CONF-781231

ENERGY

TECHNOLOGY

THIRD ANNUAL PROCEEDINGS OF THERMAL ENERGY STORAGE CONTRACTORS' INFORMATION EXCHANGE MEETING

DECEMBER 5-6, 1978
SPRINGFIELD, VIRGINIA

ORGANIZED BY SANDIA LIVERMORE LABORATORY
FOR

U.S. DEPARTMENT OF ENERGY
Assistant Secretary for Energy Technology
Division of Energy Storage Systems
Washington, D.C. 20545

Available from:

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5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed copy: $15.00
Microfiche: $3.00

CONF-781231
Dist. Category UC-94a

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PREFACE

Thermal storage technologies can contribute significantly to achievement of the goals set forth in the National Energy Act by facilitating the shift from scarce petroleum base fuels to more abundant energy sources such as coal and nuclear and by reducing total national energy use. Specifically, thermal storage technologies permit more efficient and economical use of intermittent energy sources and off-peak electrical power for applications in which there is a timing mismatch of energy supply and demand. In addition, thermal storage and transport will allow more extensive use of industrial and utility waste heat to fulfill needs currently provided by primary fuels.

In recognition of the energy savings potential of such applications, the Department of Energy has chartered the Division of Energy Storage Systems (STOR) to promote the development of thermal energy storage technologies at the national level. Overall management of the National Thermal Energy Storage Program is centralized in the Chemical and Thermal Storage Branch of STOR, while the day-to-day project management and implementation of DOE policy has been delegated to the national laboratories.

Under the direction of C. J. Swet at DOE headquarters, the Thermal Energy Storage (TES) Program has been divided into the following subprogram elements:

1. The Low Temperature Thermal Energy Storage (LTTES) Program managed by Oak Ridge National Laboratory--the objective is the development of sensible and latent heat technologies for application temperatures under 250°C.
2. The High Temperature Thermal Energy Storage (HTTES) Program managed by NASA Lewis Research Center--the objective is the development of sensible and latent heat technologies for application temperatures greater than 250°C.
3. The Thermochemical Energy Storage and Transport (TEST) Program managed by Sandia Laboratories, Livermore--the objective is the development of reversible chemical reaction technologies for applications over the full temperature range.

Additionally, Argonne National Laboratory reports directly to DOE headquarters on the use of thermal storage for electric load leveling behind the meter.

Because of the decentralized management and wide variety of projects being funded under the auspices of the Thermal Energy Storage Program, this Annual Contractors Information Exchange Meeting has been organized to give program participants a chance to place their individual project activities in perspective and to give government planners responsible for the commercialization of energy technology an overview of the TES program content. This is the third in the series of annual meetings for this program and this document provides a record of the proceedings. Each of the projects funded over the last fiscal year is described in this document but due to time constraints, only selected presentations were made from the podium.

Sandia Laboratories, Livermore was pleased to organize the meeting and assemble this documentation. It should be noted that the project reports which make up these proceedings were prepared by the responsible subcontractors--no technical editing or evaluation has been performed by Sandia.

William G. Wilson, General Chairman
Third Annual Thermal Energy Storage
Contractor's Information Exchange
Meeting

AGENDA

U.S. DEPARTMENT OF ENERGY
THIRD ANNUAL THERMAL ENERGY STORAGE
CONTRACTOR'S INFORMATION EXCHANGE MEETING

December 5 and 6, 1978
at
Springfield, Virginia

SESSION I

Low-Temperature Thermal Energy Storage

Chairman - D. M. Eissenberg, Oak Ridge National Laboratory

SESSION II

High-Temperature Thermal Energy Storage
Chairman - W. J. Masica, NASA-Lewis Research Center

SESSION III

Thermochemical Energy Storage and Transport

Chairman - W. G. Wilson, Sandia Laboratories, Livermore

LOW-TEMPERATURE THERMAL ENERGY STORAGE
PROGRAM OVERVIEW

David M. Eissenberg
Area Program Manager
LTTES Program

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Presented at: Third Annual Thermal Energy Storage Contractors'
Information Exchange Meeting
December 5-6, 1978
Springfield, Virginia

*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.

LOW-TEMPERATURE THERMAL ENERGY STORAGE PROGRAM OVERVIEW

David M. Eissenberg

1. INTRODUCTION

The Low-Temperature Thermal Energy Storage Program is a research and development program managed for DOE/STOR by the Oak Ridge National Laboratory. As program manager, ORNL has responsibility (in consultation with and with the concurrence of DOE/STOR) for planning the low-temperature storage effort, awarding subcontracts to implement the plan, maintaining technical and fiscal control of the subcontractors, disseminating the results obtained, and assisting in the transfer of the mature program elements to demonstration and commercialization. The bulk of the program is carried out through subcontracts with industrial research and development laboratories, universities, research institutes, and other national laboratories, with some support work carried out at ORNL.

In this overview, the LTTES Program objectives and scope are defined and the long-range implementation plan for achieving program goals described. Specific projects underway in support of program goals will be described in subsequent papers, either in summary form by ORNL-LTTES program staff or in more detail by contractor representatives.

2. PROGRAM OBJECTIVES

The objectives of the LTTES Program are to carry out research and development on new technologies for storing thermal energy as low-temperature sensible and latent heat, and to develop, test, and demonstrate cost-effective systems for collecting, storing, and discharging thermal energy which will have significant national impact on energy conservation in the near- and mid-term.

3. SCOPE

3.1 Storage Technology Thrust Areas

The LTTES Program is directed toward the development of thermal energy storage (TES) technologies and systems which are applicable to the near-term (by 1985) and mid-term (1985-2000). It excludes refinements of existing systems. The program is divided into three technology thrust areas:

(a) Geological storage: seasonal sensible heat or cold storage in natural underground aquifers, ponds, and subsurface earth

(b) PCM storage: decentralized daily/short-term latent heat or cold storage, utilizing devices incorporating phase-change materials (PCM's)

(c) Waste energy reuse: industrial heat reuse involving either sensible or latent-heat storage.

Of these three thrust areas, storage in underground aquifers has been further identified by DOE as having significant near-term national economic/conservation potential. As a result, a major expansion of work in the geological storage thrust area is planned in FY 1980; this proposed expansion is reflected in the long-range implementation plan.

3.2 Application Areas

Low-Temperature TES application areas include residential and commercial space conditioning (heating and cooling) and industrial, commercial, and agricultural process heat. Space conditioning applications include dispersed systems (individual buildings) and central systems (district heating). Process heat applications include within-plant cascading and transfer of cascaded process heat between plants.

3.3 Energy Sources

Heat sources to be exploited include (1) waste heat discharged to the environment from industrial or utility operations, (2) heat cogenerated in conjunction with electric power production, (3) solar heat, (4) heat generated during utility off-peak periods either by heat pumps or directly by resistance heaters, and possibly (5) natural environmental heat such as from geothermal.

Sources of cold include those (1) generated by mechanical or absorption air conditioners operating on either solar heat or off-peak electricity, (2) environmental cold collected by exchange with the ambient atmosphere during the winter, and possibly (3) reject from low-temperature industrial operations as in food processing.

The mating of these sources with a particular storage mode (geologic structures or phase-change materials) depends on the intended application of the stored energy.

4. IMPLEMENTATION PLAN

The implementation plan is a description of the logic for present and future directions in the LTTES Program. It reflects the program scope (including the technology thrust areas, applications, and energy sources) and describes an appropriate sequence of tasks for each thrust area and work element.

4.1 Geological Storage

Storage of hot or cold water in underground natural geological formations can bridge the seasonal gap between a heat or cold surplus period and a later heat or cold demand period. The attractiveness of the concept lies in utilizing geological formations for storage without significant alterations other than providing suitable input and output devices.

Aquifers, ponds, and subsurface artificial and natural cavities containing hot or cold waters and the earth itself all appear to have potential for seasonal storage of heat or cold. Of these, aquifer storage appears to have the greatest short-term potential with ponds and cavity storage considered as backups. An investigation of pond storage underway in Europe by the International Energy Agency, with funding assistance provided by DOE/STOR, will be monitored as a part of this program. Previous work on earth storage will be reviewed and a new program initiated, if justified.

In order to guide development of technology for aquifer storage to the stage where commercial systems can be designed and built, a comprehensive, multi-element, long-range aquifer R&D program is proposed that is aimed at uncovering and resolving critical technical, economic, and institutional issues. Eight work elements are included in this aquifer R&D program:

(a) techno-economic studies: Application surveys to identify and locate seasonal storage applications both nationally and, in more detail, in specific regions; analysis of the value of seasonal storage for specific applications; feasibility studies of proposed aquifer storage systems; designs and cost estimates for proposed aquifer storage projects; parametric studies to determine sensitivity of the cost of aquifer storage to the principal cost components; development of a national plan for implementation of aquifer storage technology

(b) experimental field tests: Development and operation of pilot size aquifer storage well systems to demonstrate overall technical feasibility, to develop good operating methods, to uncover and resolve operational problems, to test novel components, and to acquire a data base against which to develop and test mathematical models for predicting performance of new systems

(c) mathematical modeling: Development of mathematical models for predicting aquifer storage characteristics, including thermal recovery efficiency, hydraulic behavior, geochemical behavior, and structural integrity over multiple-storage cycles

(d) support R&D: Experimental small-scale studies aimed at increased understanding of specific areas of aquifer behavior during storage cycles, including geochemical research, structural mechanical research, and physical modeling of complex well systems

(e) technology development: Development and testing of aquifer storage system components, where not already commercially available or where optimization for the aquifer storage system is indicated, including systems for capturing winter cold and transferring it to aquifer water, down-well pumps, well casings, heat exchangers, systems for unplugging wells, systems for monitoring well performance, etc.

(f) environmental and institutional analysis: Generic analysis of possible impacts on the environment of aquifer storage systems and experiments; site-specific analyses of planned systems, where appropriate; analysis of the legal implications of aquifer storage, ownership of stored water, usage restrictions, etc.

(g) prototype systems: Aquifer selection, preliminary site analysis, test-well drilling and hydrological testing, well site selection, well system design and cost estimate, well construction, preliminary testing, performance testing with heated or cooled water over one or more seasonal cycles, incorporation into application system

(h) demonstrations: Site selection, conceptual design and cost estimate, final design, and cost estimate.

4.2 Daily Short-Term Latent Heat Storage for Building Heating and Cooling

The efficient utilization of solar energy and of off-peak electricity for space heating and cooling of residential and commercial buildings will require storage of either heat or cold to supply thermal loads during the time interval when energy is either unavailable or more expensive. These periods can range from several hours to several days. Storage elements for such applications could be in the form of central modular units, with forced convection charging or discharging, or they could be incorporated as part of building structures, as for example applications to passive solar, with natural convection and radiation supplementing or replacing forced convection for either charging or discharging. The storage in each case could be either as sensible heat or as latent heat, or a combination of the two. At the present time, it is possible to store thermal energy (either heat or cold) using commercially available heat storage systems with water or inexpensive solids as the storage medium in either modular or structural storage units. However, these systems are of limited application because of the large storage volumes required, the high initial cost, and the inherent thermodynamic inefficiency associated with sensible heat storage.

The LTTES Program focuses on identification, development, and prototype testing of novel cost-effective systems that store low-temperature thermal energy as latent heat. Applications will be for individual building space conditioning, with the transformation temperatures for systems of interest in the range of 5°C to 250°C. Both modular systems and those involving incorporation of the phase-change materials in building structures will be developed. The emphasis in each case will be on developing reliable, safe, commercially available systems that are both cost-effective in terms of the value of the stored energy and are capable of national application.

The approach to be followed in achieving this goal is to explore alternate system concepts for each application and then to select from these the one or more that appear on the basis of available information to have significant economic and conservation potential. New concepts will be identified by maintaining current awareness of technical developments and needs, issuing RFP's aimed at specific applications, and in some cases accepting unsolicited proposals. Concepts selected for development will be periodically reevaluated to insure continuing promise compared with alternate systems.

4.3 Waste energy reuse

Energy conservation through the recovery, storage, and later reuse of large quantities of low-temperature heat is the third thrust of the LTTES Program. This thrust differs from the first two in that its emphasis is not on the development of new thermal storage technology but on the demonstration of new applications of thermal storage (using new or conventional storage technology) to improve energy conservation. The approach is to uncover instances in existing industries (including electric power generation), where the application of thermal storage will allow the recovery and use of energy that otherwise would not be available and where such application would have a wide national impact. As examples are found, suitable demonstration projects will be developed and built and used to publicize both that specific application and applications similar to the one demonstrated.

The sources of energy to be utilized include industrial waste heat, cogenerated heat from electric utilities, and winter cold (captured in water by heat exchange with the environment). Applications include reuse as process heat in the same plant, use in other nearby plants or agriculture process heat, and use in district heating or cooling systems. Projects which utilize new thermal storage technologies being developed in the other thrusts of this program will be coordinated to insure timely development and demonstration.

5. FUTURE DIRECTIONS

The Low-Temperature Thermal Energy Storage Program is an important element of the national energy program. As stated in the objectives, it is focussed on making a significant national conservation impact in the near- to mid-term. To achieve that objective, truly cost-effective practical storage systems of many types need to be developed, which not only contribute to energy conservation, but do so within the constraints of the marketplace. This requires that our solutions be accepted by industry, regulatory agencies, and the consumer as the solutions of choice.

It is not clear which of the systems now being developed with funds provided by DOE/STOR/LTTES meet that test. Convincing DOE of the merits of a new technology is a necessary first step, but that is not sufficient if the goal is to bring the technology successfully to the marketplace. Thus, as the LTTES Program advances toward its objectives, the concepts being funded and those proposed for funding will be subjected to increased scrutiny with regard to their true market potential aside from the technical merits of the concepts. Although there may be many storage systems emerging as winners in the future, there most likely will be more concepts discarded than accepted.

SEASONAL STORAGE

G. D. Brunton

For presentation at the Third Annual Thermal Energy Storage Contractors' Information Exchange Meeting, December 5-6, 1978

I am going to present a status report on those LTTES seasonal storage projects (principally aquifer storage) that are not being covered by separate presentations at this meeting.

S. W. Yuan and A. M. Bloom of George Washington University have completed a final draft report on the storage of thermal energy in the earth. This report has not been published. No additional work has been contracted for at this time.

Chin Fu Tsang at LBL has completed modeling daily storage cycling into and from an aquifer. LBL hosted an aquifer storage workshop in Berkeley, May 10-12, 1978. LBL will issue a bimonthly newsletter for aquifer storage projects. In FY 79, LBL will use the data from the Auburn University field experiment to verify the "CCC" mathematical model.

TVA-Knoxville and -Chattanooga has contracted to survey the TVA service area for potential energy storage applications with an emphasis on aquifer storage. TVA geohydrologists will do a parametric study of aquifers and aquifer storage with the objective of determining a priori the suitability of various types of aquifers for thermal energy storage.

A request for proposal has been issued which covers the research, development, and construction of a prototype doublet aquifer storage system near Bellingham, Washington. The date for receipt of the proposals is December 18, 1978.

Two one-man-year sized projects are underway for FY 79 at ORNL. The first project is an economic analysis of aquifer storage by E. C. Fox. This analysis, although generic in character, will include a cost evaluation of chilled water aquifer storage at JFK Airport. The second project is the development by the Energy Division of a generic environmental impact analysis for aquifer thermal energy storage.

This summary has covered the status, not the results, of our current aquifer storage projects. In addition to these activities, we have organized a technical review committee for aquifer storage projects. The first meeting of the committee was held in Denver on November 6, 1978. Professor Stanley Davis, University of Arizona, is committee chairman. Committee members are Professor Ramey, Stanford; Professor Langmuir, Colorado School of Mines; Dr. Walters, consultant; and Dr. McClain, ORNL. The committee will meet biannually.

HOT-WATER FIELD TEST

PROJECT SUMMARY

Project Title: Experimental Study of the Storage of Thermal Energy in Confined Aquifers

Principal Investigator: F. J. Molz, A. D. Parr

Organization: Water Resources Research Institute
Auburn University
Auburn, Alabama 36830
Telephone: (205)-826-5075

Project Objectives:

(1) To inject heated water into a confined aquifer, store it for a period of time, and pump it out.

(2) To record water temperatures and hydraulic heads during the injection-storage-recovery cycle.

(3) To determine to the extent possible the feasibility of storing thermal energy in confined aquifers.

Project Status: The first of two 6-month injection-storage-recovery cycles has been completed. Relevant data have been collected and are being analyzed. During the injection period a clogging problem occurred. This problem did not, however, prevent attainment of the research objectives. Presently the injection phase of the second injection-storage-recovery cycle has been completed. During this injection the clogging problem was significantly reduced.

Contract Number: 7338

Contract Period: FY 1978, continuing

Funding Level: $287,000

Funding Source: Department of Energy, Division Of Energy Storage Systems

HOT-WATER FIELD TEST

by

A. David Parr, Fred J. Molz,
Peter Andersen and Vincent Lucido[1]

ABSTRACT

The concept of using confined groundwater aquifers for the temporary storage of large quantities of hot water has been proposed as a feasible choice for total-energy systems. The Water Resources Research Institute of Auburn University is performing a series of field experiments wherein this concept is being tested. To date, one preliminary experiment and one six-month injection-storage-recovery cycle have been completed.

The preliminary experiment involved the injection and recovery of about 7570 M^3 (2 million gallons) of water. The injection water was obtained from the effluent discharge canal of a power plant and had an average temperature of 37°C (98.6°F). The ambient temperature of the formation water in the confined storage aquifer was about 20°C (68.0°F). The injection, storage, and recovery periods were 420, 1416, and 2042 hours, respectively. The recovery period was terminated when the water temperature reached 21°C (69.8°F). About 67 percent of the injected energy was recovered. Clogging of the soil around the injection well posed a major problem during the injection period. The high level of suspended solids in the injection water was judged to be the primary cause of the clogging.

---

[1] Respectively, Assistant Professor of Civil Engineering, Alumni Associate Professor of Civil Engineering, and Field Engineers, Auburn University, Auburn, Alabama.

The second experiment involved the injection and recovery of about 54,900 M^3 (14.5 million gallons) of water. During this experiment the injection water was obtained from the formation water of an unconfined aquifer at the experimental site. The water was pumped from the unconfined aquifer, heated to a temperature of about 55°C (131°F), and injected in the confined storage aquifer. The injection, storage, and recovery periods were 1900, 1213, and 987, respectively. The recovery period was terminated when the water being withdrawn from the storage aquifer fell to 33°C (91.4°F) which was 13°C (23.4°F) above the ambient water temperature in the confined aquifer. At this point about 65 percent of the injected energy was recovered. The clogging problems that plagued the preliminary experiment were significantly reduced during the second experiment. This was apparently due to the relatively low level of suspended solids of the injection water. Periodic backwashing of the injection well also contributed to the improvement.

A second six-month injection-storage-recovery cycle is presently underway. It is being performed in essentially the same manner as the first cycle. The injection period has just been completed and the average specific capacity of the injection well is significantly better than in the previous experiment. This is encouraging since it appears that the degree of clogging will stabilize at an acceptable level when water low in suspended solids is used for injection. It still remains to be seen, however, what effects higher temperatures will have on the hydraulic conductivity of typical formation soils. Efficient total-energy systems would use injection water with temperatures as high as 200°C (392°F).

INTRODUCTION

This paper presents the results of the second hot-water injection-storage-recovery experiment performed by the Water Resources Research Institute of Auburn University. A detailed discussion of the experimental site and the preliminary experiment is given by Molz, et al. (1978)*.

BACKGROUND

The experimental field site is located near Mobile, Alabama. The confined aquifer in which the hot water was stored has a vertical thickness of about 21.3 M (70 ft) and is located between 39.6 M (130 ft) and 61.0 M (200 ft) below the surface. A fence diagram showing the location of each of the wells is given in Figure 1.

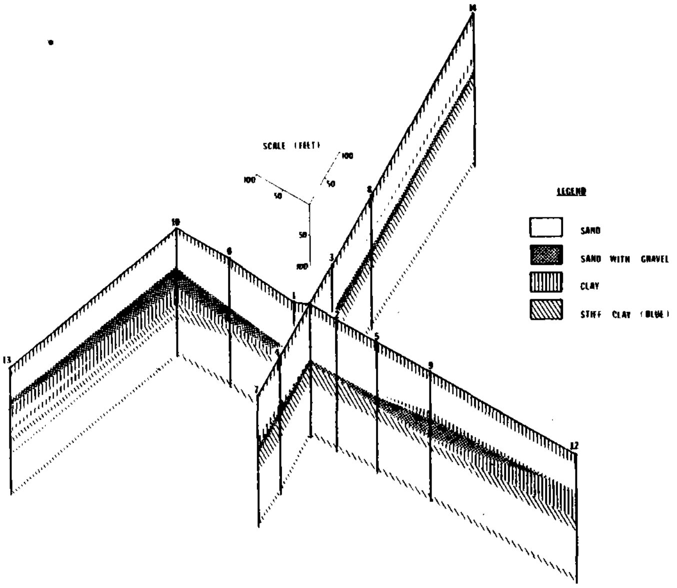

Figure 1. Fence Diagram Constructed from Well Logs

The original injection well was located at the intersection of the two principal planes in the fence diagram. A new injection well was constructed for the second experiment. Its location is indicated in the well-field layout shown in Figure 2.

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*Molz, F.J., Warman, J.C., and Jones, T.E., "Aquifer Storage of Heated Water: Part I - A Field Experiment," <u>Ground Water</u>, AWWA, Vol. 16, No. 4, July-August 1978.

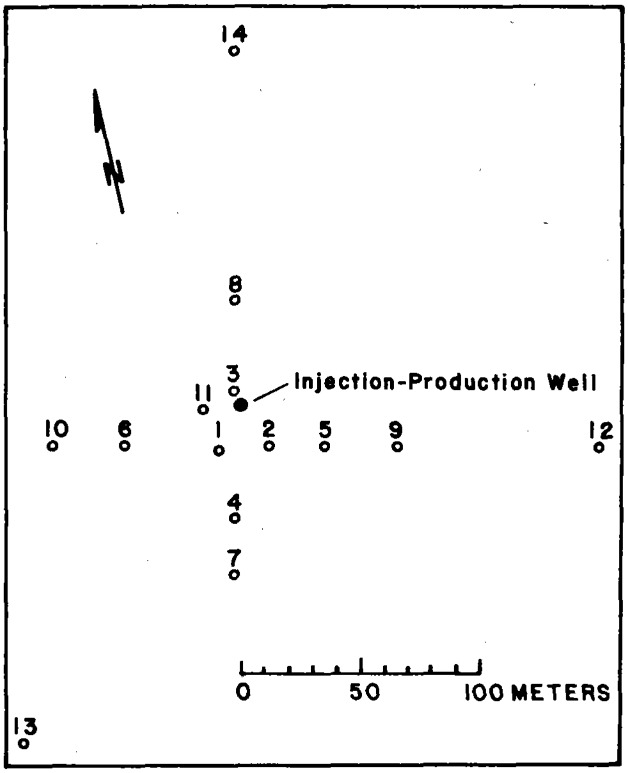


Figure 2. Well-Field Layout

The injection well screen extends from the upper confining layer about half-way into the storage aquifer. With the exception of Well 11, the observation wells are screened in the storage aquifer below the upper confining layer and are fully penetrating. Thermistors are located at 6 depths in Wells 1 through 10 and in the middle of the aquifer in Wells 12 through 14. Well 11 extends only to the upper confining layer and is screened in the unconfined aquifer region. This well serves to monitor the temperatures in the unconfined aquifer.

SECOND EXPERIMENT

Beginning March 18, 1978, formation water was pumped from the unconfined aquifer, circulated through a boiler where it was heated, and injected into the confined storage aquifer. The ambient water temperature in the storage aquifer is 20°C (68°F) and the average temperature of the injected water was 55°C (131°F). A schematic of the injection system is shown in Figure 3.

