL-4-51320-S

Contract Period: August 1979 - July 1980

Funding Level: $22,000

Funding Source: BNL/DOE

PROJECT SUMMARY

Project Title: Analysis of Vehicle Systems Using Hydrogen Storage/Alkaline Fuel Cell Technology

Principal Investigator: S. Srinivasan

Organization: Brookhaven National Laboratory
Associated Universities, Inc.
Upton, New York 11973

Project Goals: The main objective of this program is to develop low cost fuel cells for vehicular applications. Since this is a new activity, the goal in FY 1980 is to generate sufficient information for delineation of a Development Plan for low-cost fuel cells applied to automotive systems.

Present Status: Single cell and multicell alkaline fuel cell units have been evaluated at BNL. Performance is at least twice that obtained in similar units about a decade ago. Los Alamos Scientific Laboratory (LASL) is carrying out a computer simulation to evaluate selected fuel cells and hydrogen storage subsystems in a typical consumer vehicle (based on a GM X-car).

The tasks for FY 1980 will be: 1) testing and evaluation of improved hydrogen electrodes in alkaline fuel cells; 2) completion of the computer simulation studies; 3) submission of a Development Plan.

Contract Number: DE-AC02-76CH00016

Contract Period: October 1979 - September 1980

Funding Level: $150,000

Funding Source: Department of Energy

PROJECT SUMMARY

Project Title: Optical and Electrocatalytic Investigations of Oxides of Ruthenium and Iridium

Principal Investigator: Fred H. Pollak

Organization:
Brooklyn College, CUNY
Physics Department
Bedford Avenue and Avenue H
Brooklyn, N.Y. 11210
(212) 780-5356

Project Goals: The objectives of this study are to (1) correlate optical measurements of oxide film characteristics with electrocatalytic activity and (2) determine the dependence of electrocatalytic activity on crystal orientation.

Project Status: (1a) We have measured the near-normal incidence reflectivity spectrum of single crystal IrO_2 and RuO_2 with light polarized perpendicular and parallel to the c-axis in the range 0.5-9eV. This study has enabled us to obtain the optical constants of this material.

Since peak positions in ϵ_2, the complex dielectric constant, and the joint density of states agree, we have been able to verify experimentally the correctness of assumptions concerning the nature of the bonds in these materials. Experimental results for IrO_2 compare well to the band structure and density of states calculation of Mattheiss. We are thus able to confirm, in detail, the nature of the oxygen p and Ir d-electronic states. Preliminary optical measurements of RuO_2 are complete.

These results will provide important information in the investigation of the correlation of optical measurements of oxide film characteristics with electrocatalytic activity.

(1b) Tasks for FY 1980

1. Growth of larger crystals of RuO_2 and IrO_2.
2. Detailed kinetic and mechanistic studies of oxygen evolution on these single crystal surfaces using rotating disc techniques.
3. Combined electrochemical optical studies on these single crystals and on oxidized metals to determine the intrinsic source of the catalytic activity of these materials.

Contract No.: EC-77-S-02-4590

Contract Period: May 1980 - September 1981

Funding Level: $30,000.

Funding Source: Department of Energy

PROJECT SUMMARY

Project Title: Microcavity Hydrogen Storage

Principal Investigator: Robert J. Teitel

Organization:
Robert J. Teitel Associates
9145 Chesapeake Drive
P.O. Box 81921
San Diego, California 92138
(714) 565-6441

Project Goals: The goals of the Microcavity Hydrogen Storage program in FY'80 is: to prepare a two cu. ft. bed of filled microspheres for BNL tests; to establish standard procedures for characterizating testing microsphere beds; to experimentally test eight commercial grades; to select two grades for further study; to apply treatments to the two selected grades of microspheres to improve their properties; to subject specimens of the two selected grades to cyclic fill and dispense tests; to estimate a projected cost of microspheres and estimate storage costs.

Project Status: Attempts to fill larger microsphere beds was started in FY'79 but were frustrated by the procurement of suitable microspheres and the availability of facilities. This year, RJTA built a facility and delivered a two cu. ft. bed of filled microspheres to BNL. Test procedures were standardized and eight commercial grades were tested. As a result of the screening tests, it has been established that microspheres strong enough to withstand a 6000 psi crush test should have an aspect ratio between 25 and 30. Crush tests were performed in 6000 psig, nitrogen, hydrogen and helium atmospheres. Less breakage loss was observed for hydrogen and helium than for nitrogen. Two of the most promising microspheres will be selected for further study. An optimization study for the two microsphere grades was initiated and cyclic fill-dispense tests planned for FY' 81. Projected microsphere costs were estimated and storage cost information updated.

Contract No.: BNL 511197-S

Contract Period: March 17, 1980-March 16, 1981

Funding Level
$125,000 FY 80
$ 56,000 FY 81

Funding Source: Brookhaven National Laboratory

PROJECT SUMMARY

Project Title: Ammonia as a Hydrogen Energy-Storage Medium

Principal Investigator: G. Strickland

Organization: Brookhaven National Laboratory
Bldg. 120
Upton, New York 11973
(516) 345-4091

Project Goals: To develop safe and economic hydrogen energy-storage systems based on the storage and cracking of ammonia.

Project Status: This work is a new effort in the search for alternate methods of storing hydrogen. A preliminary review has shown that ammonia is substantially superior to liquid hydrogen and methanol in energy input for media manufacture from natural gas, in hydrogen energy content of the medium, and in energy cost ($\$/10^6$ Btu). Five main tasks were established. Further review is planned prior to initiating the experimental work.

Contract No.: DE-AC02-76CH00016

Contract Period: October 1, 1979 - September 30, 1980

Funding Level: -

Funding Source: Brookhaven National Laboratory

PROJECT SUMMARY

Project Title: Modification and Operation of The Hydrogen Homestead Hydride Vessel Energy Storage System.

Principal Investigator: Roger E. Billings

Organization:
Billings Energy Corporation
Hydride Research Division
18600 East 37th Terrace South
Independence, Missouri 64057
(816) 373-0000

Project Goals: The purpose of this research program is threefold. First: To study the performance of a large hydride vessel in the release of stored hydrogen at specified demand levels. Second: To determine the energy needs of the hydrogen homestead(s) and the ability of the vessel to satisfy those needs. Third: To study the safety needs of such a storage system in relation to the hydrogen homestead(s).

Project Status: The tasks specified under this contract include the modification of the existing hydrogen flow and monitoring systems, the actual monitoring of the system under operating conditions, data reduction and graphical interpretation of the resultant data, and the installation and detailed description of the required safety system. A complete description of the energy consumption associated with the homestead(s) is also required. Accomplishments to date include the completed design and installation of the specified hydrogen flow system, including the molecular sieve dryers which prevent poisoning of the metal hydride, and the design and installation of the required safety system. Data acquisition has been begun with the initial charge of the hydride vessel. The energy consumption analysis associated with the hydrogen homestead(s) has also been completed.