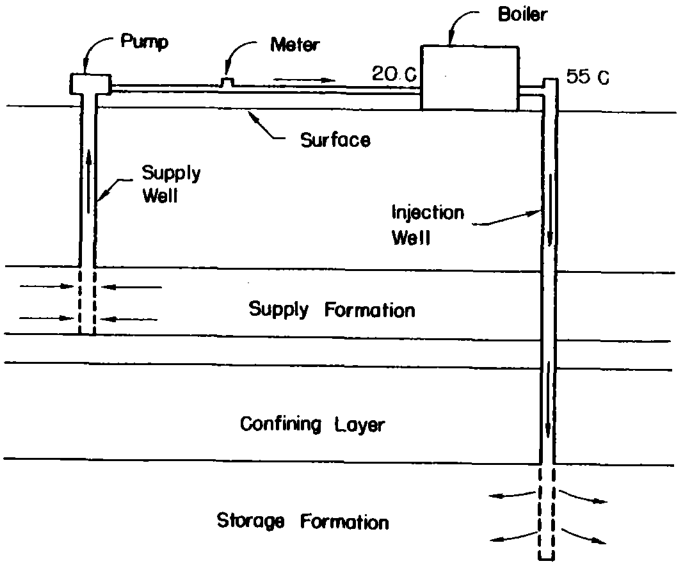


Figure 3. Schematic of Injection System

The injection rate varied from about 12.6 l/s (200 gpm) to 6.3 l/s (100 gpm) depending on the degree of clogging. Clogging was reduced by periodically backwashing the injection well. The backwashing procedure involved stopping injection and pumping two or three hundred gallons from the injection well with a submersible pump. This loosened the silt particles around the well screen and increased the specific capacity of the injection well.

The injection period continued until June 5, 1978. A total volume of 54,800 M^3 (14.5 gallons) was pumped into the storage aquifer. Figure 4 shows the cumulative volume injected versus time. The jagged portions of the line correspond to either power outages or to backwashing operations. The cumulative energy injected was nearly proportional to the cumulative volume injected since the injection temperature was relatively constant at 55^oC (131^oF).

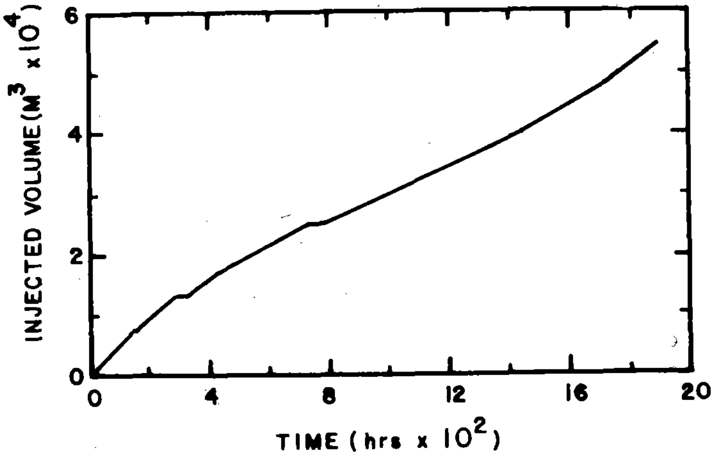
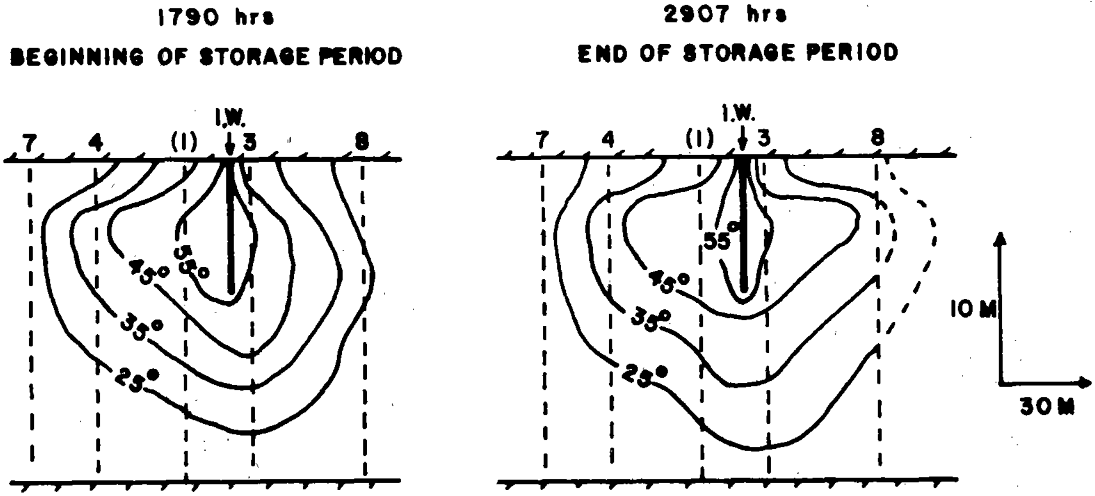


Figure 4. Injection Volume versus Time

The storage period extended from June 5 to July 26, 1978. Figure 5 shows two-dimensional isotherms interpolated from the readings in Wells 1, 3, 4, 7, and 8 at the beginning and end of the storage period. The estimated pore velocity of 0.052 M/day (0.17 ft/day) is from left to right in the figure.


1790 hrs
BEGINNING OF STORAGE PERIOD

2907 hrs
END OF STORAGE PERIOD

Figure 5. Isotherms at Beginning and End of Storage Period

The recovery period began on July 27 and ended on September 5, 1978. 1978. Water was withdrawn from the storage aquifer at a rate of 15.8 l/s (250 gpm). The cumulative outflow as plotted versus time in Figure 6 indicates that the outflow rate was quite constant. The temperature of the recovery water decreased with time from 55°C (131°F) as shown in Figure 7. Withdrawal was stopped when the recovery

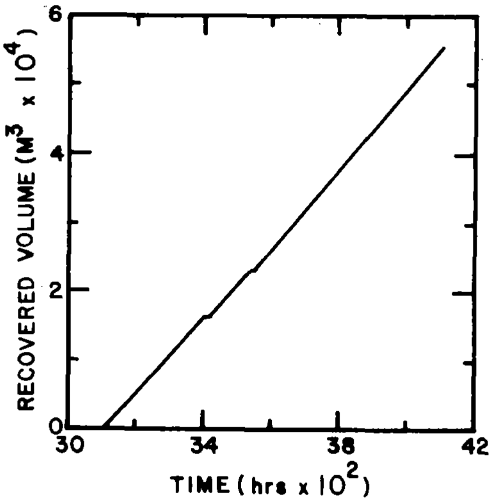


Figure 6. Recovery Volume versus Time

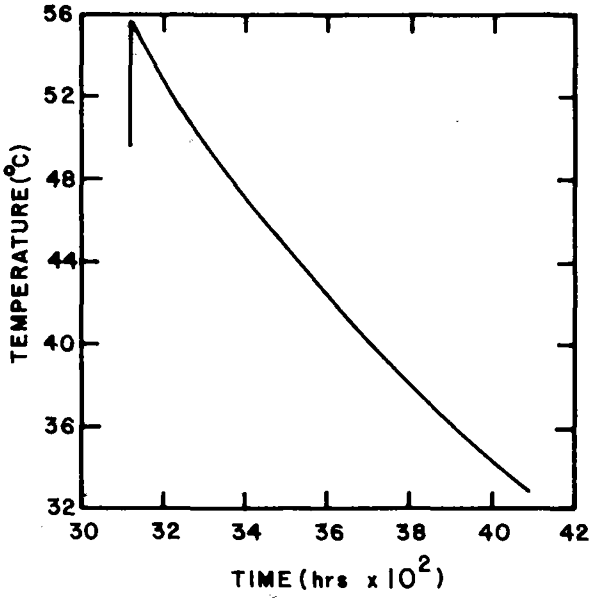


Figure 7. Recovery Temperature versus Time

temperature equalled 33°C (91.4°F). At the end of the recovery period about 65 percent of the injected energy had been recovered. This is shown in Figure 8 where the energy recovery factor, E_{out}/E_{in}, is

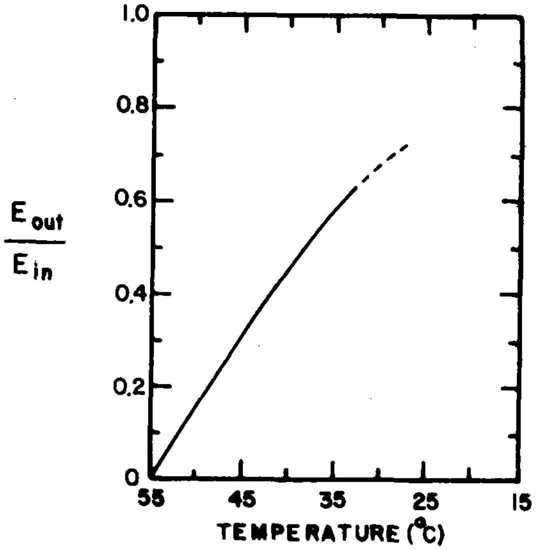


Figure 8. Energy Recovery Factor as a Function of Temperature

plotted versus temperature. It is apparent from Figure 8 that the energy recovery factor would have well exceeded 0.65 had the withdrawal continued to a temperature level below 33°C (94.1°F).

ACKNOWLEDGMENT

The writers would like to thank Professor James C. Warman, Director of the Water Resources Research Institute of Auburn University for his many contributions to the work reported herein. This project is sponsored by the U. S. Department of Energy.

U. S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Storage of Cold Water in Groundwater Aquifers for Cooling Purposes - Phase II

Principal Investigator: Donald L. Reddell, Richard R. Davison

Organization: Texas A&M Research Foundation
FE Box H
College Station, Texas 77843
Telephone: (713) 845-3931

Project Objectives: Design, develop and demonstrate a working prototype system in which water is pumped from an aquifer at 70°F in the winter time, chilled to a temperature of less than 50°F, injected into a groundwater aquifer, stored for a period of several months, pumped back to the surface in the summer time, and used to air condition buildings.

Project Status: This project is divided into two phases as follows:

Phase I - This phase consisted of construction of the facilities for the study. A pumping well and injection well were drilled and equipped. A cooling pond for chilling the water was constructed. Pipelines were installed to connect the wells and cooling pond. Observation wells were drilled to observe water pressure and temperatures at various distances from the wells.

Phase II - This phase was initiated in October of 1978 and consists of operating the project. As of December 1, 1978, two million gallons of water had been injected. This water is being pumped back out at the present time to test all instrumentation. We will begin injecting cold water shortly and continue until the end of March. From June through August the cold water will be recovered, and then the cycle repeated during 1979-80 and 1980-81.

Contract Number: 7836

Contract Period: October 1, 1978 - September 30, 1981

Funding Level: $300,000

Funding Source: Department of Energy

DESCRIPTION OF WORK

A 5,000 ft^2 cooling pond has been constructed capable of chilling an average of 100 gpm from 70°F to 40°F for a 5-month period. The pond is lined with a butyl rubber liner to prevent seepage. Water will be pumped from a well into the pond where a 600 gpm pump will circulate water through a series of spray nozzles during periods when the wet-bulb temperature is less than 50°F. Once the water in the pond reaches a temperature of less than 50°F, 100 gpm will be taken from the pond and injected into a second well. The water will be chlorinated and passed through a sand filter prior to injection.

Two wells have been drilled at the research site. The wells were completed in the shallowest groundwater aquifer in the area, the floodplain alluvium which exists extensively along the Brazos River. Dense clay from 22 to 38 feet apparently forms a slowly permeable caprock for the sand and gravel aquifer. Thus, the aquifer must be analyzed as a leaky-roof, confined aquifer. The water level in the sand and gravel is about 25 feet deep.

Both of the wells were constructed in an identical manner. The well was drilled using a reverse circulation rotary drilling rig. Surface casing was set and grouted to a depth of 18 ft. A fiberglass casing and well screen was used for 2 reasons: (1) to prevent corrosion and to allow strong chemicals to be used to remove any incrustations or plugging material and (2) to allow hot water of several hundred degrees Fahrenheit to be injected without loss of strength. Stainless steel could have been used, but it would have been more expensive.

A short-term pumping test (24 hr) was conducted on both of the wells. The injection well was capable of yielding 185 gpm with a 14-foot drawdown and the pumping well yielded 425 gpm with an 8-foot drawdown. Preliminary values of hydraulic conductivity are 600 ft/day at the injection well and 750 ft/day at the pumping well. The storage coefficient was 7.9×10^{-4} and 1.05×10^{-2} at the injection and pumping well, respectively. The values of hydraulic conductivity are large, but typical of the values expected for this aquifer. The values of the storage coefficient indicate that the aquifer in the vicinity of the injection well is a confined aquifer; while the aquifer in the vicinity of the pumping well is responding more like an unconfined aquifer. A more detailed pumping test analysis using 'leaky aquifer' techniques will be required to finalize values for hydraulic conductivity and storage coefficient. Observation wells have been drilled near both the pumped and injection wells.

TECHNICAL ACCOMPLISHMENTS AND PROBLEMS ENCOUNTERED

The Phase I part of this project was for construction of the project and aquifer evaluation only. No data have been collected to date, except for the pumping test to evaluate aquifer parameters. These results were described in the previous section. No problems were encountered except those of weather and well drillers and manufacturers not supplying their goods and services on time.

An injection period was initiated on November 15, 1978 in which water was pumped directly to the injection well and injected without aeration. Through November 27, 1978, two million gallons of water were injected with no apparent difficulty. This test was done to develop background data on the injection process prior to aerating the water. The groundwater has a natural iron content of about 7 to 9 ppm. When aerated, this iron tends to precipitate out and could cause a plugging problem in the aquifer.

Although there was no aeration of the water recently injected, there was apparently sufficient oxygen in the aquifer, well and pipeline to cause an iron precipitate to be formed at the injection well. We are presently pumping the two million gallons out of the aquifer and analyzing the water quality. We believe it will be to our advantage to aerate the water prior to injection and let the iron precipitate be removed in the cooling pond. This will eliminate it as a potential plugging problem.

DESCRIPTION OF PLANNED WORK

The construction of the project is essentially complete. By the latter part of November or first of December, we should have enough cold weather to make a substantial amount of cold water. At that time, we will begin injecting chilled water. This will continue until the latter part of March or first of April. We will then leave the water stored for a few weeks and then begin to pump the cold water out of the ground. An evaluation of the thermal losses will be made.

PROJECT SUMMARY

Project Title: JFK Airport Aquifer Storage Project: Test Well Drilling Program

Principal Investigator: M. E. Singer

Organization: New York State Energy Research and Development Authority
Albany, New York 12223
Telephone: 518-465-6251

Project Goals: The project goal is to determine the thicknesses, lateral extent, depths, and stratigraphy of the aquifers underlying the JFK Airport, Long Island, New York. This project was initiated as a result of a proposal and preliminary study by Desert Reclamation Industries of the feasibility of storing cold water in aquifers under the airport for seasonal use in the chilled-water air-conditioning system in the airline terminal buildings.

Project Status: The borehole drilling project is completed. The Jameco-Magothy aquifer ranges in thickness from 87 to 177 ft under the JFK airport. The aquifer is overlain by the Gardiners' Clay and underlain by the Magothy Clay Unit, both of which act as impermeable seals for the aquifer. Initial tests on samples of the Gardiners' Clay indicate that subsidence and upheaval due to removal and storage of water in the aquifer will not be a problem at the airport.

Contract Number: UCC Purchase Order No. 11Y13571V

Contract Period: September 1, 1978, to June 1, 1979

Funding Level: $65,000

Funding Source: Oak Ridge National Laboratory

Storing winter cold for air conditioning is now being studied for technical and economic feasibility under a joint U.S. DOE and NYSERDA grant at JFK Airport. The cold will be stored in an extensive confined aquifer. The concept, suggested by Henry Hibshman of Desert Reclamation Industries, entails the withdrawal of aquifer water in the winter during off peak hours, cooling it by employing winter cold air and storing it in the aquifer at 36°F to 38°F. During the air conditioning season the cool water will be withdrawn to supply the chilled water for air conditioning at 45°F. Water will then be recharged into the ground at another location or discharged into Jamaica Bay at a warmer temperature.

A demonstration system will be designed for the broadest application both within New York State and nationwide. The JFK site offers the opportunity to study a large installation in an urban setting. The project will address peak air conditioning capacity load of 14,000 tons. As with typical commercial sites the air conditioning load is large in relation to its heating load. This is due to the concentration of people, machinery, lighting and working hours concentrated between 7 a.m. and 7 p.m. Design of the ACES aquifer system will minimize peak load requirements and maximize off peak utilization. The system will employ hybrid operating modes to optimize the utilization of the stored cool water from the aquifer and minimize on peak pumping requirements. This might include the production of ice during off peak hours to meet peak midday energy requirements.

The program is a four phase investigation and demonstration of the technical and economic feasibility of storing winter cold for air conditioning. Phase I, a preliminary engineering and economic evaluation of the overall phan, was completed by September 1978 thru the combined effort of Desert Reclamation Industries and Dames and Moore. The Phase I investigation considered alternative methods of cooling the aquifer water (air vs Jamaica Bay water), the use of the cooling towers and dry bulb heat exchangers, developed preliminary cost estimates and addressed the technical feasibility of below and above ground systems. However, it did not investigate in detail alternative heat exchangers, institution and environmental barriers, or the cost of interconnection with the JFK power plant. Also, geohydrological data were not available on the extent and water quality of the aquifer, nor on permeability and transmissivity of the aquifer needed to refine the cost analysis of the number of wells required and to analyze the potential of subsidence. Phase Ia, Ib and II are designed to answer these questions. The feasibility study, however, suggested a potential installed system payback of 3.5 to 8 years.

Phase Ia and b are now in progress. New York State ERDA is managing Phase Ia, an exploratory drilling program at JFK Airport. Phase Ib being performed by Oak Ridge National Laboratory, is a review of the engineering, economic and technical studies from Phase I and Ia. It also includes an environmental impact analysis, and an analysis of the above ground system. NYSERDA, in cooperation with ORNL, has assembled a team consisting of Desert Reclamation Industries, the Port Authority of New York, United States Geological Survey, Dames and Moore and the Warren George Drilling Company to conduct the well drilling study. Drilling of four, 4" diameter test borings (see figure 1 for locations) and observation wells started on September 27, 1978 and was completed on November 2, 1978.

The purpose of the exploratory drilling was to refine the economics of the well system, determine the water quality of the aquifer, and to determine if there is potential subsidence of the soil over time. The four wells range in depth 429 to 500 feet as shown in Table 1. Of particular interest was the thickness and compressibility of the confining stratum, the Gardiner's Clay unit; and the thickness, permeability and transmissivity of the Jameco and Magothy aquifers. The four drilling sites were chosen to identify the extent of the aquifers (see figure 1 for locations).

Samples were taken at intervals ranging from 10 to 30 feet (more detailed samples were taken in the Gardiners Clay). Samples were logged and inspected for lithology, and drilling rates recorded on site by Desert Reclamation Industries (DRI), Dames and Moore and the United States Geological Survey (USGS). The USGS also, geophysically logged the holes for resistivity, spontaneous potential, gamma and caliper. Samples were laboratory tested by Dames and Moore for moisture density, hydrometer measurements, consolidation, permeability and sieve analysis. Port Authority personnel provided guidance during the drilling program.

The Warren George Drilling Company performed the drilling. They used a standard rotating drill bit, lined the hole with UOP Johnson revert clay, and took split spoon sample using an Osterberg Piston Sampler. Logs were also kept by the driller on the general characteristics, thicknesses and types of materials, and the drilling characteristics of the material encountered. A 4" diameter PVC casing was installed which included a 20 foot screen in the Jameco formation. The casings were gravel and sand packed and cemented. The wells were then developed so that water samples could be taken.

The thickness of the Gardiners Clay formation as revealed in the drilling program ranged from 93 feet in the farthest east boring (well #3), and from 86 feet in the south (well #2), to 53 feet in the west (well #1), to 44 feet in the north (well #4). The slope of the formation was from north, northwest to east, southeast direction.

The Jameco Magothy aquifer on the other hand, slopes from northeast to southwest. The thickness ranged from 177 feet in the farthest west boring to 87 feet in the east, and from 159 feet in the south to 148 feet in the north. Of particular interest was the highly permeable Jameco (estimated permeability from 215 to 2,000 gpd/feet^2) with thicknesses of 30 to 40 feet in well #1, 50 to 60 feet in the most southernly point, 70 to 80 feet in well #3, and 90 to 100 feet in the well #4. Highest permeability was in the boring #3.

These permeability data indicate an ideal confined aquifer, having a thick consolidated confining aquitard. It appears that subsidence should not be a major problem. However, the analyses are not completed and additional study will be required to confirm this in the site specific location.

Following completion of Phase Ia, the future studies will refine the economics, technical feasibility, institution relations and potential environmental effects of the cold water aquifer ACES program at JFK. These phases will be as follows:

Phase II - Implementation of pilot well system to examine technical feasibility, the environmental effects and institutional aspects of adding heat or cold to JFK aquifer. Demonstration pumping of the well system to determine optimum removal and recharge flow rates.

Phase III - Implementation of project to provide 25% of JFK air conditioning requirements.

Phase IV - Implementation of project to provide 100% of JFK air conditioning requirements.

In order to move the project ahead from Phase Ib to Phase II, ORNL, NYSERDA and the Port Authority must define in detail the above and below ground economics, resolve all legal and institution responsibilities, conduct an environmental assessment study, and determine how the rest of the project will be financed and managed.

The Port Authority is particularly concerned about the potential for soil subsidence due to withdrawal of water. This issue is being addressed in Phase Ia. Also of concern is the legal responsibility if damage results from this project. Finally, the Port Authority, as with many commercial facilities in New York City, gives its tenant long term energy cost plus contract leases usually 25 years and greater. Energy and maintenance costs are included in this lease and the Port Authority is reluctant to reopen negotiations with their tenant in order to finance future phases. Therefore, questions on how to finance a full scale project remain unresolved.

At this point in time, the storing of cold water in an aquifer under JFK Airport appears attractive from an economic and technical point of view. Hopefully, current studies will resolve and technical, economic, and environmental issues that must be settled in order proceed with Phase II.

ACKNOWLEDGEMENTS

The author is indebted to Henry and John Hibshman of Desert Reclamation Industries, Louis Stern and Andrew Mills of Dames and Moore, Dave Eisenberg and George Brunton of Oak Ridge National Laboratory, Dr. James Cole of New York State ERDA, and Irwin Kanowitz and Julian Soren for their technical assistance during this program. I would like to especially thank the members of the Port Authority staff including: John English, Richard Klenk and Norman Lesser for their cooperation during the drilling program.