Remaining tasks include the acquisition and reduction of experimental data into graphical and tabular form.

Contract Number: BNL 481417-S

Contract Period: May 1, 1979 - October 31, 1980

Funding Level: $60,000

Funding Source: Brookhaven National Laboratory

PROJECT SUMMARY

Project Title: Hydrogen Microsphere Safety Study

Principal Investigator: R. G. Zalosh

Organization: Factory Mutual Research Corporation
1151 Boston-Providence Turnpike
Norwood, Massachusetts 02062

Project Goals: The objective of the program is to perform a preliminary hazard evaluation of hydrogen storage and transport in hollow glass microspheres. Flammability, explosibility, and miscellaneous hazards of hydrogen filled microspheres are being assessed by laboratory testing, review of pertinent safety standards and regulations, and an analysis of potential accident scenarios. Microsphere hazards will be compared to the hazards of the other hydrogen storage modes: metal hydrides, liquid hydrogen, and compressed gas.

Project Status: Laboratory tests have been completed. Results are now being analyzed and compared to the equivalent data for metal hydrides, gaseous and liquid hydrogen. Pertinent safety codes and regulations have also been reviewed briefly. A key issue remaining to be evaluated will be a preliminary analysis of the hazards of alternative packaging forms being considered for hydrogen filled microspheres.

Contract No.: Prime: DE-AC02-76CH00016,
Sub: BNL-510190-S

Contract Period: March 1980 - January 1981

Funding Level: $28,094

Funding Source: Department of Energy/Brookhaven National Laboratory

Project Summary

Project Title: Hydrogen Production from Small Hydropower Sites

Principal Investigator: New York State Energy Research and Development Authority

Organization: New York State Energy Research and Development Authority

Project Goals: Construction and operation of a hydropowered electrolysis facility.

Project Status: Completion of program plan.

Contract Number: DE-AC02-80ET26224

Contract Period: August 1, 1980 - December 1, 1983

Funding Levels: Phases I & II - $174,900 (U.S. DOE)
Phases III & IV - Unfunded

Funding Sources: See Below

ESTIMATED FUNDING:	Phases I & II	Phase III	Phase IV	Totals
DOE/BNL	$174,900	$784,800	$ 35,550	$995,250
NYSERDA	$145,100	$758,500	$ 75,550	$979,150
Village	-0-	$849,700	$ 88,900	$938,600
TOTALS	$320,000	$2,393,000	$200,000	$2,913,000

PROJECT SUMMARY

Project Title: Study of the Behavior of Gas Distribution Equipment in Hydrogen Service — Phase II

Principal Investigator: Walter J. Jasionowski

Organization: Institute of Gas Technology
IIT Center
3424 South State Street
Chicago, Illinois 60616
(312) 567-3650

Project Goals: The main objective of this program is to identify operating, safety, and materials problems associated with the use of hydrogen in conventional gas distribution systems. Phase II was designed to determine permeabilities of commercial plastic gas distribution piping for hydrogen and methane, and leakage characteristics for mixtures of the two gases. The results, along with A.G.A. data, permitted an assessment of the U.S. distribution system's overall (hypothetical) permeation and leakage losses for different combinations of natural gas and hydrogen.

Project Status: The work on this program was completed. Permeability determinations were made for eleven samples of commercially available polyethylene pipe, using project-designed permeability cells and test loops. Ring tensile tests were also performed to compare as-received and permeability-exposed piping. The residential/commercial test loop was modified to serve in leakage experiments with varying hydrogen-methane mixtures. Extrapolating from these results, the total possible permeation and leakage losses in the U.S. distribution system were assessed.

Contract Number: JPL No. 955447

Contract Period: April 26, 1979 - June 26, 1980

Funding Level: $95,033

Funding Source: Jet Propulsion Laboratory

PROJECT SUMMARY

Project Title: Hydrogen Containment Materials

Principal Investigator: Dr. Howard G. Nelson

Organization: NASA-Ames Research Center
Materials Science and Applications Office/230-4
Moffett Field, CA 94035
FTS 448-6137, (415) 965-6137

Project Goals: The containment materials program had the overall objective of helping to develop the understanding required for the economic, safe, long-term containment of hydrogen. Specifically, through the use of model environments, existing low cost materials, having intermediate to long-term hydrogen compatibility, were to be identified; new, inexpensive, and highly compatible alloys were to be developed; and reliable accelerated testing techniques and life prediction methods were to be established. The program contained both fundamental and applied elements including an experimental pipeline-loop on which service experience was to be gained.

Project Status: Although the containment materials program has had a relatively short life, a significant increase in our understanding of hydrogen degradation of carbon and low-alloy containment steels has been attained. Probably the most significant finding is that these containment steels can be severely degraded by the presence of hydrogen, but, in a manner considerably different than that observed for the extensively studied, higher strength, martensitic steels. Our findings indicate that the primary mechanism of hydrogen degradation in low strength steels is different than in the high-strength steels, and, therefore, much of the information available on degradation of high-strength steels does not appear to be applicable to the behavior of low strength steels in hydrogen.

Tasks being terminated are Thermal Processing Task, \$60K, NASA-Ames; Effect of Stress State on Hydrogen Embrittlement, \$45K, Virginia Polytechnic Institute; Near Threshold Fatigue Crack Propagation in Pipeline Steels in High-Pressure Environments, \$75K, Rockwell International Science Center; and Hydrogen and Fatigue Properties of Steel, \$45K, Cornell University, as well as an oversight function of Hydrogen Compatibility of Structural Materials for Energy Storage and Transmission, Sandia Laboratories, Livermore.

Contract Number: ET-78-1-01-3112

Contract Period: FY80

Funding Level: \$225K

Funding Source: Department of Energy-STOR

PROJECT SUMMARY

Project Title: Production Cost Comparisons of Hydrogen from Fossil and Nuclear Fuels and Water Decomposition

Principal Investigator: Karl R. Ekman

Organization:
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103
(213) 577-9020

Project Goals: The broad objective of this project was to examine the costs entailed in producing hydrogen by technologies that rely on petroleum, natural gas, coal, thermochemical cycles, and electrolysis. Techniques for comparing these processes were developed by formulating the process data and economic assessments on a uniform and consistent basis. These data were then normalized to permit a more valid and meaningful comparative analysis of the plant investments and product costs of these processes through the year 2020.