TABLE 1

DETAILS OF HYDROGEOLOGIC UNITS AT JFK AIRPORT
- BASED ON EXPLORATORY BORINGS -

	Thickness (ft.)				Approx. Elevation of Top of Unit (ft. above m.s.l.)			
Hydrogeologic Unit	Boring 1	Boring 2	Boring 3	Boring 4	Boring 1	Boring 2	Boring 3	Boring 4
Fill and Meadow Mat	24	20	19	15	+29	+10	+10	+10
Upper Glacial Sand	108	90	105	97	+5	-10	-9	-5
Gardiners Clay	93	86	53	44	-103	-100	-114	-102
Jameco-Magothy Aquifer	87	159	177	148	-196	-186	-167	-146
Magothy Clay Unit	48	49	85	70	-283	-345	-344	-294
Lower Magothy Sand	36	36	21	17	-331	-394	-429	-364
Raritan Clay Member	--	--	--	--	-367	-430	-450	-381
TOTAL BORING DEPTH	449	471	500	429				

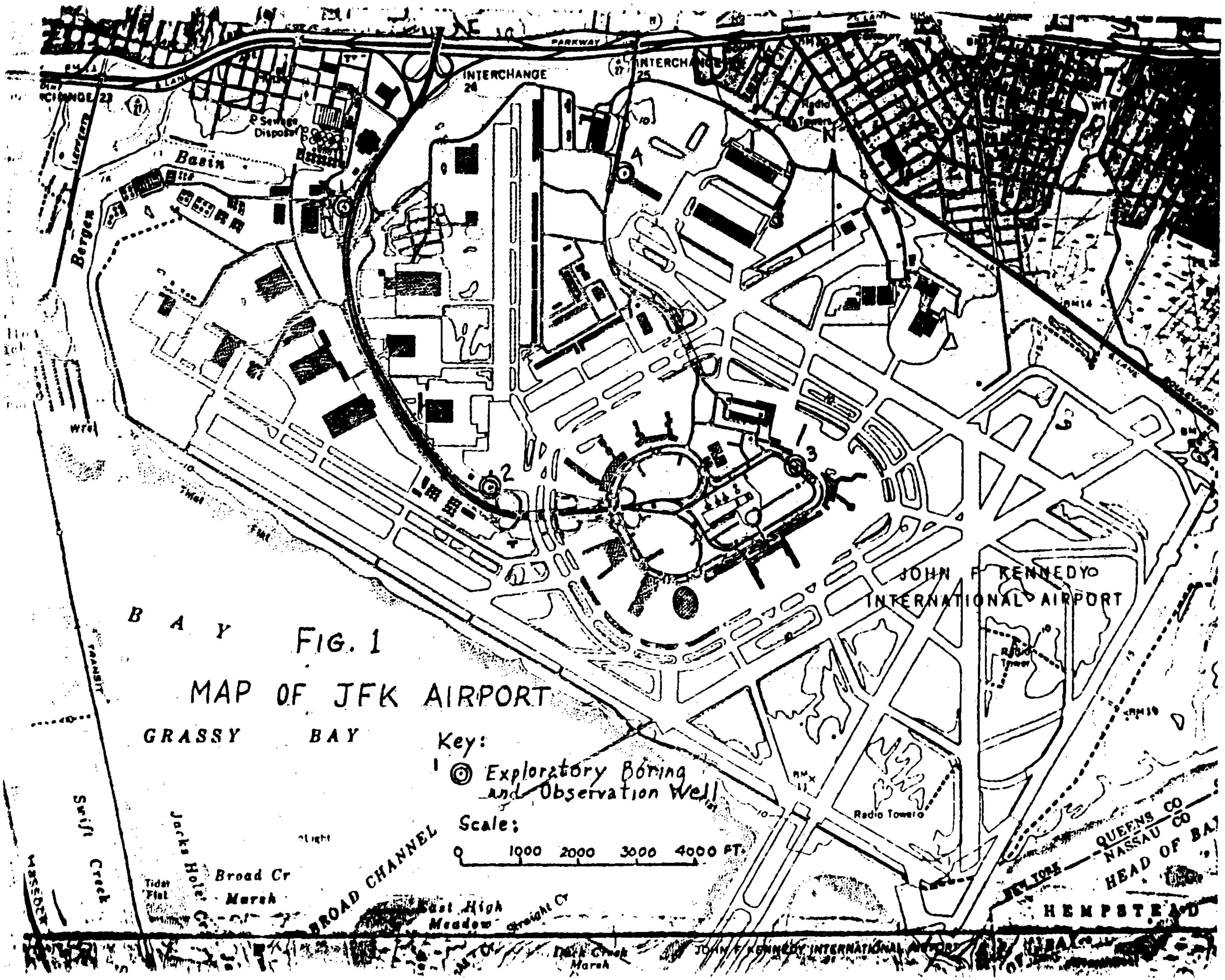


FIG. 1

MAP OF JFK AIRPORT

U. S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Title: Evaluation of Thermal Energy Storage for the Proposed Twin Cities District Heating System

Principal Investigator: Charles F. Meyer

Organization: General Electric Company—TEMPO
Center for Advanced Studies
P.O. Drawer QQ
Santa Barbara, California 93102
Telephone: (805) 965-0551

Project Objectives: To evaluate the technical and economic feasibility of incorporating thermal energy storage components (primarily based on the annual cycle) into the proposed Twin Cities District Heating Project.

Project Status: The principal effort to date has been gathering information from a number of studies which have been or are still being conducted on various aspects of a proposed cogeneration/district heating project for Minneapolis-St. Paul. The study of principal interest, whose results have not yet been completely reported, is being conducted by the Swedish firm Studsvik Energiteknik AB (formerly AB Atomenergi). They have developed a DH system configuration which includes production of hot water by power plants and peaking boilers; transmission pipeline networks; and distribution systems for the urban and residential areas of the Twin Cities. Studsvik will be a major subcontractor to TEMPO on this TES study.

Contract Number: UCC 7604

Contract Period: 14 August 1978 - 30 June 1979

Funding Level: $131,244.00

Funding Source: Department of Energy, Division of Energy Storage Systems, via Oak Ridge National Laboratory

PURPOSE

Earlier studies have shown that annual-cycle Thermal Energy Storage can significantly improve national opportunities for conserving substantial amounts of energy, with concomitant reduction in environmental pollution, through large-scale cogeneration of electricity and heat. This project will utilize the results of an ongoing study of large-scale cogeneration and district heating for the Twin Cities (Minneapolis-St. Paul, Minnesota). Comparing the capital requirements and fuel consumption of a specific cogeneration/district heating system which does not include TES to those of a system with TES, serving identical heat loads, will provide a measure of the value of annual-cycle TES.

BACKGROUND INFORMATION

A major series of studies is underway to evaluate the feasibility of installing a new, large district heating (DH) system in the Minneapolis-St. Paul metropolitan area. It would be based upon cogeneration of power and heat by Northern States Power. Among the leading sponsors and participants in the studies are the Minnesota Energy Agency, Northern States Power Company, and DOE/ORNL. Also participating are several other governmental agencies, utilities, universities, and a number of contractors and consultants.

The proposed new DH system would not send out steam, as is the universal practice in large DH systems in the United States, but hot water, as is the common practice in Europe. A Swedish firm, AB Atomenergi/Studsvik Energiteknik, under a DOE/ORNL contract, is preparing the general description of the system, based upon their experience with European systems (Karnitz and Rubin, 1978).

Supplying space heating, tap water, air conditioning (absorption cycle), and low-temperature industrial process heat needs from a central source is a more efficient way to use fuel than to burn it in many small furnaces and boilers. A particularly efficient central source is a plant cogenerating power and heat.

Neither American nor European DH systems now employ thermal energy storage to any substantial extent. This situation may be attributed to three principal factors:

- Fuel has been cheap and plentiful
- District heat has been produced largely by dedicated boilers, not by cogeneration
- Annual-cycle TES components have only been suggested, not demonstrated.

The first of these factors changed dramatically in 1973. The second is changing, principally because electric power plants using thermal cycles can, with well-understood design modifications, produce power and useful heat instead of wasting two units of heat for each unit of power generated. (Some fuel energy must be reallocated from generating electricity to increasing the temperature of cooling water to a level which is useful for district heating.) The third factor is being changed by DOE/ORNL projects such as the ones reported at these meetings, and by comparable work overseas (Warman and Molz, 1977; Werner and Kley, 1977).

Configurations so far proposed for the Twin Cities district heating system have not included TES except that which is incidental to use of large hot-water pipelines; hot water has a high energy density, compared to steam, and the DH system has significant thermal inertia.

TEMPO studies beginning in 1972 have shown that TES could greatly improve the opportunities for conserving substantial amounts of energy (with concomitant reduction in environmental pollution) through large-scale cogeneration (Meyer, Hausz, et al, 1976). If large-scale annual-cycle TES were available, it could solve the mismatch problem which limits the amount of cogenerated heat for which a market can be found. The mismatch problem arises because electricity must be generated in instantaneous response to demand (no feasible way to store electricity is available); and demands for heat seldom correspond to electric generation in time, location, or magnitude. The largest potential market for cogenerated heat is space heating — an annual-cycle load.

PROJECT DESCRIPTION

The nature of the annual heat load for Minneapolis-St. Paul is shown in Figure 1, based on a Studsvik draft report of November 1978. The high peak load (some 2600 MW thermal) occurs during the space-heating season. Note that slightly less than 60 percent of the peak heat load would be met by cogeneration. Boilers capable of handling more than 40 percent of peak load would be installed; during much of the year, they would stand idle. Additional boilers, indicated by the area at the lower right-hand toe of the load curve, would be used when peak demand for electricity requires that steam otherwise used to produce district heat be used to turn turbines and generate electricity.

In Figure 1, an area to the right of the load curve has been sketched to illustrate the benefits of annual-cycle TES. It is enclosed by a dashed line and captioned "stored heat." (Note that the load curve shows power level; areas under the load curve represent energy.) The stored-heat area is equal to the sum of the areas above the 50-percent-of-peak ordinate value, plus the small area under the right-hand toe of the curve, plus a 25-percent margin to allow for loss of heat while in storage. Thus, the amount of stored thermal energy represented by the sketched-in area is enough to meet peak heat loads with no boilers and with 20 percent less cogeneration capacity. It follows that use of annual-cycle TES could reduce capital investment by an amount equal to the total cost of boilers plus about 20 percent of the cogeneration capacity. These capital savings are one measure of the value of TES — of how much one could afford to pay for TES.

The sketch of Figure 1 represents a case in which cogeneration plants would operate more of the time and produce more heat during the course of a

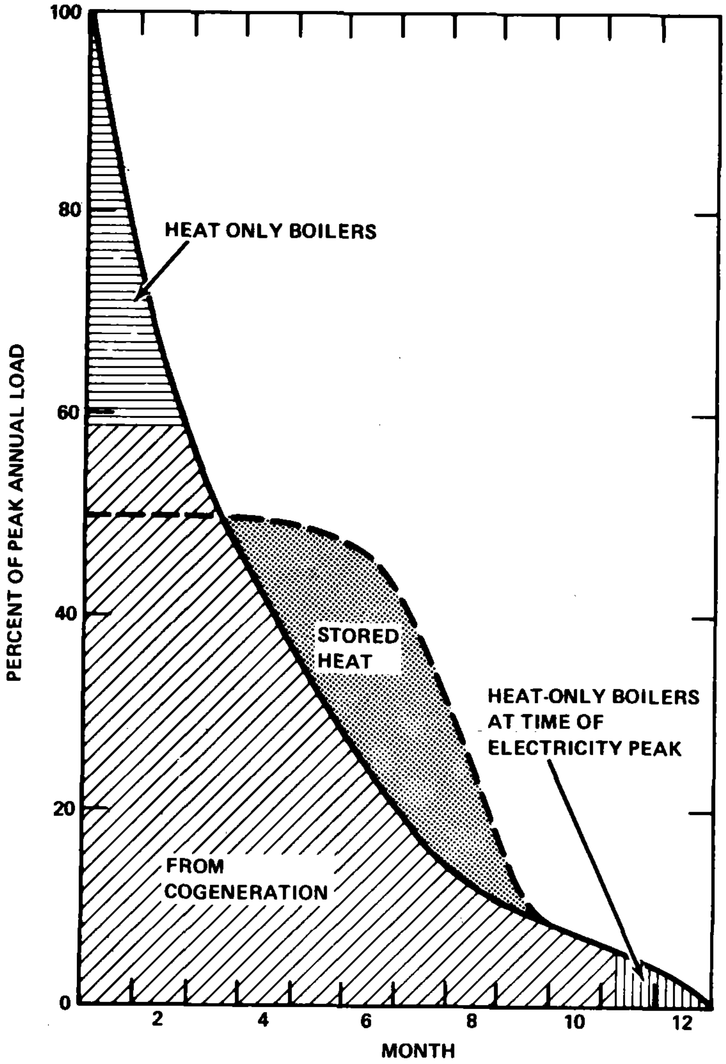
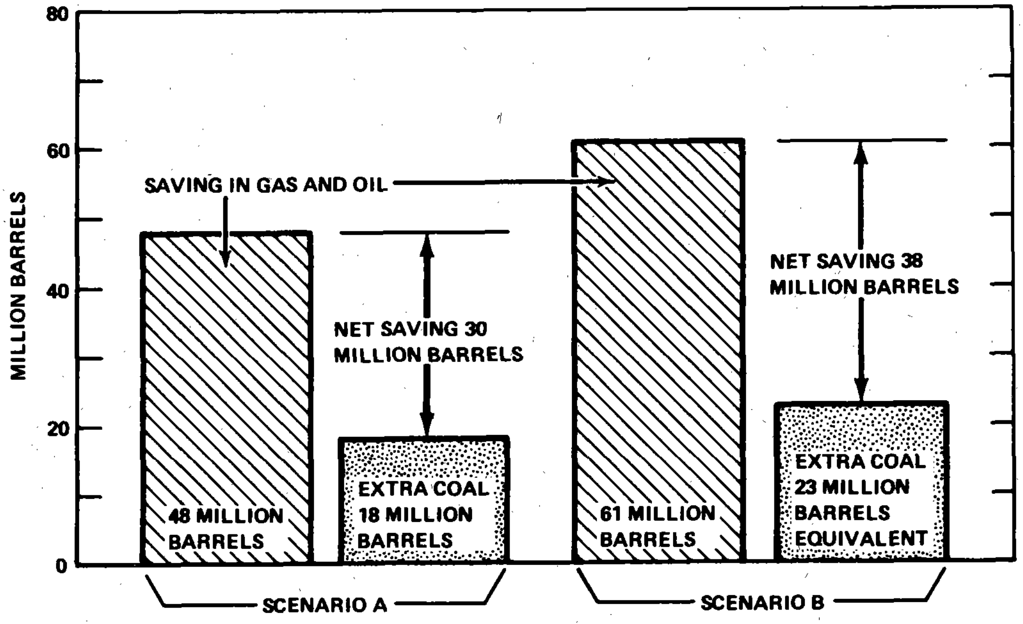


Figure 1. Annual heat load duration curve for Minneapolis-St. Paul (adapted from Studsvik report).

year than is currently proposed. The optimal shape of the dashed curve would be determined by the efficiency and reliability of the cogeneration plants. Ideally, all the heat needed for district heating would be produced by highly efficient plants generating base-load electricity, and operating at full load for 10 or 11 months of the year. The stored-heat area shown in Figure 1 would then move downward and to the right, becoming more flattened; the total cogeneration capacity could be reduced by another 20 to 40 percent. Fixed charges for capital equipment would be amortized over more of the year, further reducing the cost of both electricity and heat.

Fuel consumption is reduced, and coal (or nuclear fuel) is substituted for oil and gas, when heat is produced from cogeneration rather than from heat-only boilers. The estimated fuel savings due to district heating, supplied by a combination of cogeneration and heat-only boilers, are shown in Figure 2 for two scenarios for DH systems that do not include TES. These savings will increase when TES is included, because the amount of heat produced by cogeneration will increase and fuel consumption in heat-only boilers will decrease.



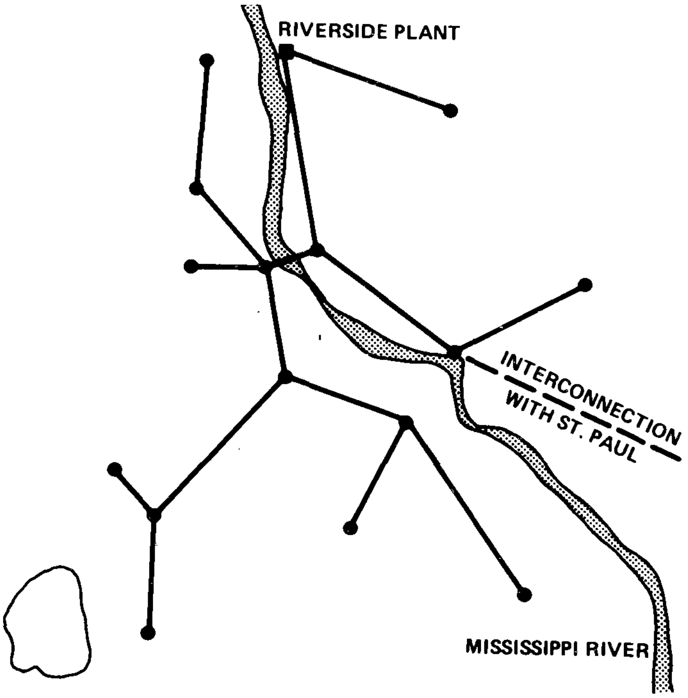
(Source: Studsvik)

Figure 2. Twin Cities fuel savings due to district heating, 1980-2000.

Beneficial effects to be expected from annual-cycle TES in reducing capital investment, fixed charges, and fuel consumption in central plants have been discussed. Another area where significant cost savings may be realized is the transmission network, illustrated in Figure 3.

Heat Storage Wells (i.e., aquifer TES) would be located at the Riverside Plant shown in Figure 3. (For purposes of this study, availability of aquifers is assumed.) For cogeneration on a large scale, TES at the central plant should be large enough to accept all hot-water production that exceeds immediate demands, and to supply hot water demands that exceed production. (Dependable storage will make possible the elimination of cooling towers or water for condensers, and thus both the capture of all useful heat produced as a byproduct of electric generation and the saving of the substantial cost of condenser cooling systems.)

TES will also be located along the major pipelines, at nodes and terminals, to help smooth load fluctuations and permit the pipelines to be operated at high capacity factors. The TES will also increase system reliabil-



(Source: Studsvik)

Figure 3. Cogeneration plant and hot-water transmission pipelines for Minneapolis district heating system.

ity, serving as a backup in case of central-station or pipeline outage (Hausz, 1977).

Figure 4 illustrates schematically the Heat Storage Well concept of annual-cycle TES at low cost and low heat loss. Two water wells are drilled deep enough – say, 500 to 1000 feet – to provide sufficient hydrostatic head to maintain superheated water in liquid form, and to avoid aquifers used for water supply. The two wells of the doublet comprise a closed hydraulic system; water pumped from one well is injected into the companion well, several hundred feet away. The heat-storage medium is the porous rock comprising the aquifer and the water filling the pores, together with the relatively impervious aquifer cap and bottom. The energy storage capacity is very large – the aquifer may be 100 feet thick, and the hot water may extend 300 or more feet radially from the well – and costs essentially nothing. The TES capacity – the rate at which heat can be stored or withdrawn from storage – is determined by the size of the wells, the pumps employed, and the flow parameters of the aquifer. A reasonable estimate is that a Heat Storage Well doublet may have a 20-megawatt thermal capacity. Multiple wells are employed to obtain larger capacities. Thus, in contrast to most TES components, only the power capacity determines the cost of storage.

Somewhat as with root cellars and ice caves, natural rocks and sand insulate the hot water stored in an aquifer. Three-fourths or more of the

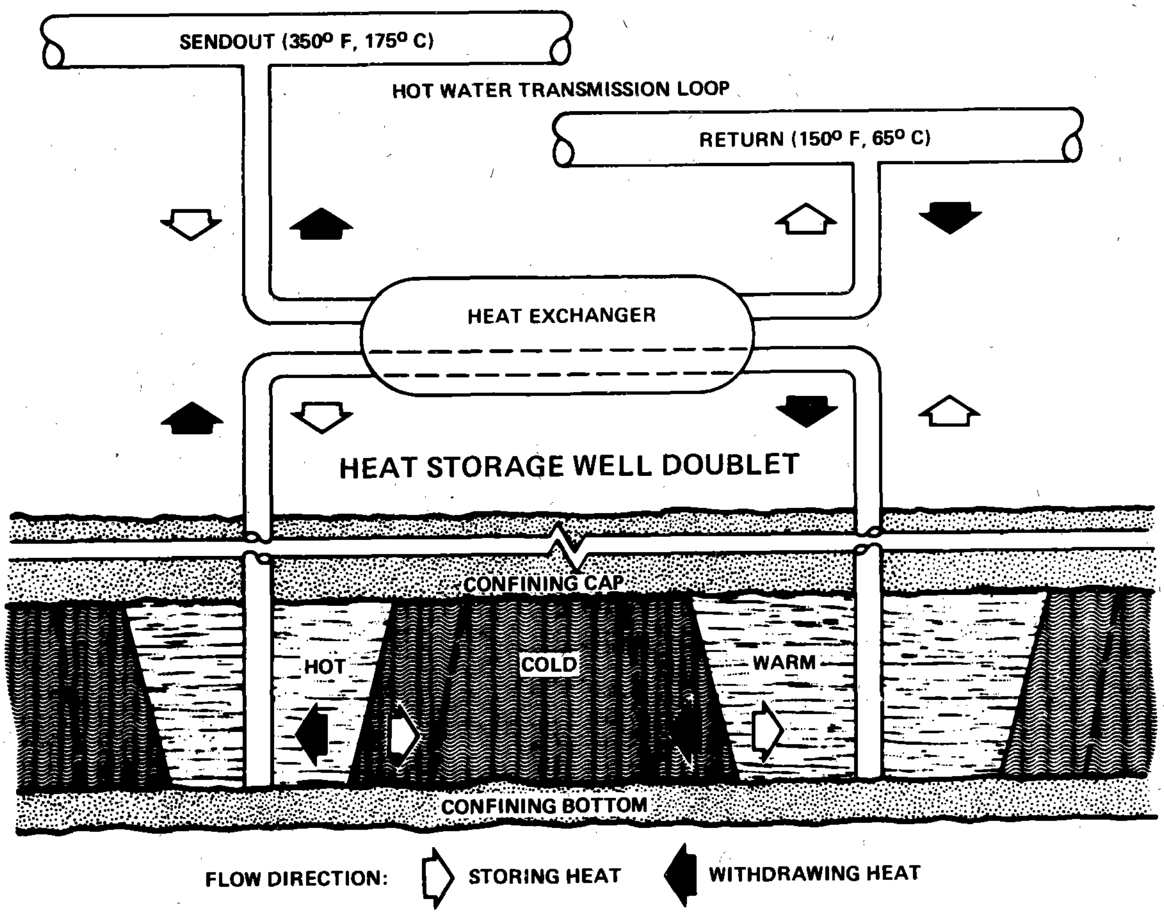


Figure 4. Schematic diagram of Heat Storage Well doublet operation.

stored heat would appear to be recoverable after six months or longer (Meyer, Hausz, et al, 1976; Tsang, 1977). This remains to be demonstrated on the necessary scale, with water injected at temperatures above 100°C.

RESULTS

No quantitative results have been obtained. Due to various delays, data on the proposed systems (Scenarios A and B) have not yet become available.

Studsvik, as a subcontractor on this project, has commenced work on characterizing the expected fluctuations of the Twin Cities heat loads. Data on hour-by-hour fluctuation of the heat loads to be served in the Twin Cities being unavailable, Studsvik is applying statistical data from Stockholm to characterize the Twin Cities heat load fluctuations (the climates are similar).

FUTURE ACTIVITIES

When adequate data to describe the heat sources, transmission network, and heat loads of the reference systems are available, the effects of incorporating TES components into the system will be analyzed. Based on very rough, preliminary analysis, the expectation is that use of TES will reduce or eliminate the auxiliary peaking and backup boiler capacity needed without TES; reduce the size of pipelines; conserve perhaps 10 to 20 percent of the fuel energy required without TES, with accompanying savings in fuel cost and environmental impact; decrease system investment cost by 5 to as much as 15 percent; substitute coal burned in central plants for oil that would be burned in auxiliary boilers; and make more flexible the siting of future cogeneration plants by eliminating the need for cooling towers or water for condenser cooling.

An interesting question will be the application of Heat Storage Wells to handle short-term (hourly to daily) fluctuations in heat loads. It has been pointed out that the cost of aquifer TES is determined almost entirely by the required capacity — the maximum rate of injection or withdrawal of hot water. To handle short-term fluctuations superimposed on annual-cycle requirements may require substantially more capacity than the annual cycle alone. Conventional TES components such as steel tanks (accumulators) used in a few European DH systems may prove superior to aquifer storage.

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DAILY/SHORT TERM STORAGE PROGRAM — OVERVIEW*

R. J. Kedl, LTTES Program
Oak Ridge National Laboratory

INTRODUCTION

Development of short-term thermal energy storage systems has been a major thrust of the LTTES Program since its inception. A wide variety of concepts are, and have been, under development. They are directed toward the storage of solar energy (active and passive) and off-peak electricity, and involve the storage of either heat or cool. Although these efforts are principally thrusted toward building heating and cooling, they could also find application in the industrial and agricultural sectors. The emphasis has been on the use of phase-change materials (PCM's) as the storage media, although some efforts involving sensible heat storage have been supported. In addition, generic efforts in support of concept development are underway.

PROGRAM DESCRIPTION AND STATUS

Projects in short-term storage can be classified into the following technology areas:

- Storage in Building Materials
- Modular Storage Units
    - Macroencapsulated PCM's
    - Bulk Containment of PCM's
- Supporting R&T

Building Materials. This implies the addition of PCM's to "conventional" building materials (concrete blocks, wall panels, ceiling tiles); thus, the building may serve as its own storage component. In this concept the room surface involved would be maintained at a temperature slightly above ambient temperature. Thermal transport to the living space would be accomplished through natural thermal convection and radiation. The radiation

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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.

component offers the prospect that occupants may experience a physiological perception of comfort at less-than-normal ambient temperatures. Development of these materials is directed primarily toward active and passive solar applications and to the use of off-peak electrical energy. Current efforts (see Table I) have been confined to the development of concrete blocks containing PCM's.

Macroencapsulated PCM's. This storage category implies the containment of PCM's in capsules (cans, sausages, bottles, etc.) which are in turn stacked in some manner in a large tank/vault that serves as the TES module. Heat transfer is accomplished by pumping the thermal transport fluid (liquid or gas) through the matrix of capsules. Development of these modules is directed toward the active solar application and to the use of off-peak electrical energy. A summary and status of the LTTES Program in this area is shown in Table II.

Bulk Containment of PCM. This storage category implies the containment of PCM in the storage module in bulk form. Advantages to this storage category are that the PCM contained in this geometry is in its most compact form and that economies may be realized because of the elimination of one layer of PCM containment when compared to macroencapsulation. The problem with this storage category is that some novel technique must be devised to add or remove heat. Response to this problem has been varied, with several rather clever techniques proposed. Development of these modules is directed toward the active solar application and to the use of off-peak electricity. A summary and status of the LTTES Program in this area is shown in Table III.

Supporting R&T. The efforts described in this category are generic and fundamental in nature and are in support of concept development. In general, these efforts are confined to the identification and evaluation of PCM's, nucleation and crystallization studies of PCM's, and analytical/physical modeling of thermal transport mechanisms. A summary and status of the LTTES Program in this area is shown in Table IV.

Table I. Storage in Building Materials

Institution	Project Description	Status
Brookhaven Nat'l. Lab.	PCM added to concrete building blocks Emphasis on polymer concrete	•Project Summary in Proceedings •Identified small polymer concrete containers filled with PCM's and sealed, then inserted into precast holes in conventional concrete blocks as a technically attractive concept •LTTES Program readjustments required dropping this effort •Final report will be written
Suntek Res. Associates	$CaCl_2 \cdot 6H_2O$ dispersed in concrete building blocks	•$CaCl_2$ chemically attacked cement •Project terminated •Final report received
TBD	RFP to develop advanced building materials capable of storing heat by virtue of PCM's included	•To be issued in 1979

Table II. Modular Storage — Macroencapsulated PCM's

Institution	Project Description	Status
Dow Chemical Company	Macroencapsulated PCM's for several temperature ranges	·Active project ·Project summary in proceedings
Univ. of Delaware — Inst. of Energy Conversion	Glauber's Salt Mixture in Chubs Cool Storage for Off-Peak Electricity	·Active project ·Project summary in proceedings
Univ. of Delaware — Mech. Engr. Dept.	Macroencapsulated PCM's for temperatures from 90°C to 180°C	·Active project ·Project summmary in proceedings ·Funded by Conservation and Solar Applications Technical management transferred to STOR (LTTES Program)

Table III. Modular Storage — Bulk Containment of PCM

Institution	Project Description	Status
Clemson Univ.	Immiscible Fluid — Direct Contact with PCM Concept	•Active project •Project summary in proceedings
Franklin Res. Inst.	TES by means of Heat of Crystallization in Saturated Aqueous Solutions	•Project completed •Final report published (TID-28330) •Several methods of thermal transport to/from TES module were investigated •The problems encountered involved solids transport and deposition
General Electric	Rotating Drum Concept	•Active project •Project summary in proceedings •Funded by conservation and solar applications •Technical management transferred to STOR (LTTES Program)
Monsanto Res. Corp.	Form-Stable Polyethylene (chemically cross-linked) as TES Media	•Project completed •Final reports published(ORO/ 5159-10 and ORNL/Sub-7398/4) •TES media developed was chemically and physically stable (250 lbs cycled 632 times) •Estimated selling price based on large volume production about 34¢/lb
Univ. of Dayton	Form-Stable Polyethylene (radiation cross-linked)	•Project under negotiation •This is an effort to reduce the cost of form-stable polyethylene by using radiation as the cross-linking mechanism

Table IV. Supporting R&T

Oak Ridge Nat'l. Lab.	Computer Modeling of Melt/Freeze TES Process	·Active project ·Project summary in proceedings
Oak Ridge Nat'l. Lab.	Experimental Thermal Transport Studies in Melting-Freezing System	·Active project ·Project summary in proceedings
Oak Ridge Nat'l. Lab.	Thermal Cycling Facility for Testing Prototype TES Units (liquid thermal transport fluid)	·Active project ·Conceptual design completed
Oak Ridge Nat'l. Lab.	Thermophysical Properties & Evaluation of PCM's	·LTTES Program readjustments required dropping this effort ·Project summary in proceedings
Oak Ridge Nat'l. Lab.	Crystal Structure of PCM's and Nucleators	·Project completed ·Results to be published in Acta Crystallographica
Pennsylvania St. U.	Computer Modeling of Solid Sensible Heat TES Units	·Project completed ·Final report published (NSF-RANN-AER-75-16216)
Univ. of Nevada - Desert Research Inst.	Nucleation and Crystal Growth Studies of Salt Hydrates	·Project completed ·Project summary in proceedings ·Final report to be published (NSF-RANN-AER-75-19601)
Villanova Univ.	Materials with Solid-State Transitions for TES	·Project completed ·Project summary in proceedings ·Final report to be published ·Identified several potential materials All had technical problems (e.g., high vapor pressure) and moderately high costs

U.S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Thermal Energy Storage Subsystem for Solar Heating and Cooling Applications (Rolling Cylinder Thermal Storage System)

Principal Investigator: C. S. Herrick

Program Manager: R. F. Thornton

Organization: General Electric Corporate Research & Development
P. O. Box 8
Schenectady, NY 12301
Telephone: (518) 385-8267

Project Objectives: Develop and construct an instrumented prototype rolling cylinder thermal (latent heat) storage system.

Project Status: Phase I of this project is subdivided as follows:

1. Analyze mathematically the interior and exterior heat transfer behavior of the rolling cylinder.
2. Conduct laboratory tests on small scale cylinders to measure the effects of system variables on performance.
3. Select construction materials based on an evaluation of corrosion problems.
4. Develop a computer model describing the behavior of a rolling cylinder thermal storage system.
5. Design, build and instrument a prototype rolling cylinder of about 200,000 Btu capacity using Glauber's salt ($Na_2SO_4 \cdot 10H_2O$).

Phase II, not included in the present funding, will be proposed as a follow-on contract. This phase will consist of comprehensive calorimetric testing of the prototype system.

This contract began on August 1, 1978. Work is proceeding well on several tasks, but none were sufficiently close to completion at this writing to warrant reporting the results.

Contract Number: EM-78-C-05-5759

Contract Period August 1978 to October 1980

Funding Level: $373,600

Funding Source: Department of Energy, Division of Solar Energy

THERMAL ENERGY STORAGE SUBSYSTEM FOR SOLAR HEATING AND COOLING APPLICATIONS
(Rolling Cylinder Thermal Storage System)

General Electric Corporate Research and Development
Schenectady, NY 12301
Contract No. EM-78-C-05-5759
Carlyle S. Herrick, Principal Investigator
Roy F. Thornton, Program Manager

August 1978 to October 1980

OBJECTIVE

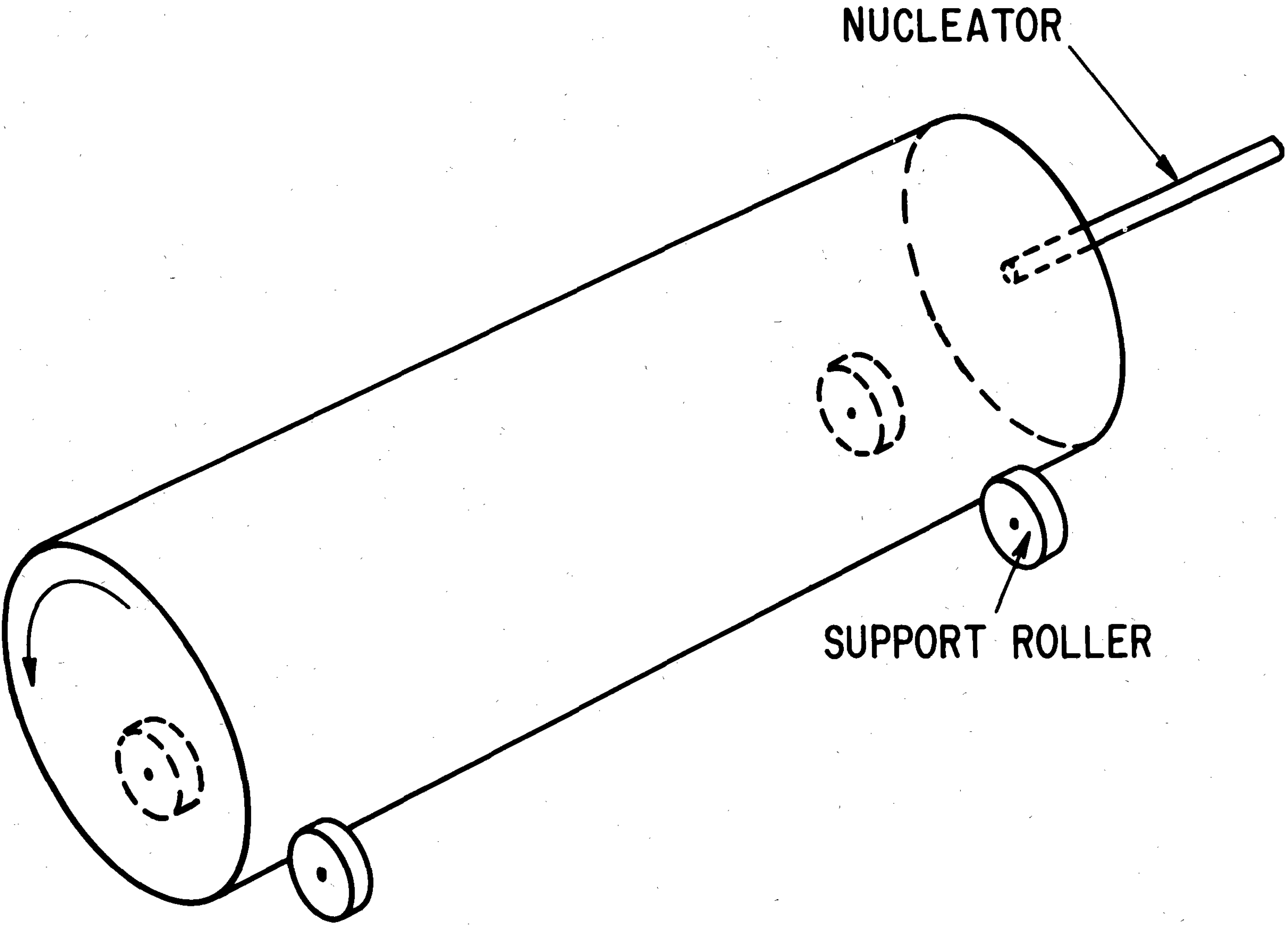
The overall objective of this program is to develop the technology and the engineering data required to implement rolling cylinder thermal energy storage in solar energy systems. The purpose of this contract is to design, and build a large, approximately 200,000 Btu prototype in an instrumented calorimeter. During the first year of the contract, the thermal characteristics of the system will be carefully defined and designs will be developed for the prototype rolling cylinder device and for its associated test equipment. During the second year of the contract, the prototype and test equipment will be constructed and preliminary checkout accomplished. A follow-on contract will be proposed the third year during which the prototype will be tested for its performance characteristics.

CONCEPT

A rolling cylinder thermal storage system using the latent heat of fusion of Glauber's salt would be considerably smaller and lighter in weight than a sensible heat storage system using water or rocks and is essentially isothermal. A water system operated over a temperature range of 20°F could store 1200 Btu/cu ft and a rock bed system could store approximately 700 Btu/cu ft. In contrast a Glauber's salt system could store 10,000 Btu/cu ft. Thermal energy storage could be used with solar collectors, heat pumps or air conditioners to reduce fuel and electrical bills and provide load leveling and fuel energy conservation.

Many of the problems with thermal energy storage systems using the latent heat of fusion of salts are solved by the rolling cylinder concept. A cylindrical container lying on its side, rotating slowly around its cylindrical axis provides just enough stirring action to keep the internal temperature uniform and very close to the wall temperature. Under these conditions crystallization occurs on nuclei in the liquid and not on the cylinder wall. The usual layer of solid does not build up on the cylinder wall, so heat transfer rates remain high as crystallization proceeds. Over 200 complete freeze-thaw cycles have been demonstrated prior to this contract on a laboratory scale rolling cylinder charged with Glauber's salt. Figure 1 shows a schematic of the rolling cylinder thermal storage device. A nucleator has been developed which reliably initiates crystallization without significant supercooling.

Glauber's salt (sodium sulfate decahydrate) has been used to illustrate the capabilities of the rolling cylinder apparatus. It was chosen because of its low cost and high latent heat of fusion, however, the rolling cylinder concept is broadly applicable to a wide range of materials.



ROLLING CYLINDER THERMAL ENERGY STORE

FUTURE ACTIVITIES

During the first few months of this contract the internal heat transfer behavior of a rolling cylinder phase change heat storage device will be studied analytically and experimentally. Based on these studies and on solar heating systems requirements a design concept will be chosen. A detailed design of a prototype rolling cylinder thermal storage system will be prepared at the end of the first contract year. During the second year of the contract, the prototype will be built and instrumented. The mechanical and electrical operation of the prototype and its test equipment will be checked. Testing of the prototype, including freeze-thaw cycling and rate calorimetry, will be proposed as a third year follow on to the present contract.

References

1. Herrick, C. S., Golibersuch, D. C., "Qualitative Behavior of a Latent Heat Storage Device for Solar Heating/Cooling Systems", General Electric Company Report No. 77CRD006 (March 1977)

2. Herrick, C. S., "A Rolling Cylinder Latent Heat Storage Device for Solar Heating/Cooling", submitted to Journal of ASHRAE, (August 1978)

3. Zarnoch, K. P., Herrick, C. S., " Latent Heat Storage in a Fifty-Five Gallon Rolling Cylinder", General Electric Company Report 78CRD175 (August 1978).

LTTES ANNUAL TECHNICAL STATUS REPORT

PROJECT SUMMARY

Project Title

"Life and Stability Testing of Packaged Low-Cost Energy Storage Materials."

Name of Contractor:

Institute of Energy Conversion
University of Delaware
Newark, Delaware 19711

Name of Principal Investigator:

Dr. Galen R. Frysinger

Current Contract Period:

September 1, 1978 - October 31, 1979

Objective:

The package integrity of the "CHUB" packaged materials will be tested to experimentally verify the ability of the package to retain the moisture within the salt mixture. The life and stability of the packaged material will be verified by thermal cycle and performance measurement.

Description of Work:

"CHUB" packages are prepared by Du Pont for mechanical and temperature stability tests. Immediate goal is a qualified "CHUB" for performance life testing.

Technical Accomplishments and Problems Encountered:

Pre-contract work indicates excellent weight retention by "CHUB" package laminates and the ability to meet handling and mechanical requirements.

Description of Planned Work:

Verification of weight retention and mechanical integrity will proceed with larger "CHUB" lots.

Thermal cycling and performance testing will continue through the year contract period.

Funding Level:

$146,000.00

Funding Source:

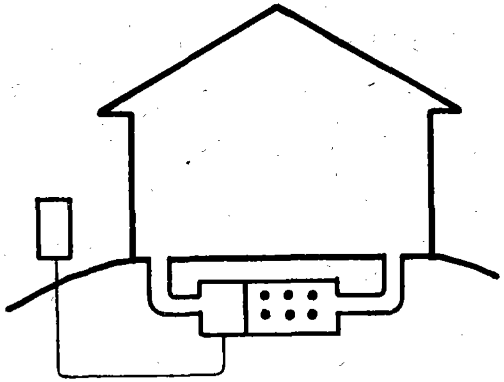
Department of Energy, Division of Energy Storage Systems

The CHUB low-cost thermal energy storage component has a wide range of applications as an air stream entrained integral heat exchange/storage unit.

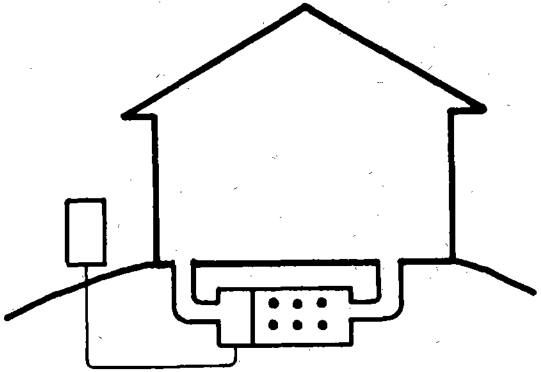
The first illustrations indicate examples of storage assisted air conditioning and heat pump applications making effective utilization of off-pleak electrical power for heating/cooling thus saving the utility fuel and generation facility costs. The CHUB may also be used with active air solar collector systems for daytime storage of heat to provide extended house heating during periods of no solar insolation. Likewise, as a passive solar system, the CHUBs can be directly irradiated by sun energy, thus storing the thermal energy for later use within the dwelling. The CHUBs also have applications in storing the heat in the dwelling to increase the thermal mass by phase change transition.

The second illustration shows the concept of storage assisted air conditioning. This application, which is the closest to commercialization, integrates the thermal energy storage with a conventional air conditioner providing the capability of using off-peak electrical power for residential cooling. The daily house heat gain is removed into thermal storage. The heat is rejected at night by the air conditioner using off-peak (lower cost) electricity, the heat being more efficiently rejected against the lower outside ambient temperature. The thermal energy storage capacity is thus renewed to absorb the next day's heat gain. The net result from the utility's point of view is that the air conditioning compressor's electrical demand is shifted from the daytime hours to nighttime hours where the utility's load demand is reduced. In this application, during the house cooling mode, the fan is under thermostatic control and circulates the house air over the frozen CHUBs to remove house heat during daytime periods to meet cooling requirements.

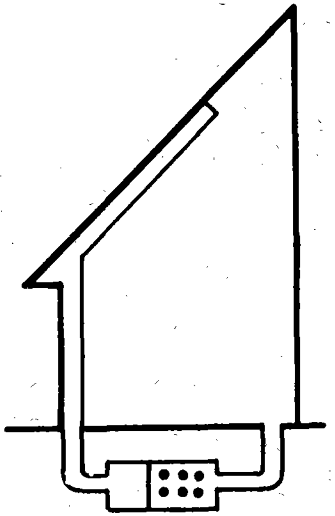
Chub Applications



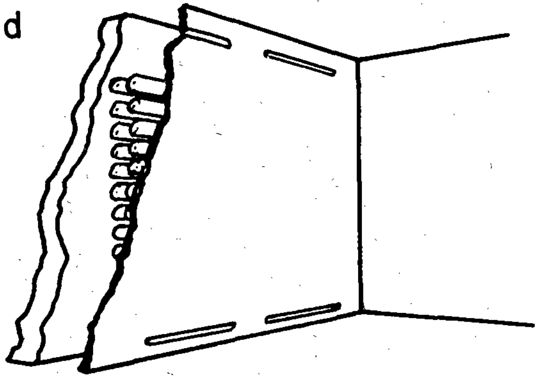
Storage Assisted
Air Conditioning



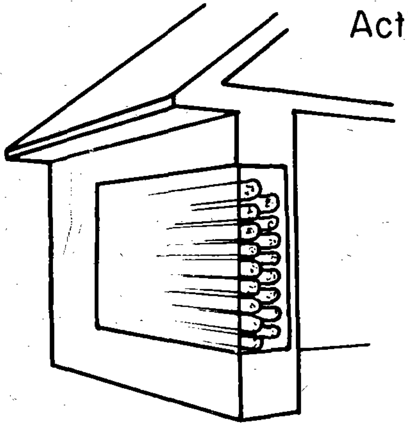
Storage Assisted
Heat Pump



Active Solar

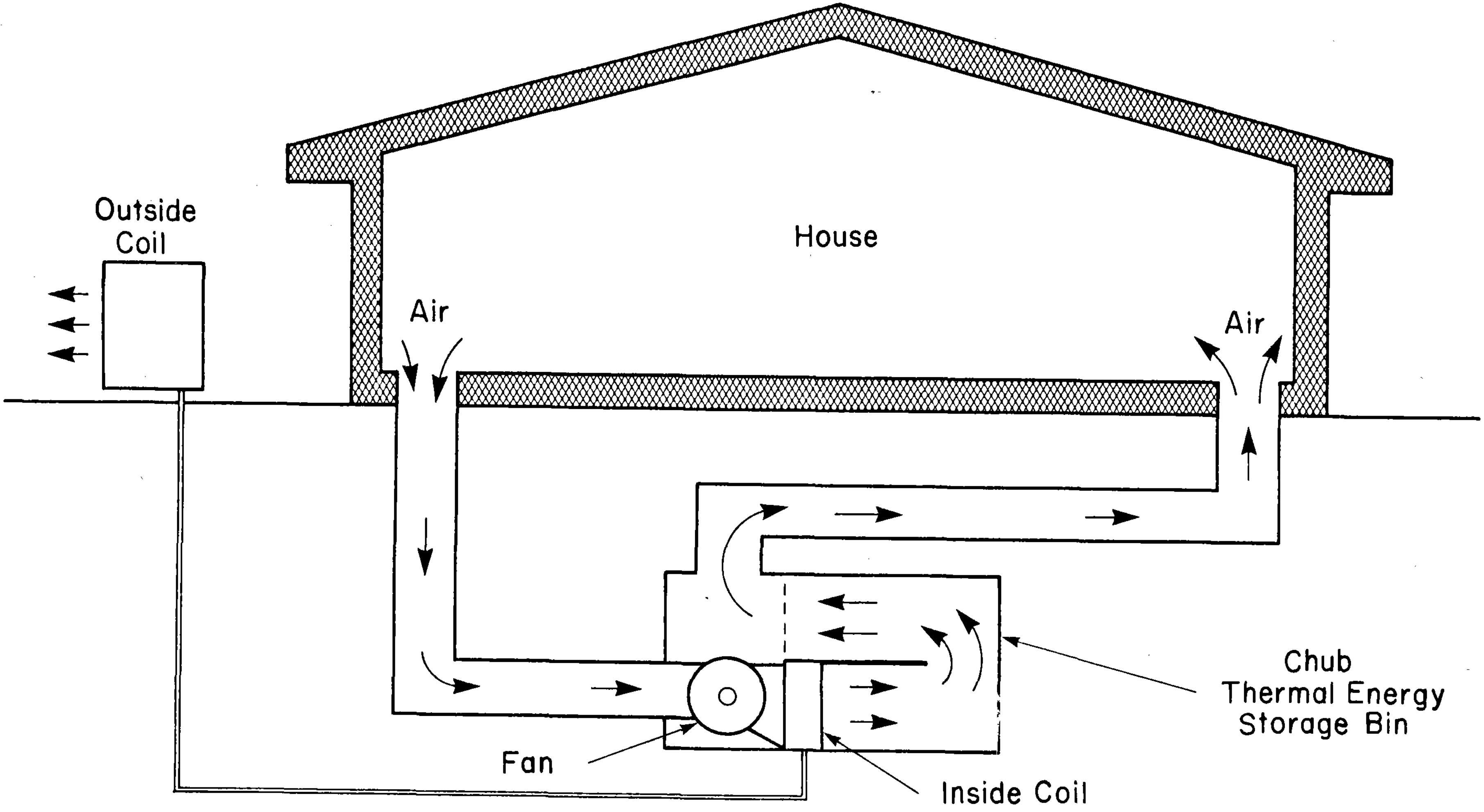


Latent Thermal Mass



Passive Solar

Storage Assisted Air Conditioning
(House Cooling Mode)



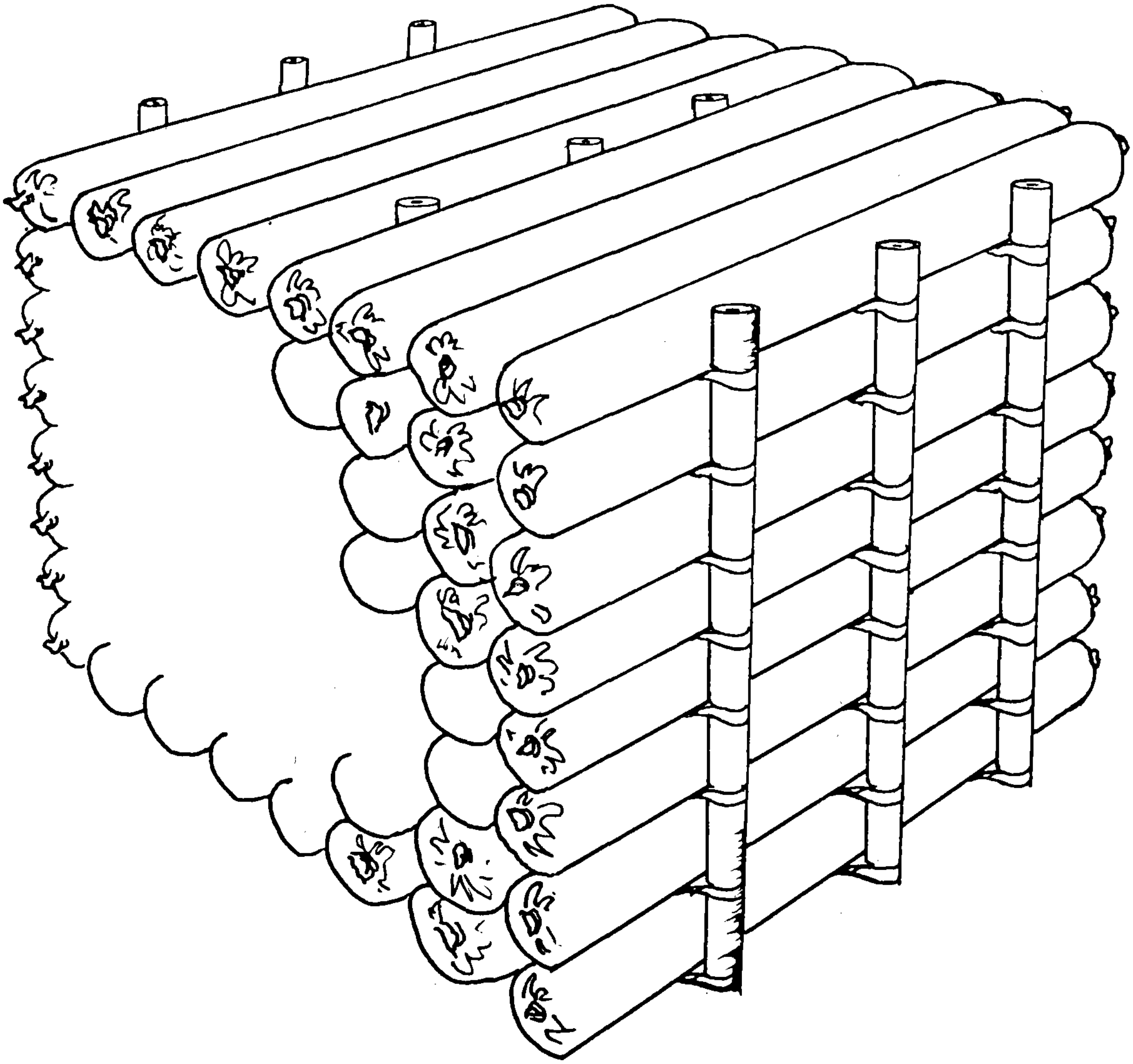
At night the compressor operation removes stored heat first freezing the CHUBs and thus preparing the house and the thermal energy storage modules for the next day's operation.