Project Status: Report finalized and issued July 1980. Conclusions reached were: Hydrogen production from natural gas is and remains the least expensive option through CY 2000, with hydrogen costs from petroleum increasing in the same ratio as natural gas. If hydrogen were produced from coal today, it would cost about the same as petroleum derived hydrogen. Thermochemical cycles are expected to become cost competitive with fossil fuels around 1995, assuming substantial process development continues and economics of large scale facilities are realized. The cost of producing hydrogen by electrolytic prcesses will remain high. By 1990, production of energy by high-temperature nuclear reactors may reach commercial feasibility and tend to stabilize overall production costs at about $10/MBtu.

Contract Number: IA ET-78-1-01-3112 (One of several tasks)

Contract Period: FY'80

Funding Level: $195K (FY'80) (For all tasks under IA ET-78-1-01-3112)

Funding Source: Department of Energy - STOR

PROJECT SUMMARY

Project Title: Advanced Hydrogen Production Concepts

Principal Investigator: D. D. Lawson

Organization: Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103

Project Goals: This activity monitors the technical progress and problems in the Advanced Hydrogen Production Concepts Element. The element has supported further development of the innovative and unusual technological findings that derive from creative basic research. It is not the intent of this activity to do fundamental or basic research, but only to extend work that has been described (literature, technical reports or by private communication) and to bridge the technology gap between very basic concepts and true larger scale applications.

Project Status: Five activities are involved in this element. The activities have been devided into two topic areas: Hydrogen Produced by Solar Radiation: 1. The hydrogen photoelectrolytic conversion activity (EIC Conf. Newton MA) has investigated practicability of semiconductor-electrolytic devises (similar to Honda-Fujishima) that use solar energy to decompose water into hydrogen and oxygen in an apparent single step process. Final report draft approved with the report due in October 1980. 2. The photocatalytic decomposition of inorganic hydrogen compounds; i.e., hydrobromic and hydriodic acids (Prof. Gray, CIT) using rhodium organic bridge complexes. The final report is in preparation. 3. Studies were conducted on the feasibility of direct high temperature thermal decomposition of water with diffusion processes for separation of the equilibrium mixture of hydrogen and oxygen into useable energy, sources (Battelle-Geneva). Report issued in June 1980. Conservation Activities: 1. A study (SRI) on the recovery of hydrogen from hydrogen sulfide was conducted. It developed a base line in terms of markets, economics and chemistry of the recovery of hydrogen from hydrogen sulfide streams in situations where hydrogen would otherwise be wasted. Report issued in December 1979. 2. Preliminary comments on the low temperature decomposition of sulfuric acid by use of high sulfur content coal to yield sulfur dioxide and carbon dioxide (JPL). Work in progress.

Contract Number: IA ET-78-1-01-3112 (One of several tasks)

Contract Period: FY'80

Funding Level: $195K (FY'80) (For all tasks under IA ET-78-1-01-3112

Funding Source: Department of Energy - STOR

PROJECT SUMMARY

Project Title: Production of Hydrogen by Electron Transfer Catalysis using Conventional and Photochemical Means

Principal Investigator: D. Paul Rillema*

Organizations:
Jet Propulsion Laboratory*
Pasadena, California - (Summer of 1980
DOE Faculty Exchange Program)
and
Department of Chemistry
University of North Carolina
Charlotte, North Carolina

Project Goals: The investigation of hydrogen production by use of electron transfer catalysts using energy from conventional or solar sources to drive the reactions.

Project Status: Work was done on alternate methods of preparing hydrogen from sulfuric acid by use of thermal or electrochemical cycles. A number of processes requiring chemical, electrochemical or photochemical methods were studied. These include the design of potential photoelectrodes and photocatalvtic membranes using $RU(bpy)_3^{2+}$ bpy = 2,2'-bipyridine impregnated nafion tubing and the design of experiments to study the catalyzed electrolytic formation of hydrogen and sulfuric acid from sulfur dioxide and water using quinones as catalysts. Experiments were carried out to determine the value of the new approaches to energy conversion.

Contract Number: IA ET-78-1-01-3112 (One of several tasks)

Contract Period: FY'80

Funding Level: $195K (FY'80) (For all tasks under IA ET-78-1-01-3112)

Funding Source: Department of Energy - STOR

PROJECT SUMMARY

Project Title: Thermochemical Water-Splitting Program

Principal Investigator: G. E. Besenbruch

Organization:
General Atomic Company
General Programs Division
P.O. Box 81608
San Diego, CA 92138
(714) 455-2090

Project Goals: This program involves experimental research and development of the Sulfur/Iodine thermochemical water splitting cycle. Specific objectives include development of a bench-scale unit which demonstrates the major aspects of the cycle, and development of engineering flowsheets for estimation of process costs and efficiency. Funding of closely related work on cycle chemistry is provided by the Gas Research Institute. Funding on solar applications of the process is provided by DOE Solar Thermal Power Office and SERI.

Project Status: Installation of the bench-scale system was completed meeting a major milestone in the overall General Atomic thermochemical water-splitting program. Operation and preliminary data acquisition in the system resulted in verification of flowsheet conditions for all unit operations which were tested. A view and modification of flowsheet section III (HI purification) was carried out and resulted in an increase in process thermal efficiency of approximately 1.5% for the total process. Consequently the capital equipment requirements were significantly reduced. The Funk panel review of the GA process was completed. Unpublished results indicate that there appear to be no real technical problems in the process. Project work centers on data acquisition in the bench-scale equipment and on demonstrating the process in the integrated DOE-STOR bench-scale system.

Contract Number: DE-AC02-08ET26225

Contract Period: October 1979 - September 1980

Funding Level:
399,205 (DOE, FY1980)
130,000 (GRI, CY-1980)
55,000 (MPC, CY-1980)
55,000 (GA, CY-1980)
40,000 (GPL, CY-1980)
99,000 (SERI, CY-1980)

Funding Source:
Department of Energy - STDR
Department of Energy - Solar Thermal Power Office
Gas Research Institute
Metal Properties Council
General Atomic Company
Jet Propulsion Laboratory (From DOE STOR)
Solar Energy Research Institute

PROJECT SUMMARY

Project Title: Thermochemical Processes for Hydrogen Production

Principal Investigator: Melvin G. Bowman

Organization: Los Alamos Scientific Laboratory
P. O. Box 1663, MS-756
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FTS 843-6014

Goals: The overall objective of this program is to contribute to the development of practical thermochemical cycles for the production of hydrogen from water using primary heat sources.

Status: The principal program tasks are:

1.0 Experimental: Studies are being conducted to obtain accurate thermochemical data and practical kinetic data for key reactions in cycles that match the heat delivery characteristics of different heat sources. Currently, reactions for the formation and decomposition of bismuth oxysulfates are being studied as steps that minimize heat requirements for solution concentration in sulfuric acid cycles designed to couple with solar heat sources. Studies in a solids decomposition facility consisting of a rotary kiln have shown that $Bi_2O(SO_4)_2$ will decompose in less than 2 minutes at temperatures ranging from 973 to 1143 K. Activities for FY-81 will consist of additional bismuth oxysulfate decomposition experiments and studies of bismuth oxysulfate reactions with sulfuric acid at different temperatures and acid strengths. Design studies will be initiated to determine the suitability of different solids decomposition systems for solar heat input.

2.0 Process Evaluation: Technoeconomic studies have been conducted to determine differences in estimated capital costs and efficiencies between water electrolysis and thermochemical cycles as paths for hydrogen production from primary heat sources. The differences found were relatively minor and within estimation error. The final best method will depend on technical advances made in both branches of technology.

3.0 I.E.A. Information Exchange: As a continuing activity reports and papers are exchanged between U. S. Laboratories and other countries participating in Annex I. of the I.E.A. Agreement on Hydrogen Production. The fourth Annex I workshop is tentatively scheduled to be held in Juelich, Germany, during the summer of 1981.

Contract No.: AL-10-05-15-0

Contract Period: FY-1980 Funding Level: $225K

Funding Source: Department of Energy/Advanced Conservation Technologies

PROJECT SUMMARY

Project Title: Sulfur Cycle Hydrogen Production Process

Project Manager: G. H. Parker

Principal Investigator: P. W. T. Lu

Organization: Westinghouse Electric Corporation
Advanced Energy Systems Division
Post Office Box 10864
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Project Goals: Major objectives include (1) providing a foundation for the long term development of efficient, long life and inexpensive electrolyzers for the hybrid electrochemical/thermochemical sulfur cycle, and (2) increasing the understanding of the electrochemistry of depolarized anode electrolysis in sulfurous/sulfuric acid solutions. Work toward these goals constitutes a portion of the overall development of the sulfur cycle. A complimentary program on the thermochemical aspects of the process is funded separately by DOE/Solar Energy.

Project Status: A series of tests has been performed with experimental electrolysis cells using various platinum catalyzed carbon electrodes. Major improvements in cell performance have been attained as indicated by measured cell voltages. When operated at 200 mA/cm^2 current density using 50 w/o acid at 50°C and 1 atm, a reference cell required 1.22 volts and degraded rapidly. After several improvements had been incorporated into electrodes and the test cell configuration, a later cell required only 0.77 volts under identical operating conditions. This cell exhibited stable operation with no measurable performance degradation. At a lower current density, 100 mA/cm^2, the cell required only 0.63 volts.

A one-week endurance test has been conducted with an intermediate cell operated at a 100 mA/cm^2 for 173 hours. This cell exhibited a stable voltage of 0.675 volts with no degradation after the first 80 hours.

Experiments have been made on two key gas separator figures of merit: diffusivity for sulfur dioxide-containing species and ionic resistivity. From diffusivity experiments several materials have been identified that have diffusion coefficients substantially lower than the reference material, microporous rubber. A cation exchange membrane material, P-4010, has exhibited an excellent diffusion coefficient, more than two orders of magnitude lower than that of rubber.

Current efforts are emphasizing reduction of precious metal loadings on the electrodes without compromising cell performance. Initial tests have indicated that cells with cathodes loaded with 2 mg/cm^2 of platinum on carbon substrates perform as well as earlier cells that used 10 mg/cm^2. A long term goal is to achieve loadings less than 0.5 mg/cm^2 on both cathodes and anodes.

Contract Number:	JPL 955380	DE-AC02-80ET25208
Contract Period:	February 79 - February 80	May 1980 - December 1980
Funding Level:	$251K	$118K
Funding Source:	DOE/STOR via JPL	DOE/STOR via BHO

PROJECT SUMMARY

Project Title: Studies on Thermochemical Water-Splitting Cycles

Principal Investigators: R. J. Remick, S. E. Foh

Organization:
Institute of Gas Technology
3424 South State Street
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(312) 567-3929

Project Goals: The purpose of this program was to assess the electrochemical oxidation of sulfur dioxide in relatively dilute (less than 50 weight percent) sulfuric acid and to determine the preferred operating conditions (acid concentration, temperature, electrode materials) for such a cell to be mated with a metal oxide-metal sulfate water-splitting cycle. Based on extensive thermodynamic evaluations of hybrid water-splitting cycles, we estimate that total cell voltages of 0.5 V or less are desired to compete with electrolytic water-splitting. Electrochemical kinetics (current density) will have a direct bearing on system cost. We estimate that current densities of about 200 mA/cm^2 or more are required for a practical cell, although this value is strongly dependent on the cost of electrode materials. Therefore, our rough performance goals were 200 mA/cm^2 at 0.5 V.

Project Status: This phase of the project has been completed.

Contract Number: 955494

Contract Period: June 1979 — June 1980

Funding Level: $75,000

Funding Source: Jet Propulsion Laboratory

PROJECT SUMMARY

Project Title: Thermochemical Hydrogen Production Management

Principal Investigator: Christopher England

Organization:
Jet Propulsion Laboratory
4800 Oak Grove Drive
Mail Stop 507/207
Pasadena, California 91103
(213) 577-9060

Project Goals: This activity monitors technical progress and problems in the program for the production of hydrogen by thermochemical cycles. Analyses of process costs, process chemistry and process thermodynamics are conducted in conjunction with the technical monitoring of DOE funded activities at industrial, academic and national laboratories.

Project Status: Continued development of the two major cycles showed good progress with the possibility of both being economically viable in light of new cost projections for synfuels. The major concern is for the relatively slow progress in developing an electrolyzer for the hybrid cycle. IGT, under JPL contract, extended earlier German work to an electrolyzer with potentially dramatic improvement of performance. Development of this concept to an operating electrolyzer is planned for this year. Progress on the sulfur/iodine cycle has been excellent in view of the level of support. The major economic and thermodynamic problem rests primarily on reducing water inventory within the cycle.

New Cycles have been proposed this year, but seem not competitive with those under development, primarily for engineering reasons.

Contract Number: ET-78-1-01-3112 (One of several tasks)

Contract Period: FY'80

Funding Level: $195K (FY'80) (For all tasks under IA ET-78-1-01-3112)

Funding Source: DOE-STOR

Meeting of the Review Committee

Friday, October 17, 1980

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Mr. C. T. Pate	Aerospace Corporation
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Mr. Laurence O. Williams	Aerospace Corporation
Mr. Charles E. Wyman	Solar Energy Research Institute

October 16, 1980

DOE THERMAL AND CHEMICAL STORAGE BRANCH
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DINNER ADDRESS

THE ROLE OF R&D IN MEETING TODAY'S ENERGY CHALLENGE

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May I first say how honored I feel to be your guest speaker this evening and let me interpret it as a manifestation of the spirit of open collaboration and mutual appreciation which we enjoy within the International Energy Agency.