The next illustration shows a thermal energy storage module consisting of 64 CHUBs capable of storing 10,000 Btu's. The CHUBs are assembled with self-stacking hardware and inserted into the duct adjacent to the air handling equipment just downstream from the cooling coil.

The photograph of the CHUB component shows four units - the two on the right-hand side being frozen and the two on the left-hand side being thawed. For the application of the storage assisted air conditioning, the transition point has been adjusted to 55°F for humidity control.

The composition of the CHUB materials and their performance are shown in the next illustration. The seasonal system rating of 50 Btu's/lb. of CHUB material is based on the requirements for the worst-day design criteria, even though it must be realized that the average air conditioning day throughout the season would involve only a shallow cycle , i.e., only partial melting of the CHUB material.

A typical residence (1,800 - 2,000 sq. ft,) would require 27 modules (270,000 Btu's) which would have a nominal weight of 5,400 lbs. and require a volume of 125 cu. ft. within a 5-ft. cube. The cost for providing this home thermal energy storage unit for storage assisted air conditioning is broken out in the last illustration. A total material cost of $205.90 is related to an installed selling cost to the consumer of $595.80, which is a three-five year payback to the consumer if the utility passes on 30-40% of its savings to its customer.



THERMAL ENERGY STORAGE MODULE
(PROTOTYPE DESIGN FOR STORAGE ASSISTED AIR CONDITIONING)

20" CUBE

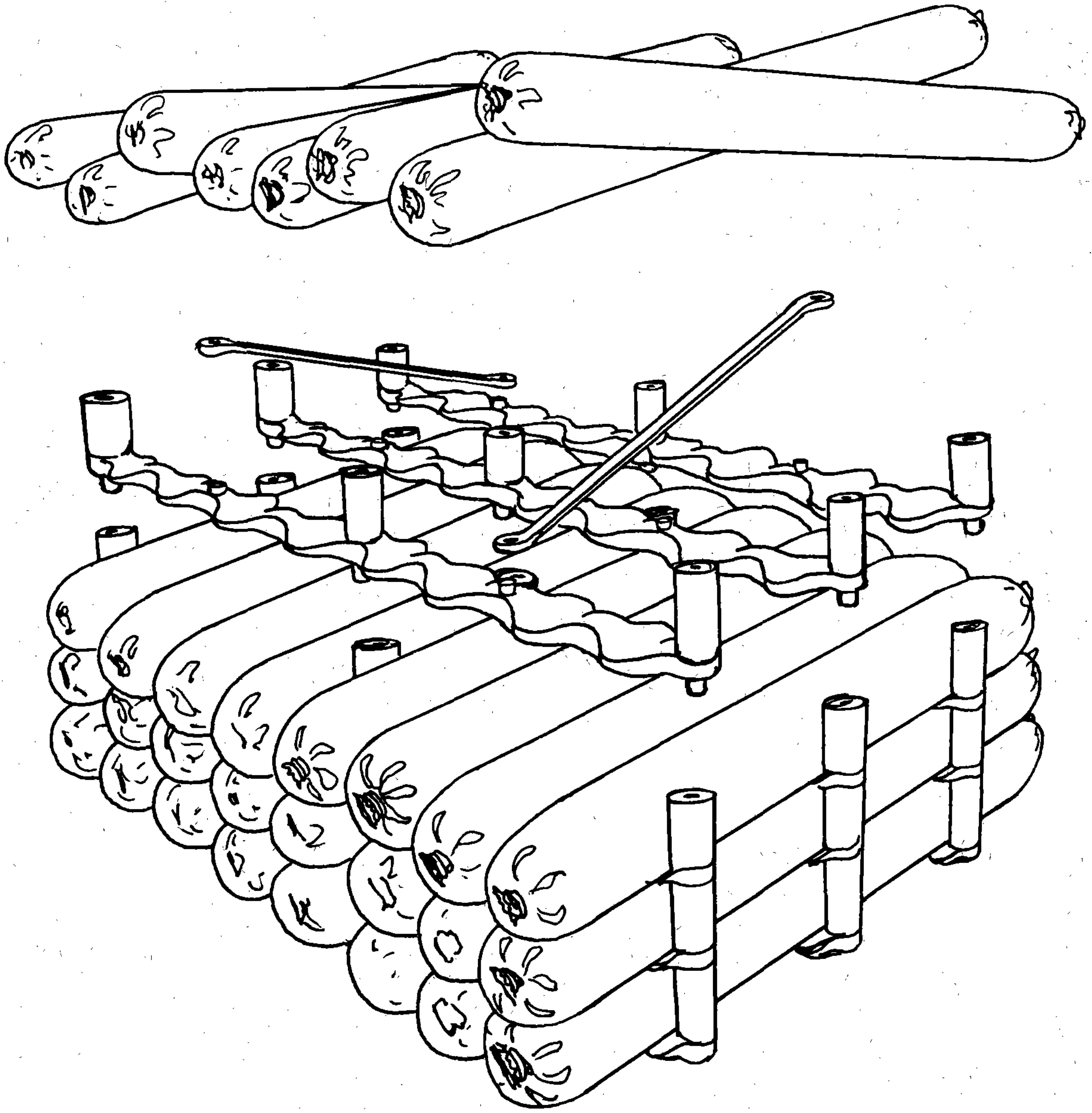
64 - 20 INCH LONG BY 2 INCH DIAMETER "CHUBS"

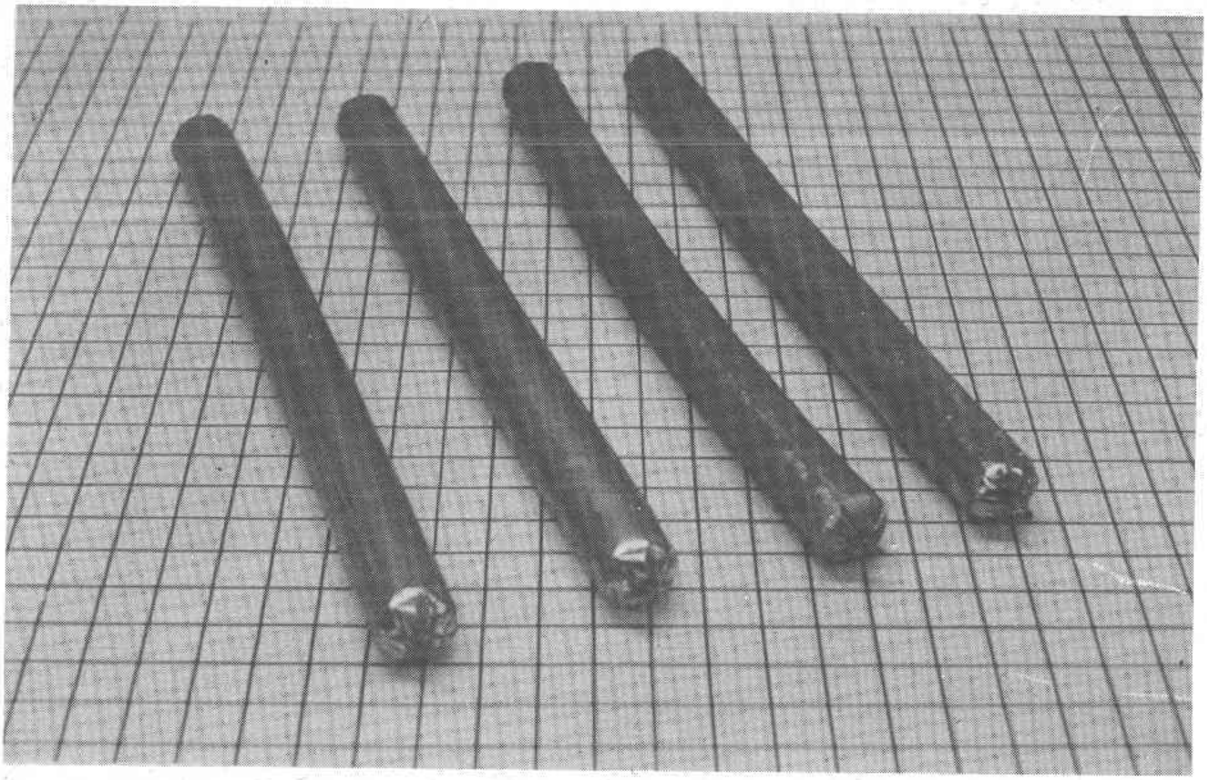
10,000 BTU

200 LBS.

50% AIR FLOW VOLUME

2,160 BTU/CU. FT.





"CHUB" COMPONENT

Materials

Sodium Sulfate Decahydrate
(Composition per U.S. Patent # 3,986,969, October 19, 1976)

	Weight Percentage
Na_2SO_4	32.8
H_2O	41.7
NaCl	6.7
NH_4Cl	6.2
Nucleating Agent: Borax	2.6
Thickener: Minugel F.G.	7.9
pH Stabilizer: Boric Acid	1.8
Dispersing Agent: Tetrasodium Pyrophosphate	0.3
	100.0%

Packaging

Multi-ply laminate (DuPont) heat sealed and packaged using "CHUB" machine

Performance

	Cal/gm	Btu/lb.
Glauber's Salts (90°F Theoretical)	60	108
Stabilized Glauber's Salts (55°F Theoretical)	45	80
Laboratory Calorimetric Data (Multi-cycled)	35	63

Part III - Distribution of Costs by Type

Unit	All Materials	Fabrication -Direct	Fabrication - Overhead	Shipping	Profit	Total
$/Ton	76.26	20.53	43.44	25.80	54.64	220.67
$/House	205.90	55.43	117.29	69.66	147.52	595.80
%	34	9	20	12	25	100

THIRD ANNUAL THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Experimental investigations of thermal flow in freezing and melting systems

Principal Investigator: Ralph M. Deal*

Organization: Oak Ridge National Laboratory
Building 9204-1, M.S. 3
P.O. Box Y
Oak Ridge, TN 37830
Telephone: (615)-483-8611, extension 3-5700

Project Objectives:

(A) Assessment of a computer model for thermal energy storage for phase change materials (PCM)

(B) Collection of fundamental data on heat transfer in freezing and freezing processes in a variety of materials

(C) Provide a facility for the testing of proposed PCM materials

Project Status:

(A) A facility is operating with temperature control for each of two thermal reservoirs and recording of temperatures on a millivolt recorder.

(B) The use of a laser as a probe to measure gradients in the liquid phase has been tested and shows promise.

(C) An LSI-11 computer system to take data and analyze it and to control the experiment is now being tested.

Contract Period: FY 1978

Funding Level: $30,000

Funding Source: Division of Energy Storage Systems, U.S. Department of Energy

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*Guest at ORNL on sabbatical leave from Kalamazoo College, Kalamazoo, Michigan.

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.

PROGRAM PROGRESS DURING FY 1978

Starting in July 1978 the following results have been obtained:

1. The Experimental Facility. An experimental facility has been built for the investigation of heat transfer in materials undergoing phase transformations. The initial experimental cell for the phase change materials (PCM) is a one-in. thick Plexiglas box of inside dimensions 4" x 6" x 3 1/2", one 4" x 6" face of which is an aluminum plate closely coupled to a set of copper tubes through which thermostated water is forced (see Fig. 1). The facility allows the thermostated water to come from either of two 55-gal drums at different temperatures (see Fig. 2). Bare copper-constantan thermocouples are located 1/2", 1", 1 1/2", and 2 1/2" from the aluminum face. The reference junctions are located in a highly regulated water bath.

Data collection so far has been limited to recording thermocouple voltages on a 1-MV recorder through a crossbar scanner. An LSI-11 data acquisition, processing, and control system is nearly ready to be added to the facility. It will allow selective gathering of data and control of the temperature of the aluminum face to fit any desired schedule. The LSI-11 system runs with a foreground/background monitor in RT-11. Twenty-eight K of core and two floppy disks provide program and data storage; a serial interface is included to allow further storage on a remote computer. Forty analogue input channels are amplified to give a full 12-bit conversion of 0-10 mv, corresponding to a few tenths of a degree F. Two analogue and two digital outputs allow control of the temperature of each reservoir.

2. A Potential Thermal Gradient Probe. Studies of the deflection of a laser beam upon travelling through the liquid phase show promise as a method of exploring the temperature gradients in the system.

a. No convection case. Assume the aluminum face is up and is providing heat to melt the PCM. To the extent that Plexiglas is a better insulator than the PCM, the thermal gradient will be vertical throughout the cell and uniform at a given distance down from the face. A horizontal beam of light in the z direction passing through w cm of the liquid PCM will emerge from the PCM with a net deflection of α:

$$\sin \alpha = \frac{n_{PCM}}{n_{air}} \sin \int_{0}^{w} \frac{\partial \, \ell n \left(n_{PCM}\right)}{\partial y} \, dz$$

where y is the vertical direction. The integral is over the path, and so averages the vertical component of the gradient of the log of the refractive index over that path. With judicious choice of cell width, w, for a given temperature gradient, deflections can be easily measurable, yet the variation in the distance from the aluminum face over the path can be kept within 1 or 2 mm.

b. Convection case. If the cell is oriented so that the aluminum face is vertical, convection currents dominate the thermal transport through the liquid during melting but seem to conform to paths that preserve a zero component of the temperature gradient parallel to the face in the horizontal direction. A laser beam along that direction will allow exploration of the thermal gradients in the liquid.

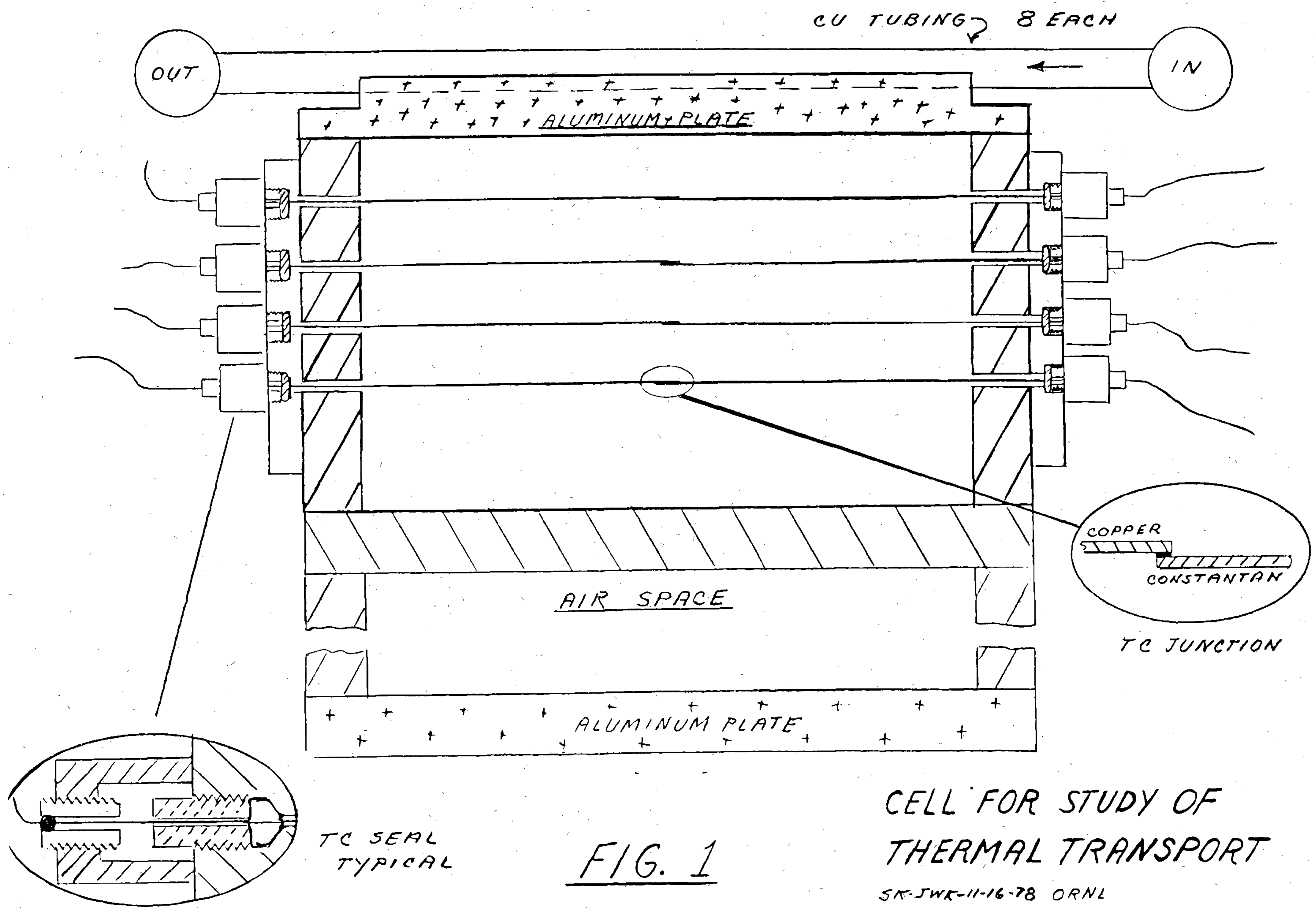


FIG. 1

CELL FOR STUDY OF
THERMAL TRANSPORT

SK-JWK-11-16-78 ORNL

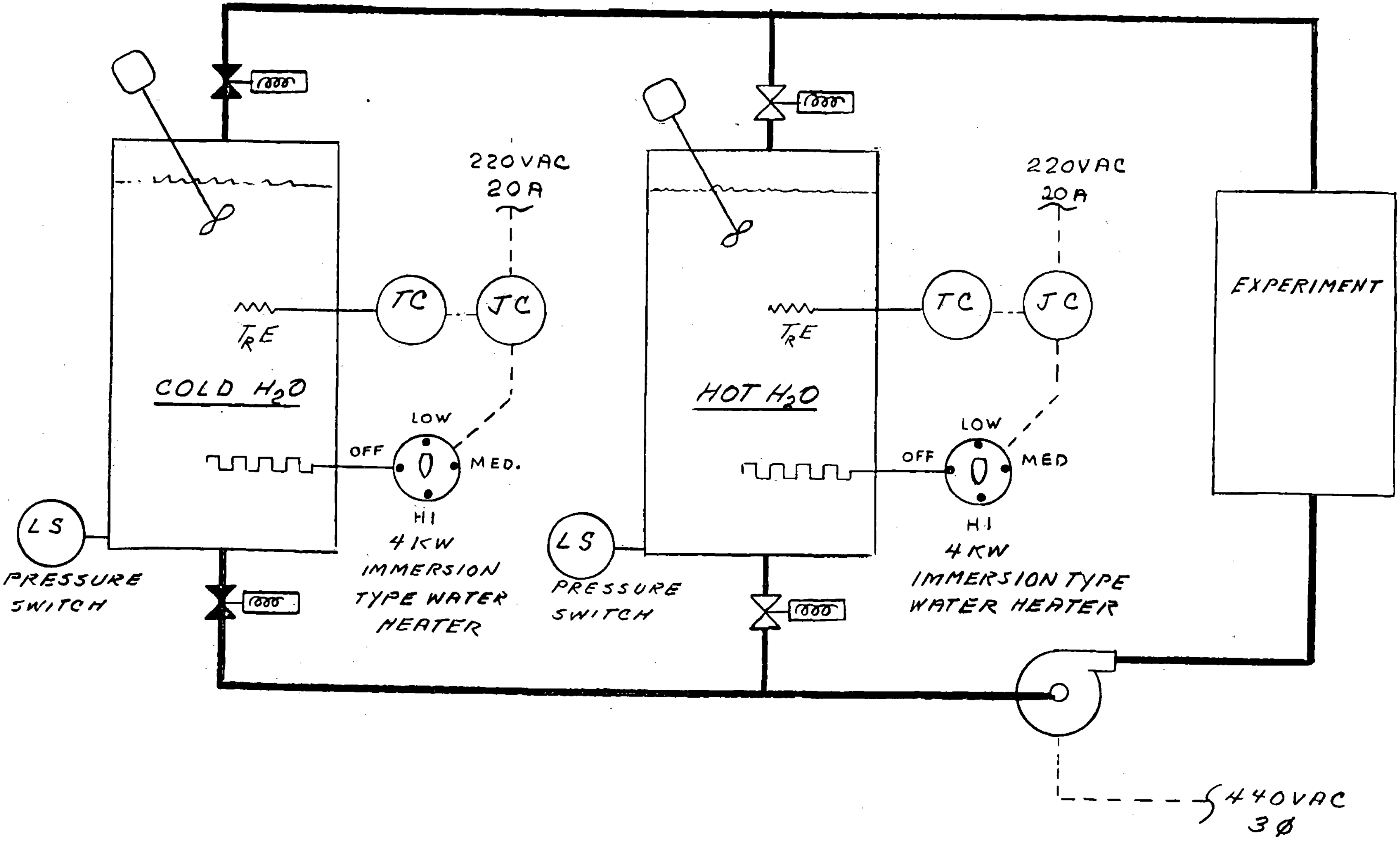


FIG. 2

LOOP FOR STUDY OF
THERMAL TRANSPORT

SK-JWK-11-16-78 ORNL

3. Results to Date. Initial studies have been directed towards assessment of a thermal energy storage program wirtten by Alan Solomon of ORNL (see the paper in this proceedings by Solomon). Results shown in Fig. 3 indicate the degree of agreement between the computer predictions and experimental results for an abrupt increase of the temperature of the aluminum face from below to above the melting temperature of n-octadecane, a simple wax. The initial temperature of the solid wax was 68°F; the temperature to which the aluminum face was taken was 105°F. The computer model was rún with literature values for the thermal properties of n-octadecane and a time step of 0.0005 hrs with 84 subintervals in the 3 1/2" depth of the cell. The experimental curves in Fig. 3A show the temperature of each probe over nearly eight hrs. The computer output curves in Fig. 3B show temperatures calculated at the same position as the experimental probes except that the highest probe, 1/2" from the aluminum face, is modelled by plotting calculated temperatures at three positions, 11/24", 12/24", and 23/24" from the aluminum face. Note the shift in the time of melting at each of these three positions. The position of the thermocouple itself is in the range 11/24" to 13/24" from the aluminum face, the uncertainty arising from some bends in the wire despite the tension maintained on the thermocouple wires. With some care, convection can be minimized with the aluminum face on the top of the cell. More elaborate assessment studies await the expension of the computer code to include convection.

4. Plans for Future Experiments. Eventually, various PCM's will be taken cyclically through a variety of temperature schedules to assess the model and to provide primary data for the assessment of proposed systems for low temperature thermal energy storage.

FIG. 3A

WAX 8NOV'78 EXPER.

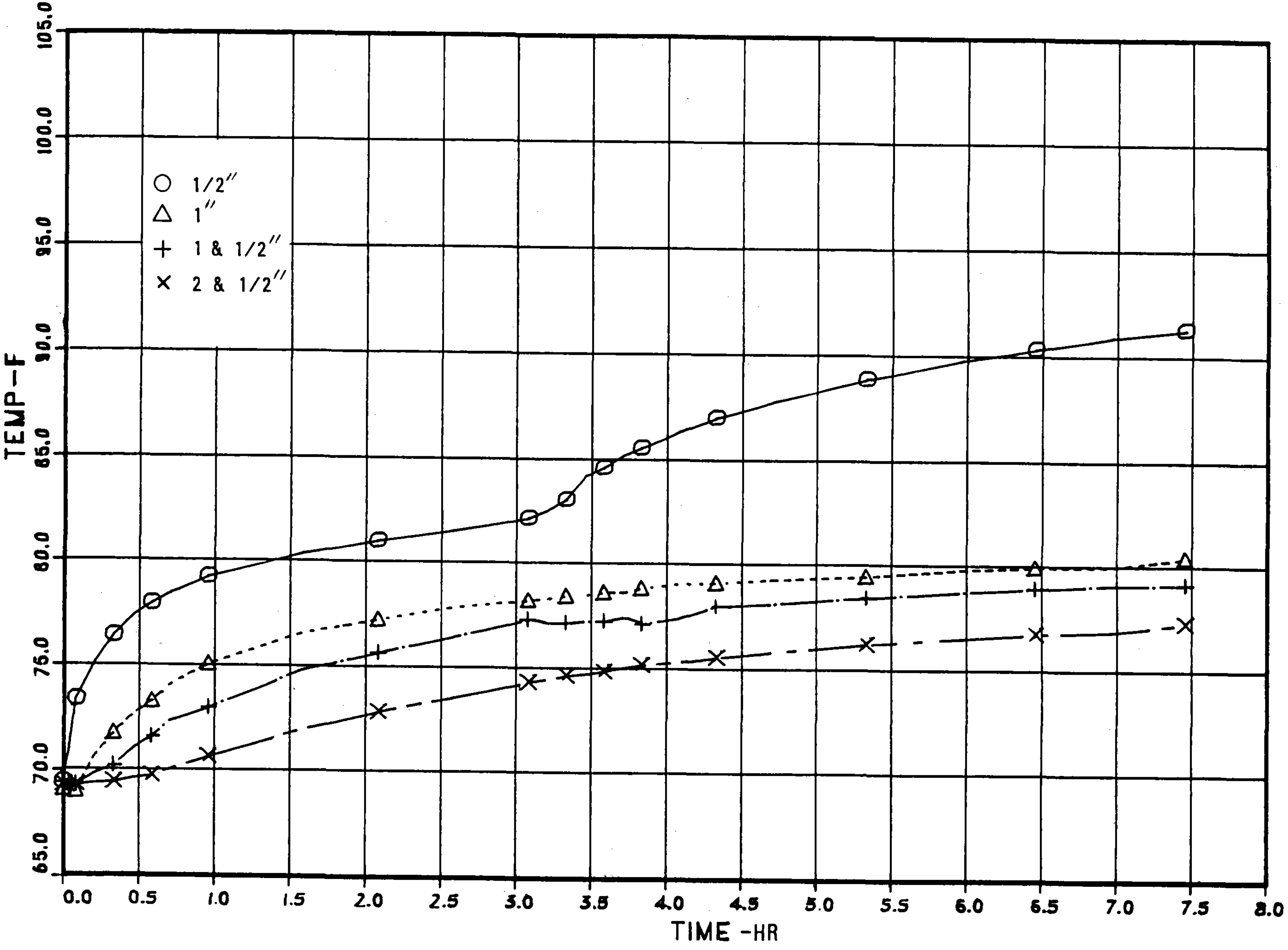
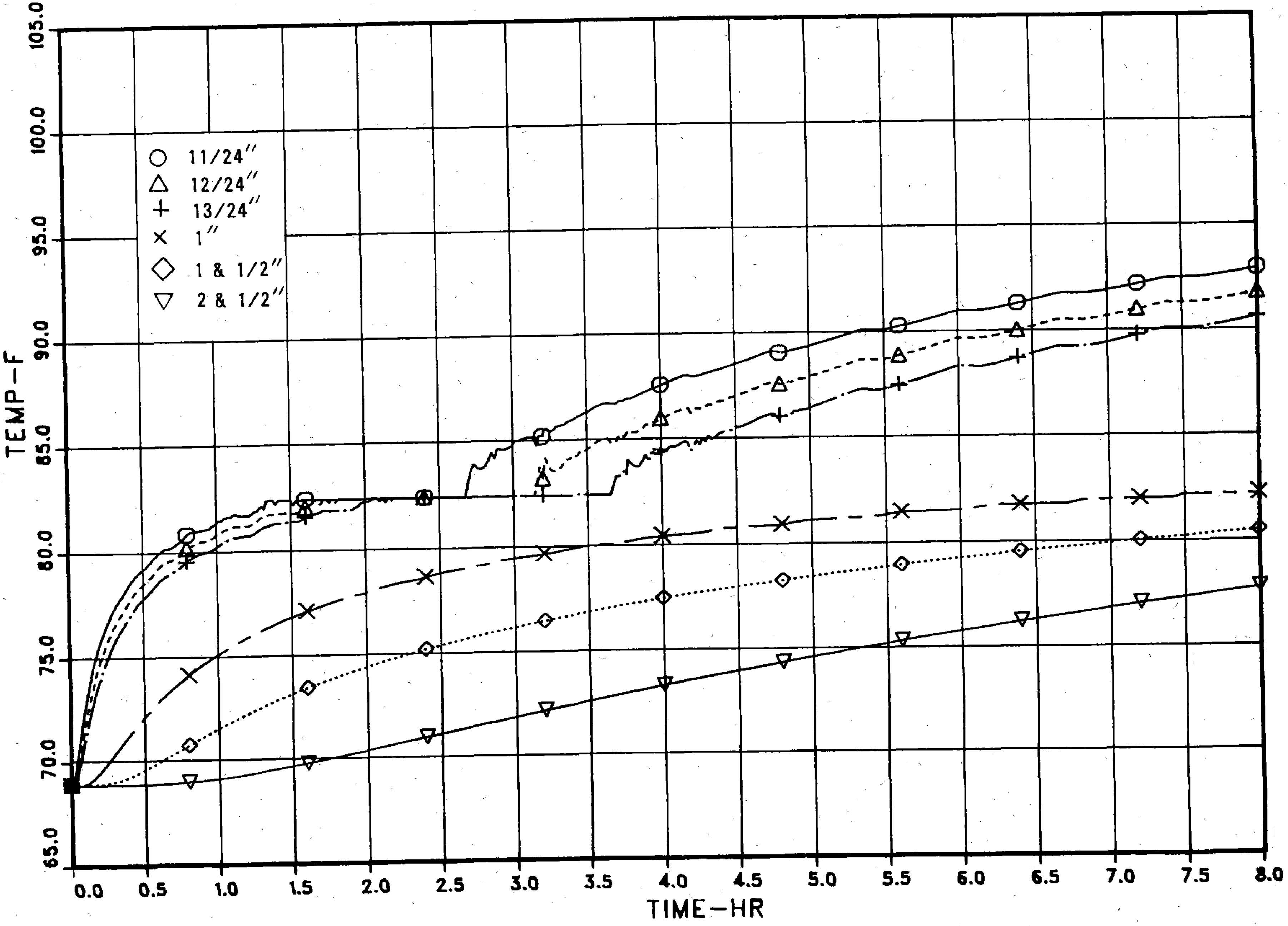


FIG. 3B

C18 $K_L=K_S$ 3.5" .0005HR 1/24" CN=.5



U.S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: ANL Storage Assessment and Field Test Program

Principal Investigator: Joseph G. Asbury

Organization: Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Project Objectives: The objectives of the assessment program are to analyze storage technologies that interface with electric supply systems to: *i)* determine their cost-effectiveness, *ii)* specify commercialization strategies, and *iii)* define R&D needs and opportunities. The objectives of the field test program are to evaluate the performance of near-commercial and advanced customer thermal storage technologies under U.S. operating conditions. Customer acceptance, load-leveling benefits, and development needs will be determined.

Project Status:

Assessment Program: Comprehensive assessments of storage resistance heating, storage air conditioning, storage heat pump, solar/storage/resistance, and solar/storage/heat pump technologies have been performed. Alternative strategies for commercializing customer storage have been analyzed and reported. Work is underway on comparisons of after-the-meter storage technologies and before-the-meter technologies (pumped hydro, compressed air, thermal electric batteries).

Solar storage concepts, including seasonal and stratified thermal storage have been analyzed. A general theory to specify and analyze the role of storage in solar-thermal applications is being developed.

Field Test Program: Electric storage heating systems are being installed in residences in Maine and Vermont. Roughly twenty (20) sample and twenty (20) control residences will have been equipped in each state before the end of the 1978-79 heating season. Data will be collected and preliminary benefit-cost analysis performed during FY 80. A thermal storage test facility will be established at Purdue University during FY 80.

Contract Number:

Assessment Program:	ANL 189 #49961
Field Test Program:	ANL 189 #49897

Contract Period:

Assessment Program:	FY 76 - FY 81
Field Test Program:	FY 78 - FY 81

INTRODUCTION

This project, which is supported by the Technical and Economical Analysis Branch and the Thermal Storage Branch of the Division of Energy Storage Systems, is divided into two main program areas: i) an assessment of storage technologies in electric load leveling and solar energy applications and ii) an experimental evaluation of thermal storage devices.

I ASSESSMENT OF STORAGE TECHNOLOGIES

Storage for Electric Load Leveling

Electric load leveling is one of the most important applications of energy storage technology. To assess the technical and economic feasibility of energy storage for electric load leveling, Argonne has performed case studies of the benefits and costs of alternative storage technologies in specific electric utility service areas. Here, we report the results of the analysis of three after-the-meter (customer) thermal storage technologies -- space heating, space cooling, and domestic water heating -- and two before-the-meter (utility) mechanical storage systems -- underground pumped hydro storage (UPHS) and compressed air energy storage (CAES).

Method. A case studies approach was used to evaluate the marginal savings and costs of each storage technology in representative electric utility service areas. (The method and general approach have been described in more detail elsewhere.[1,2]) The ANL cost allocation model SIMSTOR is used to calculate the utility savings associated with each storage technology. SIMSTOR uses hourly load and tri-hourly weather data (in the case of customer TES systems) together with the storage system performance characteristics to generate load profiles over the full annual (8760 hours) cycle. It then calculates the incremental utility capital and fuel costs to meet the incremental loads. SIMSTOR incorporates a storage charge/discharge optimization routine and a load dispatch model and observes operating constraints such as scheduled and forced outages and the cycle time of each type of generating unit. The model also calculates transmission and distribution system costs for dispersed energy storage systems. Storage system cost data were obtained from system vendors, HVAC system distributors and installers, and research and development groups.

Study Results. Utility benefits depend on such storage characteristics as: storage efficiency, storage discharge period, charge/discharge ratios, and aggregate installed storage capacity (MWh). Here we present results for two representative utilities: a small winter-peaking New England utility and a large summer-peaking Midwestern utility. Figures 1 and 2 show annualized marginal benefits ($/yr/kWh) for storage systems having 10-hour discharge periods and representative device efficiencies. The utility benefits, which represent annualized marginal capital cost savings plus levelized fuel savings, are shown as a function of installed storage capacity.

To provide a consistent basis for comparing the storage technoliges, we used utility cost of money in calculating the annualized utility benefits and the storage equipment costs. This is equivalent to assuming utility ownership of the customer TES systems, although in practice this need not be the case and, from the point of view of the utility, may not be desirable. The annualized storage system costs are show to the right in each figure. For the CAES and UPHS systems, the costs are representative of the large scale systems (8,000 to 10,000 MWh) located in favorable geological settings.

In the winter-peaking service area (Fig. 1), the TES space heating system shows the greastest benefits at low market penetration. Here the TES system provides transmission and distribution (T&D) benefits that are not provided by the central station UPHS and CAES technologies. The TES T&D benefits gradually decrease, until at 400 MWh, additional storage produces nighttime peaks on the distribution system. The maximum benefits occur at that capacity where the marginal benefit curve intersects the marginal cost curve. The savings and cost values presented in Table 1 correspond to these optimum installed storage capacities for CAES and UPHS. The values presented for TES space heating and water heating, however, correspond to market saturation of these technologies. Table 2 shows the effect of different storage technologies on a summer peaking utility having predominately coal-fired intermediate generating plant. As shown in the table the incorporation of CAES, involving oil fired gas turbines, causes an increase in oil consumption for this particular utility.

Figure 2 shows results for the summer peaking utility. In this case TES space heating does not save overall utility capacity but does improve the operating characteristics of the generating plant mix. TES water heating provides the greatest marginal benefits, however, total capacity is severely limited by the existing appliance stock. The interpretation of these curves parallels that given for the winter peaking utility.

On the winter peaking utility TES space heating provides maximum net utility benefits as well as the most favorable benefit/cost ratio. On the summer peaking utility TES water heating has the best benefit/cost ratio and TES space cooling provides the maximum net utility benefits and the second best benefit/cost ratio. Current studies are extending these results to other utility systems and providing sensitivity analyses of key storage and utility characteristics.

Table 1. COMPARISON OF STORAGE TECHNOLOGIES FOR WINTER PEAKING UTILITY

Technology	Storage Capacity (MWh)	Peak Reduction (MW)	Oil Savings (10^3 bbls)	Average Benefits ($/yr/kWh)	Storage Cost ($/yr/kWh)	Net Benefits (10^6 $/yr)	B/C
TES Space Heating	1062**	70	95	4.62	0.91	3.94	5.1
TES Water Heating	357**	40	58	10.25	2.96	2.60	3.5
CAES - Daily	730*	77	82	5.02	3.00	1.48	1.7
UPHS - Daily	648*	59	125	5.26	3.14	1.37	1.7

*Installed capacity that maximizes net system benefits, where net benefits equal total utility benefits less storage costs.

**Installed capacity that corresponds to conversion of all existing conventional appliances to storage appliances.

Table 2. COMPARISON OF STORAGE TECHNOLOGIES FOR SUMMER PEAKING UTILITY

Technology	Storage Capacity (MWh)	Peak Reduction (MW)	Oil Savings (10^3 bbls)	Average Benefits ($/yr/kWh)	Storage Cost ($/yr/kWh)	Net Benefits (10^6 $/yr)	B/C
TES Water Heating	1,050**	106	161	8.56	3.02	5.83	2.8
TES Space Cooling	9,480*	1,380	323	6.86	3.45	32.29	2.0
TES Space Heating	5,450**	0	-109	1.28	0.97	1.71	1.3
CAES - Daily	17,200*	1,950	-925	3.58	3.00	9.94	1.3
UPHS - Daily	13,300*	1,320	655	3.77	3.14	8.39	1.3

*Installed capacity that maximizes net system benefits, where net benefits equal total utility benefits less storage costs.

**Installed capacity that corresponds to conversion of all existing conventional appliances to storage appliances.

Storage for Solar Applications

The ongoing Argonne system studies have analyzed the role of TES in a number of important applications. Here, we describe two recent studies: i) seasonal storage for 100% solar space heating of buildings,[3] and ii) stratified sensible heat storage for improved solar-thermal system performance.[4]

Seasonal Storage. In solar heating of buildings, load requirements occur only over the winter season with the collector unit remaining essentially idle during the rest of the year. Recently, a number of solar system designs have been proposed, some built, that incorporate storage capacities on the order of one or several months' supply. The rationale for these "seasonal" solar schemes is to permit solar collection over a much greater fraction of the year, with energy stored for periods extending over several months or longer before actually being used to meet load. By improving utilization of the available solar input over the full year, a seasonal system will reduce the collector area requirement relative to that of a comparable diurnal system while providing the same total energy to load. The resultant savings in collector area costs represent a major economic benefit of seasonal storage. A second benefit is to lessen, or eliminate altogether, requirements for a backup energy supply and the associated problems of load management. Against these benefits must be weighed the added capital cost of the seasonal storage unit.

We have analyzed seasonal solar systems consisting of conventional flat plat collectors and a sensible heat storage medium. A concise system model has been developed under the assumption of a fully-mixed, uniform temperature, storage medium that permits efficient simulation of long-term (multi-day) system thermal performance over the course of the year. With this model we have solved for the thermal performance of seasonal solar systems that are designed to supply 100% of load without backup under "reference year" weather conditions. Provided the storage vessel is extremely well insulated, we find substantial performance gains for the seasonal over the diurnal system, with the annual fraction of useful solar energy delivered to load greater by as much as a factor of two for the reference year conditions.

Based on these performance and sizing findings we have estimated unit break-even costs of seasonal storage by comparing the capital and fuel costs of conventional space heating technologies against those of seasonal solar systems. At costs below the break-even estimates, the seasonal solar system has an economic advantage over the conventional system. We have also made cost comparisons between seasonal and diurnal solar systems. Results for Madison are shown in Fig. 3. For the range of collector costs and conventional system costs considered in the paper, the corresponding storage break-even costs range up to a high value of about 15¢/gallon ($40/m^3) for extremely well insulated tanks, and high competing fuel costs.

Although the storage break-even costs are dependent on the costs assumed for collectors and for the conventional technologies, the qualitatively low range of estimates is symptomatic of a seasonal storage system. In simplest terms, the value of each increment of storage capacity is set by the cost difference between the aggregate energy input to storage (divided by storage efficiency) and a comparable amount of competing conventional fuel. For a seasonal system, thermal energy is cycled through the device only about once per year, leading to a relatively low annual energy throughput and hence to a low storage break-even cost. By contrast, in diurnal solar applicatins, energy is cycled through the storage device numerous times over the heating season, increasing proportionately the total energy throughput and the storage break-even cost.

Stratified Storage for Solar Heating. In solar heating systems employing sensible heat storage (SHS), the collector losses tend to increase linearly with the quantity of stored heat, thereby reducing the rate of solar heat delivery to SHS and ultimate load. This tendency can be mitigated to a useful degree if the SHS is stratified, with some additional improvement in the delivery of stored heat to useful load. Two types of stratified SHS are approximately realizable in practice, namely serial or time-ordered (exemplified by the rock bed) and temperature-ordered (buoyancy-ordering in liquid tanks).

We have carried out an extensive analytical treatment of solar-thermal systems embodying idealized unstratified (fully mixed) or stratified SHS. Results from the theory provide a direct evaluation of the gains in sun-to-load heat transfer from stratification for any combination of load and insolation time patterns. Based on the analytic treatment we have developed simulation models of each type of stratified SHS. In general, we find three major features of stratified systems that account for their performance gains over fully-mized systems.

1. When the load draw of a solar-thermal system is reasonably constant over the hours of collection and the heat exchange to load is effective, either type of stratified SHS gives somewhat better collection efficiency than does the fully mixed (FM) SHS. The main reason is that the stratified storage delays the return of the warmed collector output to the collector inlet, thus giving a head start to the stratified system which is never overcome by the FM system.

The difference in collection efficiency is typically only a few percent for liquid-cooled collectors but may be much larger for air-cooled collectors. The reason is that the stratified system is rather insensitive to the temperature rise across the collector $(\Delta T)_C$ while in the FM-case performance degrades substantially as $(\Delta T)_C$ increases. The temperature rise $(\Delta T)_C$ is typically relatively large for air collectors because of the small coolant heat-capacity flow.

2. The most reliable advantage of stratified SHS in domestic-hot-water (DHW) and similar systems is the discharge behavior during noncollection. The stratified SHS delivers its stored heat with minimum load flow, and the more or less fixed overnight integral draw leaves the stratified SHS at a lower starting temperature than in the FM case. That is, more heat is delivered to load overnight and more heat will be collected the following day.

3. Turning to the special aspects of temperature-ordered SHS, these are clearest for DHW-like systems. Consider such a system after an hour or several of solar-heat collection with small load draw. Under these circumstances, even the coldest region of the TO-SHS, the bottom, may be at temperature substantially greater than the cold-water supply ("mains") temperature T_O. If a substantial load draw now begins, the influx of cold water is immediately available to the collector, so that collection efficiency is abruptly increased. At the same time, the hottest water available is being delivered to the load so that both collection and delivery of heat is simultaneously maximized. The effect on system efficiency may be quite substantial as illustrated in Fig. 4. Most hot-water loads are intermittent in nature so it seems likely that the realization of TO-SHS would result in significant increases in efficiency for all

applications such that daytime load is a major fraction of total load. Laundries, schools, and car-wash establishments come to mind.

II EXPERIMENTAL EVALUATION OF THERMAL ENERGY STORAGE

The experimental evaluation program includes two principal activities: i) the TES Field Test program and ii) the TES Test Facility.

Field Tests. By validating TES performance under actual U.S. operating conditions, the field tests will: i) establish baseline cost and performance characteristics for thermal storage technologies, ii) identify R&D needs for adapting commercial European TES heating systems and for improving prototype U.S. cool storage systems, and iii) establish cost and performance goals for advanced TES concepts.

The ANL field tests are evaluating brick and hydronic storage heating systems. The experiments are being conducted in two winter-peaking service areas. The experiments will span two full heating seasons (78-79 and 79-80). ANL has overall program management responsibility while the Universities of Maine and Vermont are responsible for management of the local research efforts.

In Vermont, Central Vermont Public Service, Vermont Electric Cooperative, and Green Mountain Power are cooperating with the University of Vermont in testing 13 dispersed ceramic units, one central ceramic unit, and six central hydronic units in 20 residences. A set of 20 control residences is also being monitored. In Maine, Central Maine Power is working with the University of Maine in testing 15 dispersed ceramic units. An equal number of control residences is being monitored.

Data collected in the two experiments include: indoor and outdoor temperatures, TES device load, and utility system load. Customer acceptance of TES is also being determined through customer surveys. Both experiments involve close cooperation with state utility regulatory commissions.

TES Test Facility. The thermal energy storage test facility is being designed to complement the TES field tests and to provide DOE, its contractors, and others with a capability to evaluate advanced TES concepts and systems. In addition, the facility will be used to validate TES testing procedures and standards.

Purdue University has been selected as the test facility site. The test facility will incorporate existing constant temperature rooms and a small calorimeter chamber to be developed. Initially, sensible heat storage systems will be tested, but it is contemplated that heating and cooling storage systems of both sensible and latent types will be tested in the laboratory. The facility shall be set up to handle testing assignments from ANL and DOE.

It is anticipated that the ASHRAE testing standard currently under development will be evaluated at the Purdue facility. The standard will be examined to determine its suitability for evaluating commercial and near-commercial TES systems and its appropriateness for duplication by commercial testing laboratories and by TES manufacturers' R&D laboratories.