Perhaps it is not just a coincidence that a European - and a convinced European - addresses an American audience the day after the United States celebrated Columbus Day. America - Europe, New-World - Old World, it is a relationship of nearly 500 years now, with evidently a strong evolution in the character and balance of this relationship. The Europe of to-day is no longer the Europe of Columbus' time. At that time, progress towards unity was achieved through weddings between royal families; currently, it is through institutional measures - the Treaty of Paris signed in 1951 and the Treaties of Rome signed in 1957 which led to the Establishment of the European Communities - that Europe tries to reach this unity, notably in the economic, social and political fields, in order to maintain its role on the world scene.

On 1st January 1981, Greece - one of the birthplaces of our civilization - will join our current 9 Member States - Belgium, Denmark, France, the Federal Republic of Germany, Ireland, Italy, Luxemburg, Netherlands, United Kingdom - Europe will be at the time larger in population than the Soviet Union by about 8 Million souls, larger also than the United States by about 50 Million souls. The European Economic Community is already second in the World in terms of gross domestic product, the first in terms of import and export volume.

Nevertheless this Europe is facing formidable challenges for the future : in terms of population, the future position of Europe in the world will be very small - not even going back as far as Columbus' time, one should recall that the European population represented 20% of the world's in 1900. In the year 2000 it will be less than 5% of the then world population of 6 to 8 billion people. The same consideration applies incidentally to the United States. Also Europe's population is ageing : as an example, again in the year 2000 the young Arabs of less than 15 years of age will be more numerous than the young Europeans of the same age class, while in 1950 the ratio was only 40%.

Europe has very little natural resources in its own territory and must import most of its primary raw materials - mineral as well as vegetal. It corresponds thus to an immense factory which produces manufactured goods not only with raw materials bought from outside but also with energy acquired from outside, and there lies a formidable challenge.

Since the invention of the steam engine by James Watt and the ensuing industrial revolution, the economics of all our industrialized countries require energy as an essential ingredient of their development, if not of their survival. Securing adequate energy resources is one of the most pressing problems of the European Community; a problem which the 1973 oil crisis already underlined, but which the second oil crisis of 1978 has greatly exacerbated, and the most recent events - the Iraq-Iran war - let us believe that there is little hope of improvement in this area.

The impact of the 1972-1973 oil crisis was painful but short-lived. Supplies were restored and oil prices began to fall in real terms in the years that followed; a positive response to the energy challenge began very quickly to seem less pressing, but the 1978 crisis has shaken the most inveterate optimist about our energy future.

Between January 1978 and May 1980, the oil price has increased by 140%. In 1978, oil accounted for 55% of our total energy consumption in the European Community. We imported 9 million barrels a day at a cost of over 70 billion dollars; that is equivalent to some 3% of our combined gross domestic product. This year we can expect to spend about 120 billion dollars to import a smaller amount.

These financial burdens are heavy : these extra 50 billion dollars represent a loss of resources equal to nearly half of what the US, the most powerful nation in the world, spents on defence; they depress our economies and encourage inflation, which is running currently at about 14% in Europe.

- the trade balance of the Western industrialized countries has gone from a surplus of 30 billion dollars in 1978 to a deficit of about 50 billion dollars in 1980;

- the economic growth rate in Europe has gone down from 3.4% in 1979 to 1.5-1.8% in 1980; 1.5% is about a third of what is considered necessary to solve on a long term basis the problems of employment and of the necessary structural adaption of economies to the new realities of this world. We need at least 3% growth to avoid a degradation of the current unemployment problem, which affected 8 million people in the Community this summer, and this should be coupled with an inflation of no more than 4.5%.

Our troubles are as nothing compared with those of the developing countries that are unlucky enough to have little or no oil of their own. The indebtedness of the Third-World - for oil supplies alone - increased from 7 billion dollars in 1973 to 43 billion dollars last year : many of them have already exhausted their international credit.

Yet all the pressures in the developing world are towards increased oil consumption. Their high levels of population growth, the steady movement out of villages into the cities, the development of more intensive forms of agriculture, the shift from agriculture to industry, all of these will tend to push-up energy consumption. Merely to maintain their present - I repeat present - standard of living, the growing populations of the Third World will need 50% more energy by the year 2000.

Unless there is a radical change in the prospects for alternative sources, this will mean importing 10 millions barrels of oil a day compared with the figure of 4 million barrels a day at present. That is, if the oil is available, and if they can pay for it.

The energy problem is a problem on a global scale. How we try to resolve it in the industrialized world will impact very heavily on the prospects for the less fortunate elsewhere. How we approach it in Europe will affect the New World as well at the Old and vice versa. Our interdependence is self-evident. Our response to the energy challenge must avoid the risks of damaging competition with the developing world for scarce oil resources and also damaging competition amongst ourselves in the industrialized world. We have to act in concert in engineering an energy revolution with the longer term interests of all of us together in mind.

The Western industrialized countries are effectively working closely together across the Atlantic and the Pacific, notably through the International Energy Agency. They have begun to make a determined effort to cut out wasteful energy use, to move out of oil and to find replacements to provide the means to return to steady economic growth. At the Summit of the 7 main industrial nations - and those include four members of the European Community - in June this year in Venice, new foundations were laid for a coherent energy plan which complements the agreement already reached at the Tokyo Summit of 1979. These nations have now pledged themselves to policies which are expected to reduce the share of oil in their total energy demand to about 40% by 1990.

"Away from oil" is thus emerging as a common objective of our Western world. How to achieve it is left to the initiative of each nation or group of nations and indeed there are differences in the various energy policies.

As far as Europe is concerned, an agreement exists within the Community on the basic principles of an energy policy. It takes the shape of measures undertaken both by Member States and by the Community itself through its executive body, the Commission.

The Commission does not claim that everything in the energy sector should be regulated on a centralized basis at Community level. A large part of the strategy on which the Member States have agreed can be implemented only at national level. But - and this has always been the Commission's intention - these measures must be co-ordinated and where necessary, supplemented and reinforced by Community measures.

In June 1980, the Council adopted a resolution concerning the objectives for 1990 and the convergence of the policies of the Member States, together with a resolution concerning new lines of action in the field of energy saving. These texts provide a reference framework to guide national policies and a gauge of the effort which the Community is making to help solve the world energy problem. They give the Commission the basis for co-ordinating, stimulating and if necessary complementing national measures.