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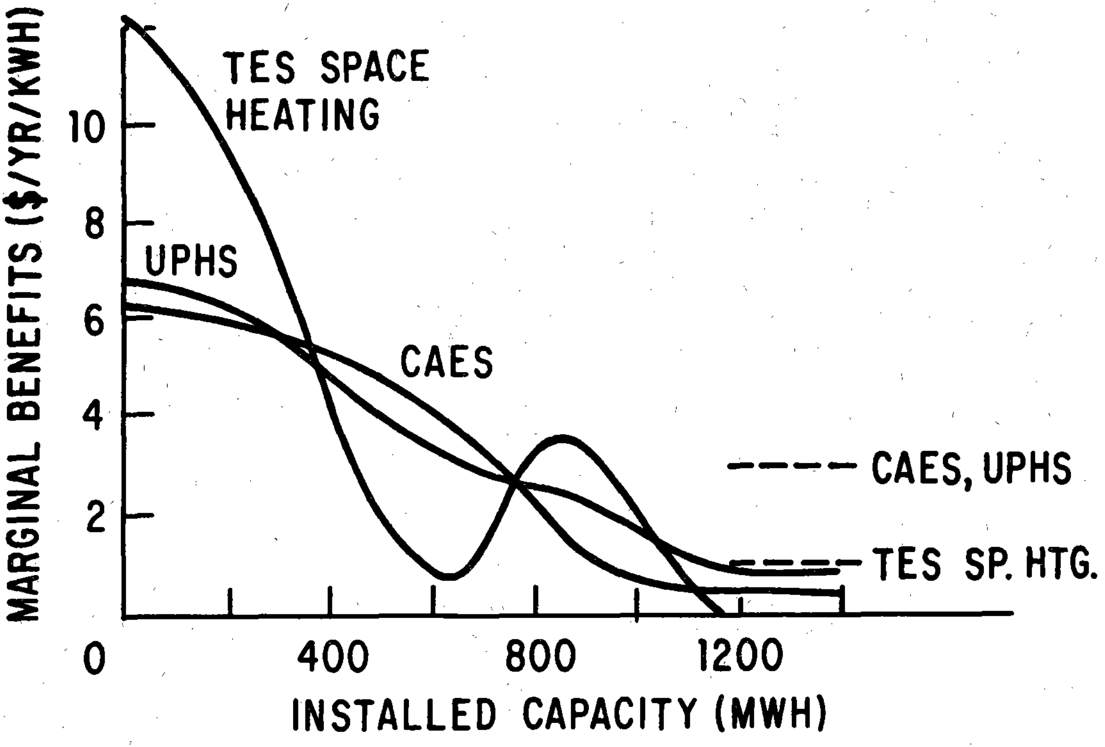

Fig. 1. Marginal Utility Benefit Curves for Winter Peaking Utility.

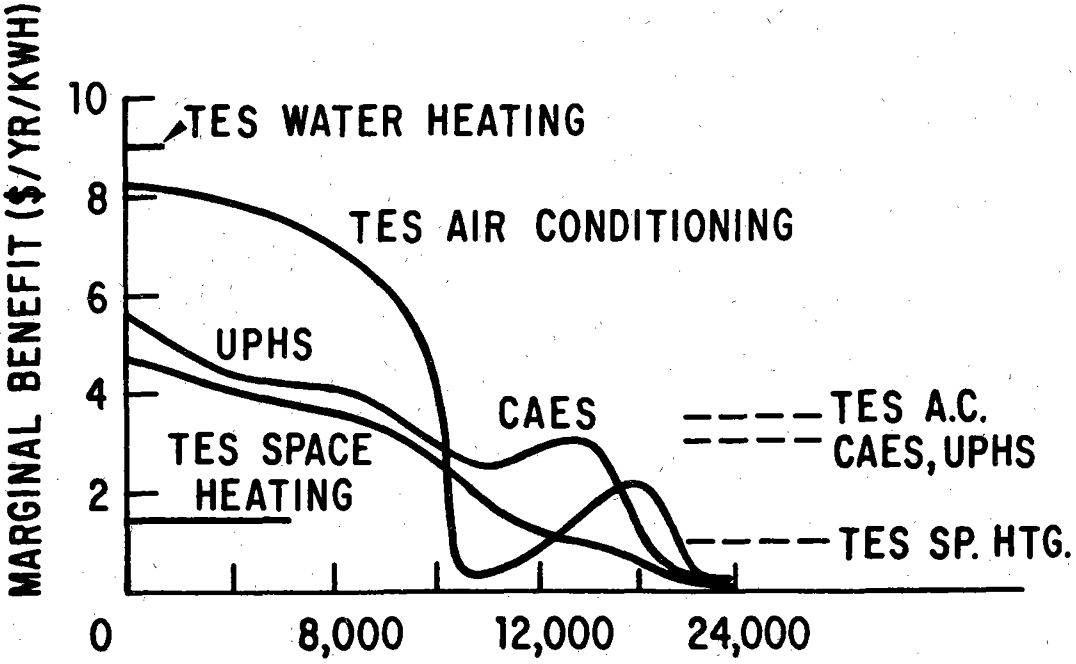

Fig. 2. Marginal Utility Benefit Curves for Summer Peaking Utility.

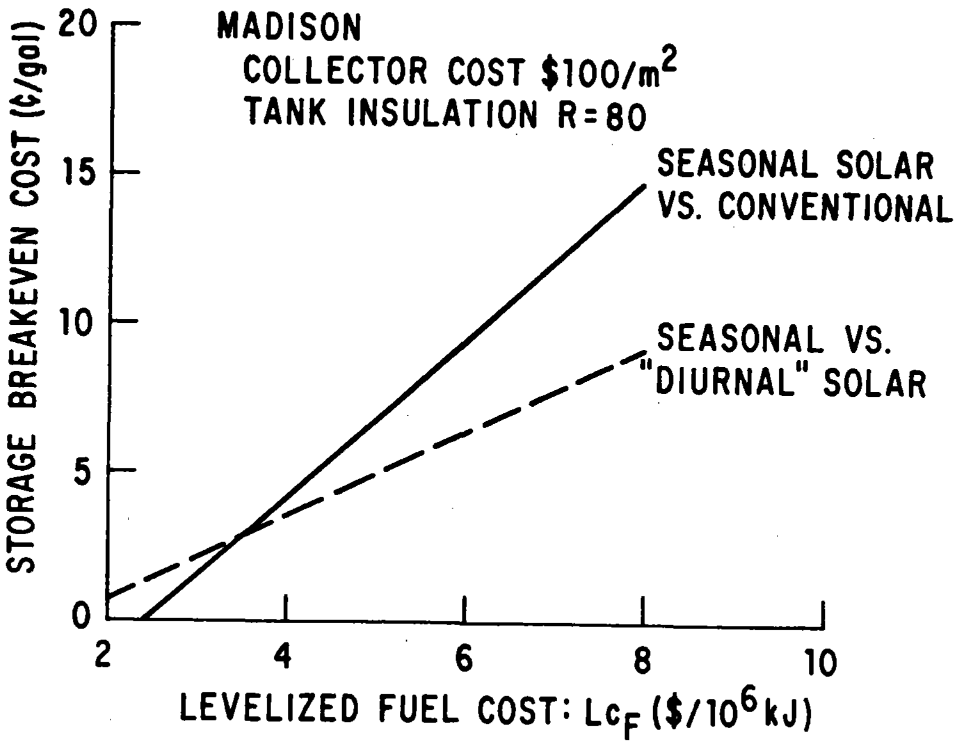

Fig. 3. Unit Break-Even Cost of Seasonal Storage for Comparisons of a Seasonal Solar System against a Conventional Heating Device and against a "Diurnal" Solar System.

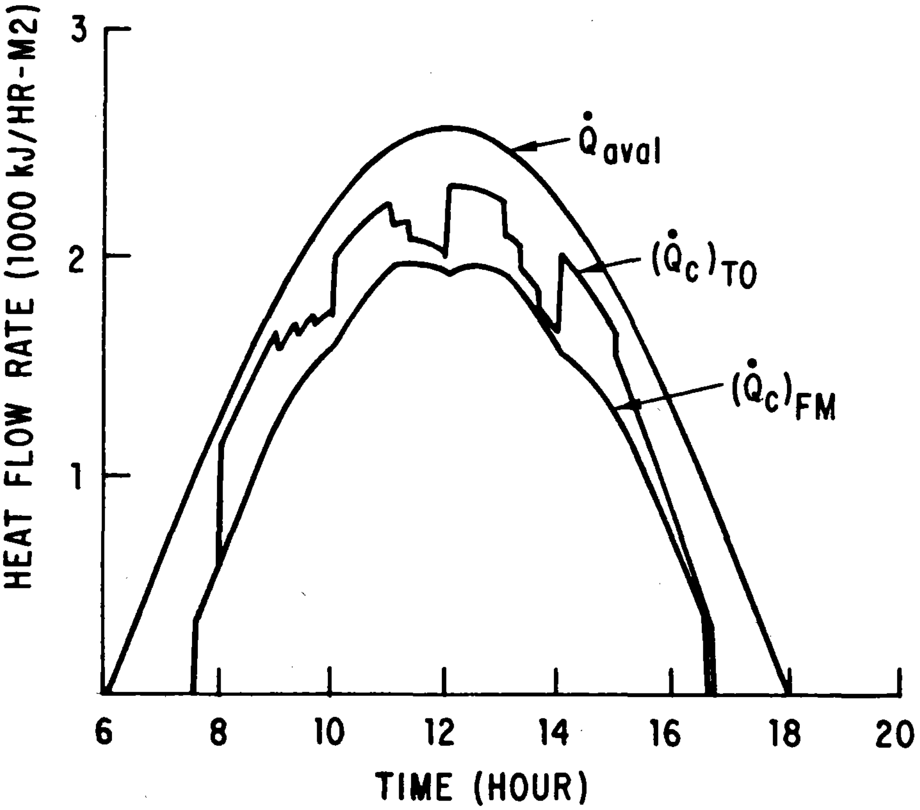

Fig. 4. Comparison of Collection Heat Rates for Temperature-Ordered Stratification $(\dot{Q}_c)_{TO}$ and Fully Mixed Sensible Heat Storage $(\dot{Q}_c)_{FM}$ for Intermittent DHW Load during Collection (1-Hour) Load Draws beginning at 8, 10, 12 and 14 Hours). $\dot{Q}_{aval}$ is the Collector Heat Flow with Infinite Heat Capacity.

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, Pennsylvania 15236
Telephone: (412) 892-5600

Project Objectives: To assess the potential for waste heat recovery in the food industry and to evaluate prospective waste heat recovery systems employing thermal energy storage.

Project Status: The project tasks were:

(1) Waste heat availability and applications survey.
(2) Waste heat recovery system design.
(3) Assessment of potential fuel and energy savings in the food industry.
(4) Commercialization plan development.

The project has been completed and the development of demonstration plans is proceeding.

Contract Number: EC-77-C-01-5002

Contract Period: 8/31/77 - 9/30/78

Funding Level: $96,195.00

Funding Source: Department of Energy, Division of Energy Storage Systems

ADDITIONAL BACKGROUND

The project was conducted by Westinghouse with the cooperation of the H. J. Heinz Company. Heinz arranged access to two of their manufacturing plants within the Heinz U.S.A. Division and permitted Westinghouse personnel to analyze factory and food system operations. Besides the selection of the two survey sites, a waste heat availability study was performed at each site and recovery system concepts were developed and evaluated.

DISCUSSION

Survey Site Description & Selection Rationale

The Heinz U.S.A. Division operates eleven factories engaged in a variety of thermal food processes. Two of those factories, located in Pittsburgh and Lake City, Pennsylvania, were selected as survey sites for the project. The Pittsburgh Factory is a large multi-building facility employing over 2,000 production people and specializing in foods processed with steam and hot water. The factory's main products are baby foods and juices, canned soups and canned bean products. At the Lake City Factory, approximately 150 employees are employed in the preparation of frozen desserts. Lake City operations are conducted in a modern single-story building having a total floor area of approximately 70,000 ft^2. These factories were selected as survey sites since their products and processes are common to a large segment of the food industry – nearly 13% on the basis of total energy consumption. This fact would lend attractiveness to any recovery system concept stemming from the project since the potential for a significant industry impact would be correspondingly large.

Waste Heat Availability Study

The Pittsburgh Factory operates several food systems that produce hot waste water. To eliminate the possibility of product contamination, waste water is not recycled nor is waste heat recovery currently attempted. Instead, the waste water streams are collected by a drain system that transports them from the factory via clear water and sanitary sewer systems. The factory waste heat survey shows the individual waste streams flow at a variety of temperatures in the 120 to 200°F range. When merged, the average stream conditions will be 145°F at 720 gpm during first shift operations and 145°F at 550 gpm during second shift. As an indication of waste heat availability, the waste streams could yield 6.9×10^{10} Btu annually if their temperatures were reduced to 75°F by heat exchange with incoming fresh water. This recovery potential is significant representing nearly 6% of the factory's current energy demand.

The Lake City Factory has two independent refrigeration requirements – blast freezing and cold storage. The refrigeration effect is provided by an ammonia system driven by ten rotary and reciprocating compressors. On the discharge side of the compressors, the condensers are arranged in two separate groups. One group primarily serves the blast freezer and its heat rejection therefore peaks during production hours and subsides to a relatively low level during off-production periods. The second group, however, serves a storage freezer and its heat rejection rate is more uniform over the entire day. Thus, the factory actually has two independent sources of refrigeration waste heat that behave differently with time. They could therefore be linked with two independent waste heat applications whose energy demands also follow different time patterns. Waste heat availability estimates were performed for the Lake City Factory using assumed ammonia vapor conditions, factory electrical consumption data and compressor nameplate information. The estimates show an annual waste heat availability at the condensers of 4.0×10^{10} Btu which is larger than the factory's total energy consumption (gas and electricity combined) by approximately 50%.

Waste Heat Applications

Three separate energy demands that could use the available waste heat were selected for study at the Pittsburgh Factory. They involve the heating of boiler make-up water, fresh water for food processes and factory clean-up water.* Thermal storage would be required in the latter case and conventional heat exchange in the make-up and process water cases. A clean-up water application involving thermal storage also exists at the Lake City Factory and could be supplied by the blast freezer refrigeration system. In addition, a continuous demand (in cold weather) also exists for heated air which is blown beneath the freezer floors to prevent soil freezing. This demand represents an ideal application of waste heat from the storage freezer system.

Waste Heat Recovery System Design and Evaluation

Several recovery system concepts to satisfy the waste heat applications identified above have been considered for use at the Pittsburgh Factory. A multi-building system is shown schematically in Figure 1. In that concept, waste water streams at various temperatures are collected from processes occurring in three production buildings. The high temperature streams (i.e., those above 140°F) are collected in the high temperature accumulator (HTA) while all low temperature streams are channeled to a low temperature accumulator (LTA). The LTA and HTA will be insulated and will serve as surge tanks between the waste water source and application points. From the HTA, waste water flows on demand to the high temperature heat exchanger (HTHX) located in the Power Building. At the HTHX, heat is transferred to incoming fresh water as it flows to various food processes. When those demands diminish while hot waste water is still available at the HTA, the system will automatically divert the flow of heated fresh water to storage. Water that accumulates in storage during the production period would then be used during third shift for clean-up purposes.

Waste water collected in the LTA will flow to two low temperature heat exchangers (LTHX) also located in the Power Building and mounted in parallel. Waste heat will be applied at that location to preheat fresh water for food processing and for boiler make-up. The parallel heat exchanger arrangement is necessary since the food processing and make-up applications require water from two different sources — on-site wells and the city water main, respectively.

Estimated materials and installation costs for the multi-building system total to \$359,400. Allowing an additional 15% for engineering brings the total system cost to \$413,300. At current fuel prices, the system will yield a return on investment (ROI) of 34% per year and reduce factory energy consumption by 5 - 6%.

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*Production operations generally extend over a one or two shift period. A thorough clean-up is performed daily when production ends.

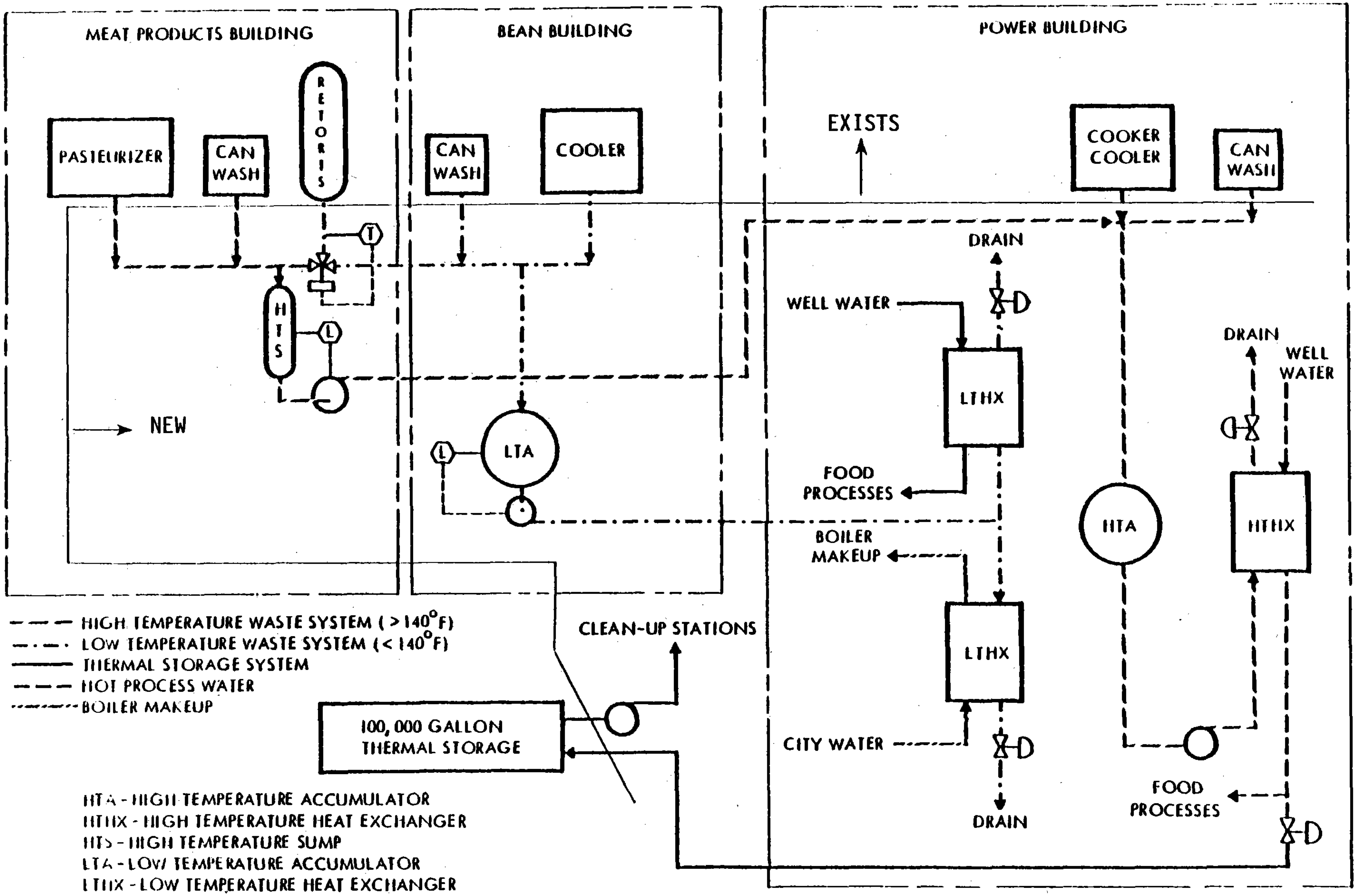
A single-building concept for the Pittsburgh Factory is depicted in Figure 2. In that system, hot waste water flowing at rate W_W will be pumped to a plate heat exchanger where heat will be transferred to cold fresh water circulating at rate W_F. Fresh water circulation from storage will occur whenever hot waste water is available and the storage tank temperature is less than a set-point value. With those conditions satisfied, energy storage will occur if W_F exceeds the process flow rate, W_P. If W_F is less than W_P, all heated fresh water will flow directly to the food processes or to clean-up stations. System performance studies have been completed and a sampling of results is presented in Figure 3. For a particular heat exchanger size (UA = 750,000 Btu/hr-F), the effects of retort cut-off temperature, T_{CO}, and the flow ratio, W_F/W_W, on ROI and annual heat recovery are demonstrated. To the right of the peak in each ROI curve, W_F exceeds W_P and storage capacity is needed which adds a significant new component to the total system cost. This, combined with the diminishing ability of increasing W_F to increase heat recovery, causes the ROI decline after the peak is reached. As indicated in Figure 3, the system design procedure should specify a minimum acceptable ROI and system parameters (UA, T_{CO} and W_F/W_W) will then be selected to yield that ROI with maximum heat recovery.

For the Lake City Factory, two recovery system concepts have been evaluated. The first system, shown schematically in Figure 4, will apply refrigeration waste heat from the blast freezer compressors to heat fresh water for later use during third shift clean-up operations. The system will be located in an existing water distribution system at a point between the softener exit and the first clean-up station take-off. The system heat exchanger will operate as a desuperheater and under normal conditions, vapor will exit the unit with 5 - 10°F of superheat still remaining. The vapor will then flow to the existing condensers to complete the heat rejection process. For low storage temperatures, the circulation pump will energize sending water from storage to the heat exchanger and back to storage. During production hours, heated fresh water will accumulate in storage to be available for local clean-ups during production and for the general plant clean-up when production ends. System performance predictions are presented in Figure 5.

The second Lake City system would apply refrigeration waste heat to warm freezer floor air. Its annual ROI is estimated at 12 - 14%. System details are presented in the final report but they have been omitted from this paper primarily because thermal storage is not a system feature.

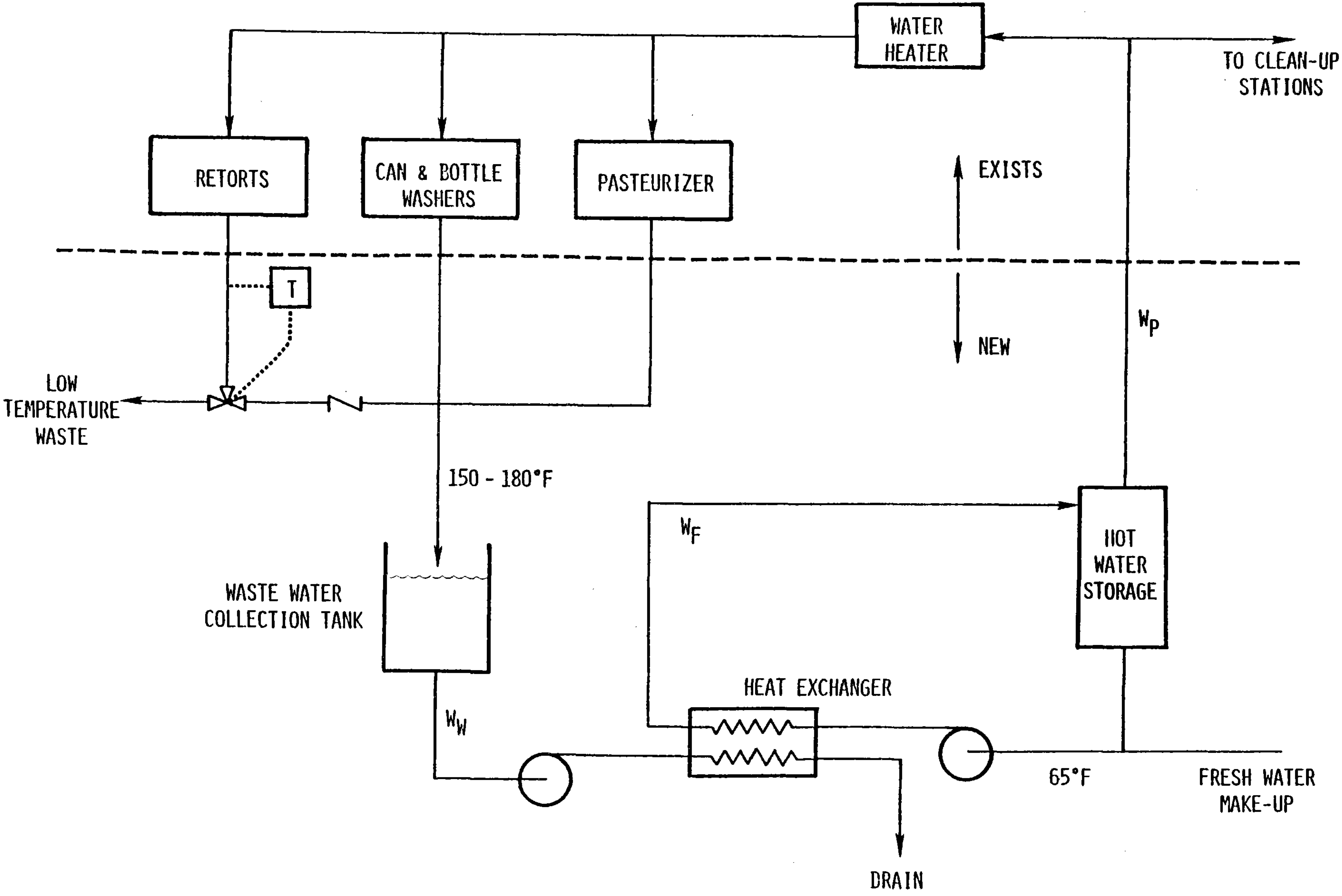
CONCLUSIONS

Based upon the study, it appears that waste heat recovery from certain food processes is feasible and can be performed economically using available, off-the-shelf hardware. Extrapolating results from the Pittsburgh Factory and Lake City studies to the canning and frozen food industries yields projected savings of 6.4×10^{12} Btu annually which corresponds to nearly 0.7% of the total energy currently consumed annually by the entire Food and Kindred Products industry. To further evaluate and optimize recovery system design and to determine actual costs and benefits, demonstration projects should be undertaken. The projects would be publicized widely within the food industry and the results would be used effectively to acquaint the industry with system design and performance.