The adopted strategy involves the following guidelines :

a) to reduce to 0.7 or less the average ratio for the whole Community between the growth rate in gross primary energy consumption and the growth rate in gross domestic product. The present objective for 1985 is 0.8.

b) to reduce the consumption of oil in the Community as a whole from the current 54% to a level not exceeding 40% of gross primary energy consumption in 1990.

c) to increase the use of coal and nuclear energy so that these two sources together cover 75% of primary energy requirements for the production of electricity. This compares with about 52% at present and will mean considerably speeding up coal firing conversion and new capacity, and the increased ordering and commissioning of nuclear plants.

d) to encourage the use of renewable energy sources so that they make a contribution to the Community energy balance in 1990. The contribution will nevertheless remain modest in this time frame. It is estimated that even by the year 2000 renewable energies (hydro power, geothermal energy, wood, biomass, solar energy, etc.) will not account for more than 4.7% of our total energy needs.

e) to adopt a prices policy encouraging the achievement of the Community energy objectives.

These guidelines complement earlier guidelines laid down in the first instance in 1974 and reviewed at regular intervals. Some concrete results can already be underlined notably in the field of energy saving : the reduction in the Community energy consumption between 1973 and 1979 is significant. Even if this is partly due to the slow down in economic activities, it has been estimated that a yearly saving of 7 to 8% has been achieved. This represents nearly half a billion barrels per year or more than 15 billion dollars per year at current prices. As a whole, the dependance of the Community on energy imports has been reduced since 1973 from 63 to 54%. We appear to be on the right track but there is a lot more to be done.

Research and Development has a significant role to play in this respect and it is no surprise that energy R & D has received the highest priority in the Community policy in science and technology - in fact 2/3 of the overall research funds are allocated to energy. It is interesting to note that if this priority is recognized at the decision-making level in our Member States, the perception of the general public on these priorities is somewhat different. I will come back later to this point.

The action of the Community in the field of energy R & D has several aspects :

- the coordination of programmes conducted at national level. There is no direct financial intervention of the Community which acts only a forum for consultations between the interested parties.

- the execution of specific research programmes either within the Commission's own laboratories grouped in the Joint Research Centre or through association with national research and development bodies. In the first instance, research is financed at 100% by the Community, in the second, the Community contributes in general half of the total cost, the other half being financed by national authorities or the contractor itself. Through this partial financial contribution, the Community adds some leverage to the coordination of national programmes.

If R & D programmes have been an activity carried out by the Community since its inception, it is only fairly recently (1973 for the hydrocarbons sector, oil and natural gas, 1978 for the other sectors) that it has been decided to add a new volet covering demonstration activities, and one may now speak of Energy, R, D & D in the Community. Due to the financial risk involved in new methods and technologies and/or to their high cost of investment, the Commission has launched a scheme to assist the financing of projects in the energy sector. These projects aim to demonstrate the industrial and commercial viability of the relevant technologies and methods, in order to encourage utilization and promote their spread within the Community.

In general the regulations on demonstration projects state that the Community's financial contribution may not exceed 40% of the total cost of the assisted project, and that half the support is repayable by the recipient if the methods developed are exploited for industrial and commercial purposes (100% is repayable in the case of hydrocarbon projects). Furthermore, the recipient undertakes to permit the dissemination of the results of the work performed.

So far about 35 million $ (M$) have been allocated annually since 1974 to the oil and natural gas sector. They cover projects dealing with improved production techniques, transport techniques for natural gas, improved prospection and drilling techniques and storage techniques.
Solid fuel, i.e. coal projects have been allocated about 70 M$ for the 5-year period 1979-1983. It is foreseen that this sum will be insufficient and its doubling has been proposed to the Member States.
Geothermal energy and solar energy projects have been allocated each 32 M$ for the same five year period. Again an increase in the appropriations has been requested in view of the large success of the first invitation to submit projects.
Finally energy saving projects have available about 80 M$ for 4 years 1979-1982. 30 M$ have already been allocated and it is foreseen to request again an increase in appropriations.

It would been tedious to list all the technologies and methods covered so far by these projects. It should be only underlined that they cover a wide spectrum ranging from large, ambitious advanced technology industrial ventures - 1.5 M$ in average per hydrocarbon project and 5 to 7 M$ in average per coal gasification or liquefaction project - to the support of simple demonstrations at the level of local communities and small business notably in the solar energy and conservation areas (350,000 $ on average per project).

Going back to Research and Development before describing our main lines of action, a few figures might help to put things into perspective :
in 1979 the Europe of the Nine spent about 46 billion $ in research, while at the same time Japon spent 22 billion $, the United States 56 billion $ and Soviet Union 29 billion $, that is respectively 1.9, 2.0, 2.3 and 3.2 with respect to their Gross Domestic Product. Europe ranks thus fourth in this respect. In Europe, and the same pattern applies to the US, roughly half of the total financing comes from public funds, the rest from private industry. In Japan the private sector contributes more. On the other hand, defence research represents only 22.4% of the public financing in the Europe of the Nine while in the United States it accounts for more than half of government R & D financing. This leads to a situation where for civil R & D financing, credits are roughly comparable on both sides of the Atlantic.

But the comparison stops there. In Europe the credits are spent in nine - soon 10 -different nations with their own research structures, their specific traditions and speaking 6 - soon 7 - different languages. How can we combat the negative effects of such a fragmentation? We must by all means avoid wasteful duplications or divergence in research objectives, co-ordination at Community level is an absolute must, and that is why I mentioned it in the first instance.

Secondly, the Community's own research has to concentrate on a few essential subjects and not disperse itself in all possible areas of science and technology. The funds allocated at Community level represent no more than 1.8% of the overall R & D spending in Europe. If spread evenly, these funds would not have any noticiable impact on research activities. On the contrary, if they are concentrated, their impact can be felt and that is why we put so much effort in the energy field. In overall energy research, the Community share is about 10% of the total and in the specific area of new energies -including fusion - it goes up to 30%. Selectivity is our essential preoccupation when defining our Community research programmes.

Where are we orienting our efforts right now? Five disciplinary research sectors can be identified :

- energy conservation
- nuclear energy-fission
- new energies comprising fusion and renewable energies - solar and geothermal
- synthetic and replacement fuels; this covers at the research level, hydrogen production
- coal production

to which a sixth horizontal sector has to be added
- energy systems modelling.

In the field of energy conservation, EC research funds have been multiplied by a factor of 10 between 1974 and 1979 while in the Member States the corresponding factor is about 4. This indicates that this sector is receiving much attention. Research at Community level is essentially conducted through contracts with national laboratories and industry; 38 M$ are currently assigned for that purpose for a four year period starting July 1st 1979. Five sectors are considered : in the domestic sector, priority is given to heating systems, their control, heat pumps, insulation materials and new building systems. In the industrial sector, mainly energy intensive processes, essentially in the chemical and metallurgical industry are considered. Moreover special efforts are devoted to the improvement of heat exchangers, industrial heat pumps and ORC engines. In the transportation sector priority is given to the improvement of the thermodynamic behaviour of engines and to the development of a public transport system. In the energy transformation sector, fluidized bed combustion and burning of low grade fuel is emphasized. In the energy storage sector efforts are mainly concentrated on electricity storage for vehicles and power stations, and a small number of thermal and mechanical energy storage systems which are application oriented. A modest start in the latter area of energy storage is planned also for in-house research and in the new four year programme of the JRC - and more specifically of its Ispra Establishment - about 7 M$ will be spent on this topic.

Nuclear research - for fission energy - has always been an important component of the Community research : it is one of the tasks assigned specifically by the Euratom Treaty. The in-house research component through the JRC programme is the most important in this area; it is complemented however by a significant effort of research by contract. The currently decided programmes represent no less than 550 M$ expenditure over the next 4 years. This sum is particularly significant if one recalls that all this research is related solely to the problem of nuclear safety, no development of reactor systems, a generally very costly item, is performed at Community level.
The main areas investigated are

- reactor safety, which receives a very large fraction of the total effort
- radioactive waste management and disposal
- improvement of safeguards techniques, and
- decommissioning of nuclear power plants.

The public concern about these problems justifies the large Commissions intervention. It is worth mentioning that the independence of judgment of the Commission - which is not linked to a specific development in this field - constitutes a non negligible asset which is fully recognized by decision-makers and public opinion.

In the area of new energies again in-house research and research by contract complement each other :

- The fusion programme is a model case of co-ordination of research; nearly all of the research conducted in Member States is integrated in the Community programme through the so called association contracts, so that full coherence of the actions is achieved. Furthermore the single largest experiment in the fusion field, JET, - a large Tokamak machine comparable in size to TFTR currently being built in Princeton - is the object of a joint undertaking with its own specific status. The Community finances 80% of JET whose construction is estimated at about 280 M$. JET should start operation in 1983.

  The other parts of the fusion programme represent another 280 M$ over 5 years, while the Joint Research Centre is devoting 37 M$ in the next 4 years to fusion technology problems.

- the effort in the field of new energies is concentrated on solar and geothermal energies /
  In the solar field, work is focussed on 8 items

  - solar energy applications to dwellings
  - thermomechanical solar-power plants - a 1 MWe central tower power plant realised by a consortium of European industries will be soon put into operation in Sicily
  - photovoltaic power generation
  - photochemical, photoelectrochemical and photobiological processes
  - energy from biomass
  - solar radiation data
  - wind energy, and
  - solar energy in agriculture and industry.

65 M$ are allocated over 4 years for research by contract in these areas while in-house research represents an effort of about 34 M$ also over 4 years.

Geothermal research work deals with integrated geological, geophysical and geochemical investigations in selected areas, subsurface and surface problems related to the use of natural hydrothermal resources and hot dry rocks.

Research, exclusively by contract, is allocated 26 M$ over 4 years.

In the area of synthetic fuels and replacement fuels, attention is currently being given to the type of action that should be initiated in this area. If one excepts synthetic fuels from biomass, which is investigated under the solar energy programme, so far the only significant activity is in the field of hydrogen production and utilization. The main part of this activity is concentrated at the Joint Research Centre; Ispra is focussing on production techniques essentially through thermochemical or hybrid processes, while research by contract also covers electrolytic production as well as transport, storage and utilization problems. Over the next 4 years the consolidated effort represents some 32 M$.

Finally, as far as coal is concerned, research is concentrated on improvement of mining techniques and coal upgrading. This research obeys special financing rules, with no budgetary envelope determined a priori; the effort can be estimated at some 23 M$ per year.

To complete this panorama of our Energy R & D activities, I would like to underline the importance that we attach in the Community to the horizontal activity of energy systems analysis.

This activity is currently allocated 9 M$ over 4 years. It comprises the improvement and further development of the medium and long term energy models, the development of new concepts for energy systems representations, the development of new means for better communication between model builders and model users and a contribution to world energy modelling. National models - when they exist - too frequently ignore the behaviour of other countries, and thus present the risk of leading to fully irrealistic conclusions, for instance by "exporting" their problem to a neighbour, who perhaps on his side is doing the same in the reverse direction. With the very integrated economic relationship existing between European Community Member States, this deficiency could be particularly damaging and an integrated approach is absolutely compulsory; hence the interest of a Community activity which has already led to the establishment of a model implementing team regrouping experts of the Member States.

In summary, it appears that our Energy R & D activities are covering adequately the vast field of energy technology. No major gaps can be identified, even if in some areas - thermal and chemical storage synfuels - some reinforcement may appear necessary. Pointless duplications of effort are avoided through close co-ordination with national programmes, although improvements are of course always possible.

International co-operation beyond the level of the Community can further contribute to avoid this pointless duplication and to enhance the efficiency of one's own research effort. Indeed, there is a strong international component in the most of the research activities described. We participate in several IEA cooperative programmes, namely :

- in the energy R, D & D strategy exercice, which was led here in the US by Brookhaven
- in fusion in the 3 programmes, super conducting magnets, plasma/wall interaction (textor) (where we are acting as operating agent) and radiation damage in fusion materials
- in energy conservation, in the programme on heat storage
- in solar energy, in the programmes on
  - . performance of systems for heating and cooling
  - . testing of collectors for heating and cooling
  - . solar instrumentation package (where again we are acting as operating agent)
  - . treatment of meteorological information
- in biomass conversion, in the programme setting up a biomass technical information service
- and last but not least, in the hydrogen programme that Dr Swisher has outlined in one of the meeting's papers.

In the nuclear field, we are associated with the work of the NEA(OECD) and we participate in the International Atomic Energy Agency activities; a cooperation agreement with the IAEA on safeguards R & D will be signed very soon. The European Communities also takes an active part together with the USA, Soviet Union and Japan in the INTOR design exercise. INTOR is possibly the next step in large fusion machines which could be built at international level.

Furthermore, we have established cooperation through several bilateral agreements :

- with Sweden, Switzerland, Spain - these countries in particular participate in our fusion programme as if they were Members of the Community
- with Canada on radioactive waste disposal and energy conservation (we have recently adopted in this respect the Canadian energy bus concept)
- with Israël, on photochemical conversion;
- with the United States finally, mainly in the field of nuclear reactor safety and safeguards.

As I mentioned early in my talk, developing countries have an acute energy problem and in our co-operation with these countries - mainly the countries of Africa, the Caribbean and the Pacific which have signed the Lomé convention with us - we are injecting an energy R, D & D component. So far we have no R & D programmes specifically designed to their specific needs but our own programmes are generally usable as such for their purposes, at least in the energy field.

All this looks fine, and indeed we have no reason to be dissatisfied with the development of our programmes; this view is fortunately shared by our Member States who finance us. Nevertheless there is always room for improvement and problems are never completely resolved.

Our current main problems relate mostly to the end of the R & D cycle rather than to its initial phase - the selection of research avenues - or to their actual execution - if one excepts the constant fight against inflation in programmes appropriated on a multiannual basis.

The first problem which requires constant attention is how to ensure an adequate dissemination of information on research results. R, D & D is not an end in itself, it must transfer its results to industry, to policy-makers, to regulatory agencies for further use. Valorization of research results - as we call it - requires all our attention. Our efforts are oriented towards a better availability and accessibility of information, in particular to small and medium business which cannot spend as much effort as big agencies on information retrieval. Improvement in our publications systems are in course, particularly with a view to getting the results understandable to the non-specialists; contractors meetings of the type of the present one are organized more frequently and considered to be an excellent way to exchange and disseminate information. Furthermore, small groups of experts are compiling catalogues of present and planned R & D projects in a specific area. Our experience with the catalogues on Energy Savings in houses and on heat pumps has been so far extremely good. Those who benefit from this type of processed information are firstly the planners of research work and those, who, responsible for external relations, are seeking opportunities and ways and means of co-operation; secondly those who perform research are interested in discovering who their colleagues are and precisely what they are doing in other institutes and laboratories; thirdly but not lastly those who are, or may be, the potential users of the research results.

Efforts for improving the transformation of research results into industrial processes or products - valorization - have been entrusted to a special unit within the Commission and our Joint Research Centre obtained this year approval for a specific programme funded at level of 1.5 M$ over 4 years to assist these efforts with some in-house technical support.

Our second problem in energy R & D is to reach the right balance between two conflicting objectives, on the one side the Commission's institutional obligation to make available research results to "the Member States as well as to persons and undertakings which pursue, on the territory of the Member States, a research or a production activity justifying access to such information", on the other side to protect as much as possible the intellectual property rights of our contractors in order to avoid that working for the Community would become so unattractive for the contractor that he will not even care to bid. We have devised a patents and licenses system which represents a sort of compromise in this respect. Its main elements are as follows :

- the contractor has the obligation to investigate exploitation or to exploit inventions resulting from Community sponsored work;
- he has the exclusive right to do so himself or to grant exclusive licenses to Member States or persons/organizations within the Member States - not necessarily of European origin;
- in case the contractor does not exploit or license the invention, the Commission, which anyway gets a royalty - free license "for its own purposes" - can sublicense the invention; to this end, parties are invited for a non-exclusive license via publication in the Official Journal of the European Communities;
- if there is no response within 6 months after publication, the Commission can grant exclusive licenses;
- if there is a positive response within 6 months, the Commission invites interested parties and the inventor to settle the matter between them.

It should be mentioned that once one tries to transpose this kind of system to international co-operation, one runs into trouble, and it should noted that the most difficult item which had to be dealt with in the IEA co-operative agreement on hydrogen has been the clauses on intellectual property rights.

Our third problem is in the area of the evaluation of R, D & D results - what the Germans describe as "Erfolgskontrolle". The problem is not so much to evaluate if the research has been conducted properly, but to evaluate the relevance of these research results to our more general policy objectives, relévance not only from a technical point of view but also from a financial and manpower point of view. In other words the main question is whether the potential impact of our research is sufficiently identified to justify the means it is allocated.

The question is far from being academic,and my personal experience of having to defend research budgets shows that decision-makers are less and less inclined in our tight economic environment to give us a blank check in the research field. The methodology for this type of evaluation of R & D results is in my view still very primitive, and we are working actively on its improvement. The conduct of audits on research projects by independent experts is one of the ways currently investigated. Our solar energy and hydrogen programmes are being now submitted to such audits.

A particular aspect of evaluation of research results is the sanction of the general public. Its perception of research is certainly (in our highly democratic western societies) a factor in the decision making process of our political masters. It is certainly not the determining factor : as we will see, policy makers may adopt explicitely our perception of priorities rather than the one emerging from public opinion, nevertheless, the latter has an implicit influence on political decisions.

The Commission asked a group of experts to conduct a survey of public opinion on research. The survey took place in 1977 i.e. after the first oil crisis but before the second oil crisis of 1978; I personally feel that the later one would not have influenced very much the results of the survey and they may considered to be still representative of to-day's opinion. A sample of 9,000 people in the nine Members States was interviewed and the results are the following :

- On the general view of attitudes to science :
  80% of the people consider that science has been playing an important role in the changes in people's life that have come since 1950,
  89% of the people consider that there are still good things to discover in science,
  81% consider that science can help to improve the life of developing countries,
  69% affirm that science is one of the most important factors in the improvement of our daily life, while 5% consider science as dangerous,
  66% nevertheless consider that scientific discoveries can have very dangerous effects (apart from military applications),
  81% consider that it is the role of the State to subsidise scientific research,
  79% believe that European States should get together to pool their scientific research.

- On the difficult question of determining if government subsidies for scientific research should be spent more on projects which would give results in a short time (a year or two) or a long time (15 or 20 years), opinions were nearly equally split with a slight favour for long time research.

These results are very favourable to science, more than the regular press comments about the disillusionment with science and advanced technology would indicate. Also, the feelings are clearly towards joint European research.

With regard to priorities to be assigned to specific lines of research, people expressed the wish to see funding increased in eight areas and in the following order of priority :

(1) medical and pharmaceutical research

(2) research to increase agricultural resources to meet the world's food needs

(3) research on reduction and control of pollution

(4) research on new form of energy

(5) research on prevention and cure of drug addiction

(6) research on safety of nuclear installations

(7) research on educational training and methods

and last

(8) research on road traffic safety.

They also expressed the wish to see funding limited or reduced in the following four areas and in the following order :

(1) research on space exploration

(2) research on armement and national defence

(3) research on speeding up public transport

(4) research on forecasting and weather control.

One may comment at infinitum on these results; I will limit myself to the point that the public perceives priorities rather differently than we technocrats do, they attach much more importance to issues that touch them directly : illness, hunger in the world, pollution, rather than, for instance, energy issues that are nevertheless vital for our future. We should not ignore this element.

Mr Chairman, Ladies and Gentlemen, I have tried in these few minutes to give you an overview of the problems we are currently facing in Europe in the context of a global energy crisis, and how we try to use R, D & D to meet one of the most exciting challenges of this century. May it give to you a better understanding of the situation of the Old World.

Mutual understanding is an ingredient for co-operation between us, a co-operation which I feel remains highly desirable not only for strict political or economic reasons but also because of our common past and present ties.

Thank you for your attention.