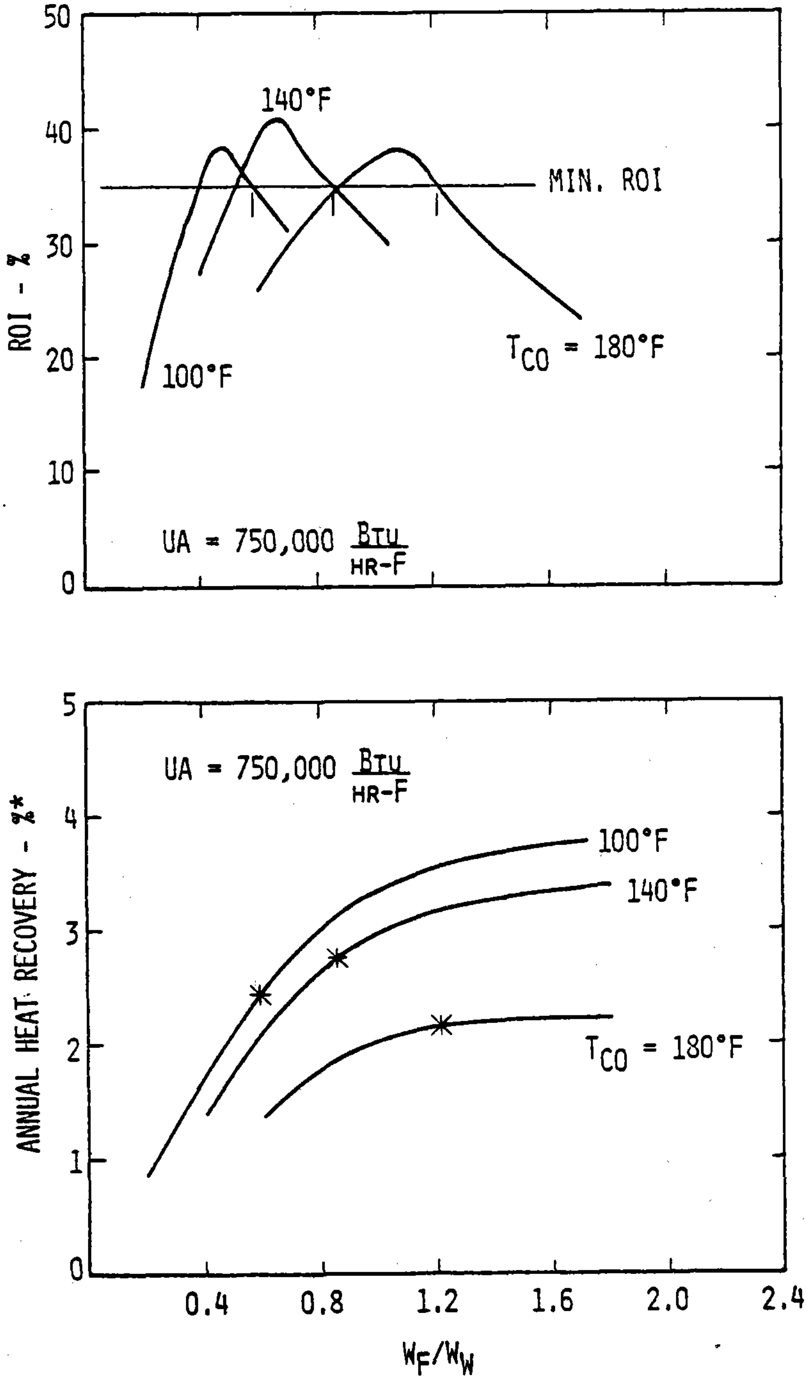
WASTE HEAT RECOVERY SYSTEM — PITTSBURGH FACTORY

Figure 1



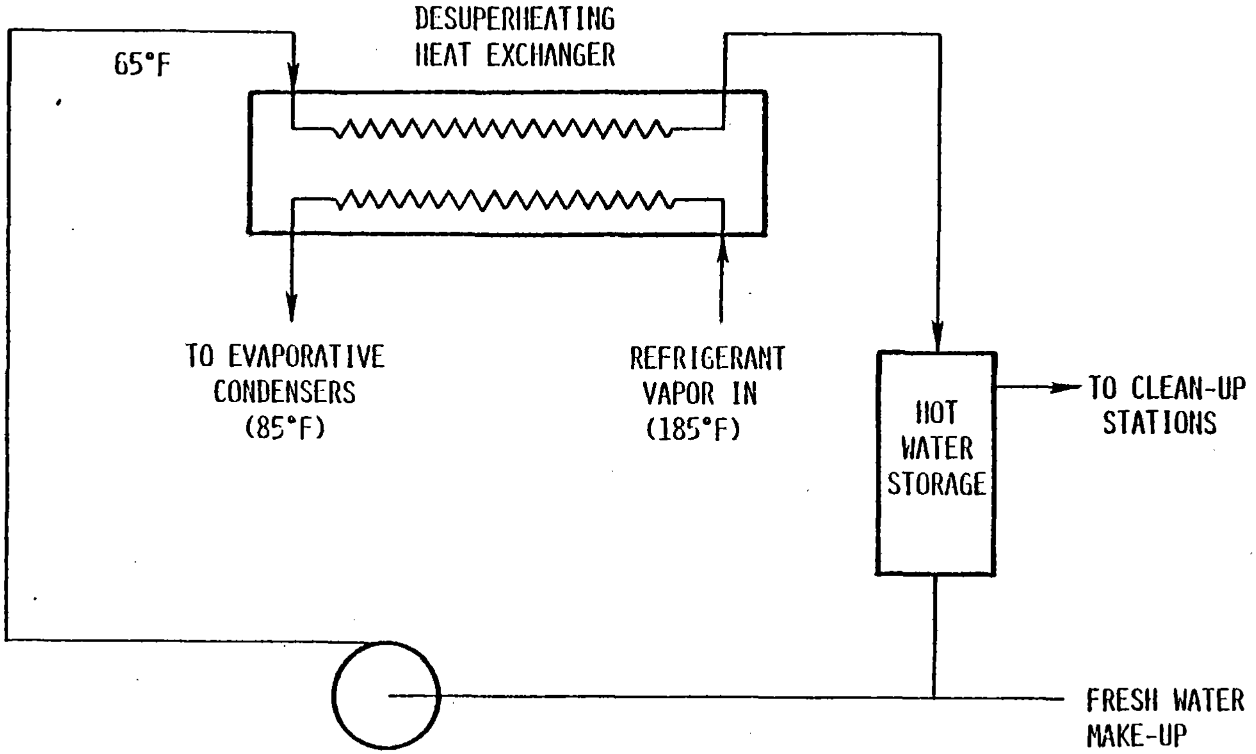
WASTE HEAT RECOVERY SYSTEM — PITTSBURGH FACTORY
MEAT PRODUCTS BUILDING

Figure 2



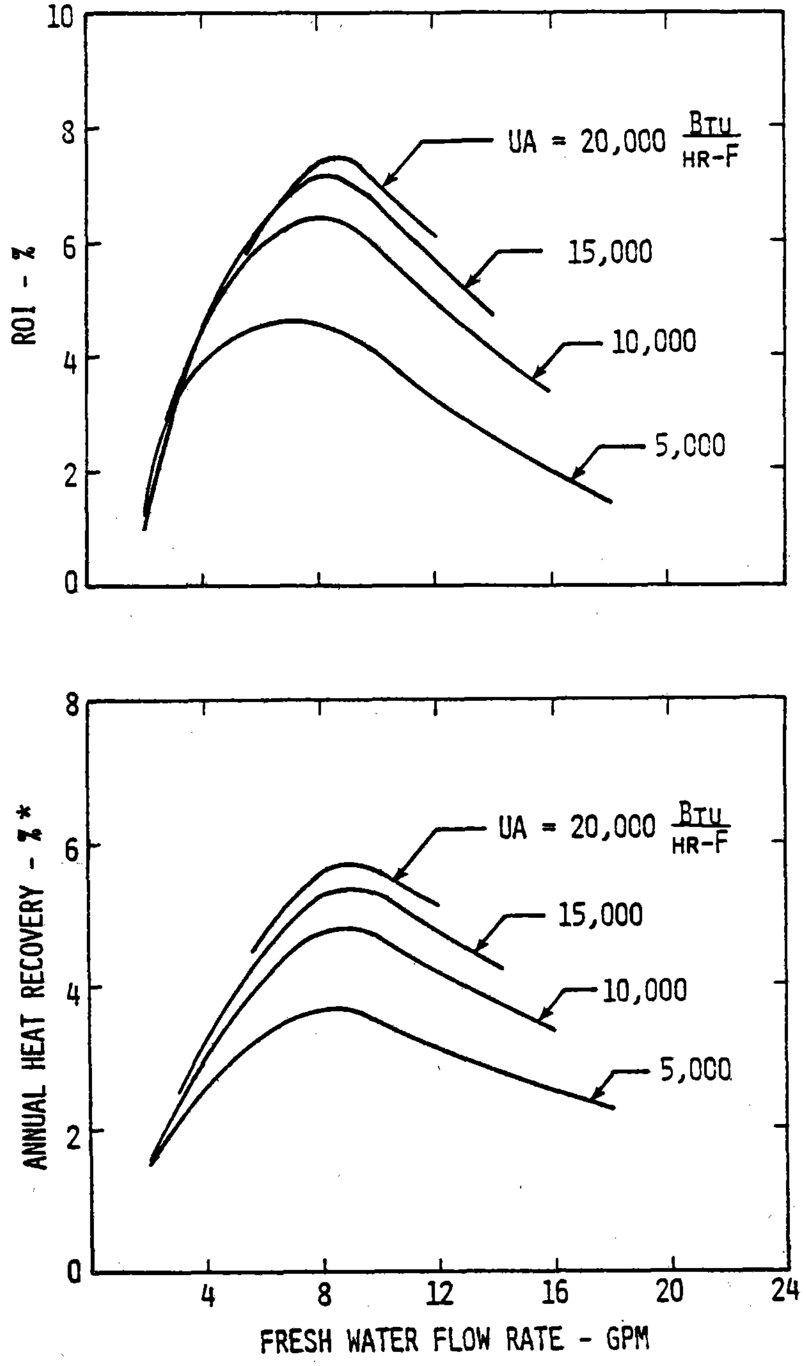
SYSTEM PERFORMANCE PREDICTIONS — PITTSBURGH FACTORY
MEAT PRODUCTS BUILDING
Figure 3

* % of current annual energy consumption



WASTE HEAT RECOVERY SYSTEM — LAKE CITY FACTORY

Figure 4



SYSTEM PERFORMANCE PREDICTIONS — LAKE CITY FACTORY

Figure 5

* % of current annual energy consumption

U.S. DEPARTMENT OF ENERGY

THIRD ANNUAL

THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Application of Thermal Energy Storage to Process Heat and Waste Heat Recovery in the Aluminum Industry

Principal Investigator: L. B. Katter and R. L. Hoskins

Organization:
Rocket Research Company
York Center
Redmond WA 98052

Project Objectives: Identify application of low-temperature energy storage techniques in the primary aluminum smelting industry which provide significant energy conservation at competitive economics. Quantify the projected national savings from these applications.

Project Status:

Aluminum smelting plants reject very large quantities of waste heat ranging from 250°F to 400°F. During the initial phase of this study, a system has been identified that can utilize this waste heat for comfort heating and hot water in nearby communities. Energy is stored as hot water in steel tanks or aquifers. Analytical trade-off studies conducted for a site specific system (Intalco Aluminum Company and Bellingham, Washington) indicate that a single aluminum plant can provide heat for 12,000 equivalent residences and costs less than existing conventional fuels. A follow-on program is being negotiated to conduct detailed analytical, economic, and implementation studies for Bellingham, Washington.

Contract Number: EC-77-C-01-5080

Contract Period: August 30, 1977 through October 30, 1978

Funding Level: $90,000

Funding Source: Department of Energy, Division of Energy Storage Systems

RRC-79-H-232

APPLICATION OF THERMAL ENERGY STORAGE TO PROCESS HEAT AND WASTE HEAT RECOVERY IN THE ALUMINUM INDUSTRY

The rapid rise in the price of imported petroleum initiated in 1974 has precipitated an aggressive effort to develop energy conservation techniques in the United States. Many techniques which have formerly been technically feasible, but economically unattractive, deserve reevaluation against a background of rapidly rising energy costs. In many cases, energy is rejected to the ecosphere at an otherwise usable state simply because a use for this energy does not coincide with the time at which the energy is available. The role of energy storage is to hold such energy in a usable state until the demand for it arises.

The primary aluminum smelting industry is a large user of prime (electrical) energy. Its waste energy streams are usually of low grade, but high magnitude. The very large amount of low grade energy from this industry makes it an attractive subject for conservation.

There are few uses for the low grade energy. Many of these are currently not established needs, i.e., one could develop a use, but the use currently does not exist. Large-scale heated greenhouse complexes, heated aquaculture, alcohol distillation (for gasoline augmentation), and enhanced crop production through open field soil warming are possible low grade energy uses which do not currently exist. Space conditioning for human comfort is the only widely established demand for large quantities of low grade energy. This end use is the only one which affords direct and immediate reduction of the national dependence upon imported oil. Comfort conditioning tends to be strongly cyclic in energy demand on a daily and annual basis. Through energy storage, the utilization of the constant energy source by a variable demand is enhanced.

A team composed of Rocket Research Company (RRC) (as prime contractor) supported by Intalco Aluminum Corporation and Bonneville Power Administration has conducted a detailed technical and economic evaluation of the benefits to be derived from application of thermal energy storage techniques to process heat and waste heat recovery in the aluminum industry.

The Intalco Aluminum plant in Ferndale, Washington, has served as a typical aluminum plant for the study described herein. Intalco supplied detailed operational data on the plant and assisted in the evaluation of plant installation and operation variables. Bonneville Power Administration, the supplier of electrical power to the Intalco plant, supported the program economic analyses with data on electrical power rates and availability on both a local and national level.

The program was initiated with a literature and aluminum industry survey. The literature search and survey were aimed at determining the magnitude of potentially recoverable waste energy on a national basis and in assuring that the Intalco Aluminum plant was typical of those in the industry, so that detailed study results obtained with their plant were valid on a nation-wide basis.

Following the national survey, review was made of the aluminum plant waste heat sources. Based on preliminary engineering and economic analyses, the aluminum waste heat source to be utilized for recovery was selected. A hot water district heating system with hot water storage was established as the baseline application. Test measurements were made at the Intalco Aluminum plant to verify the magnitude of and temperature of the waste energy streams.

Following system definition, a detailed trade study was conducted to arrive at a system configuration which represented an optimum utilization of the waste heat from the Intalco plant (both from technical and economic viewpoints). Preliminary cost analyses were conducted to determine the capital cost of installing the system.

The major waste heat sources in primary aluminum industry are the cast house, anode baking ovens (prebaked anode cell plants), and the electrolytic reduction cells.

The electrolytic reduction cells consume approximately 80% of the energy used in the primary aluminum plants. This figure includes the fuel value of the carbon consumed in the anodes. Considering only the energy used directly in the plant, i.e., natural gas, fuel, and electricity, the reduction cells account for over 90% of the energy consumed within the plants.

While the exact percentage varies widely from plant to plant, approximately 50% of the total energy input to the reduction cells is converted to thermal energy and must be removed from cell to maintain the proper cell operating temperature. Much of this energy is picked up along with the air and pot gases by the primary air pollution control system.

The gas temperature and the amount of energy entrained in the primary air pollution control system gases varies, depending upon the cell type and the plant operating parameters; however, the large majority of available energy ranges from 250°F to 400°F. The total quantity of waste heat available from 30 (of 31) aluminum plants is 7.39×10^9 Btu/hr.

Of the various waste heat recovery applications examined, district heating via hot water shows the greatest fossil fuel replacement potential. The waste heat available and hence the potential for energy savings for the waste heat recovery application is estimated to be over 80% of the total recoverable waste heat from the primary aluminum plant sources.

District space and water heating systems using hot water have been widely used in Europe and elsewhere for many years in both residential and commercial heating applications. The energy sources for these systems have included dedicated boilers, cogeneration with thermal electric plants, and in some limited instances, waste heat recovered from nearby industrial process plants. In the United States, due to the low cost of energy, district heating systems have been primarily for large commercial applications and usually with steam.

The temperatures involved in the hot water district heating system vary from system to system, depending upon somewhat arbitrarily chosen system operating constraints. In Denmark, for example, by law, the maximum temperatures allowed in internal installation are 194°F. The district heating temperatures compare very favorably to the 185 to 300°F temperature, at which bulk of the recoverable energy in primary aluminum plants is available. Figure 1 is a schematic of the system proposed for the Intalco Aluminum Corporation plant with Bellingham, Washington as the user.

Energy storage plays an important role in efficient utilization of the recovered process energy for district heating applications. As aluminum production is essentially a a continuous process, the energy which could be recovered from the process and utilized is produced at a constant rate 24 hours per day, 365 days per year. The energy requirements, however, of district heating systems vary widely on both a daily and seasonal basis. An energy recovery system sized to handle the daily peak demand energy storage would be under-utilized during all but the peaking portion of the demand cycle and would be unable to utilize the excess energy. Incorporation of energy storage in the district heating system reduces the peak energy demand from the source and allows the same energy supply to meet the energy demands of a greater number of users.

The same type of load leveling problems that occur on a daily basis also occur on a seasonal basis. District heating requirements are higher during the winter months than during the summer. Depending upon the location, the average energy demand for the year (yearly load factor) is less than 35% of the peak load.

Six basic types of thermal energy storage systems were examined in detail for use with the district heating system. These storage concepts were: 1) unpressurized hot water in steel tanks (storage temperature less than 212°F); 2) unpressurized hot water insulated heat storage ponds (less than 212°F); 3) moderately pressurized hot water tankage (212 to 250°F); 4) aquifer storage (less than 250°F); 5) unpressurized hot oil tankage; and 6) hot oil/rock hybrids (less than 275°F). Latent heat of fusion and rock bed thermal storage systems were ruled out initially due to their high cost.

Each of the various storage systems was evaluated on the basis of the following criteria:

a. Initial storage system capital cost -- $/Btu of storage (based upon estimates shown in Figure 2).

b. Recurring maintenance cost -- $/Btu/year (based upon initial cost and industrial experience where applicable).

c. State-of-the-art (subjective evaluation of degree to which storage system technology will be developed by the estimated wide-scale implementation date (1985) for district heating system).

d. Safety, reliability, and potential environmental hazards (subjective evaluation).

e. Peak storage temperature capability.

f. Site applicability -- extent to which storage system is site specific, i.e., can only be used at some sites and not others.

g. Energy utilization (evaluation of the effect of storage system on the ability of system to maximize the energy recovery from the aluminum plant, i.e., seasonal storage capability).

h. Storage efficiency (evaluation of the extent to which energy placed in the store can be recovered from the store).

The site applicability of aquifers was based upon a very preliminary study of known aquifers located in proximity to the various aluminum plants. The storage efficiency of aquifer storage systems was based upon efficiency estimates in the literature. The storage efficiencies of the other concepts were based upon detailed heat transfer analysis.

DISTRICT HEATING SYSTEM FLOW SCHEMATIC

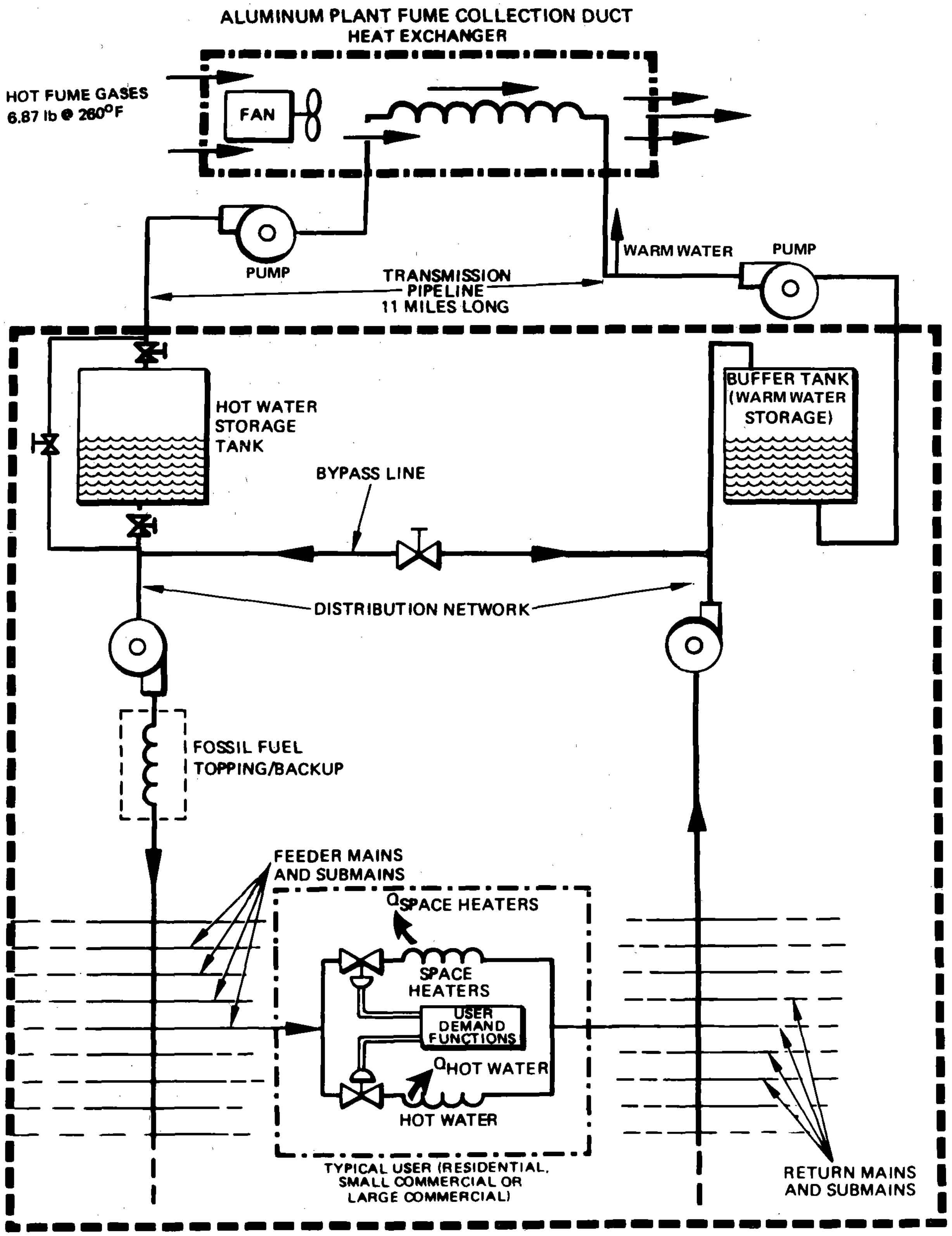


Figure 1

INITIAL STORAGE SYSTEM CAPITAL COST

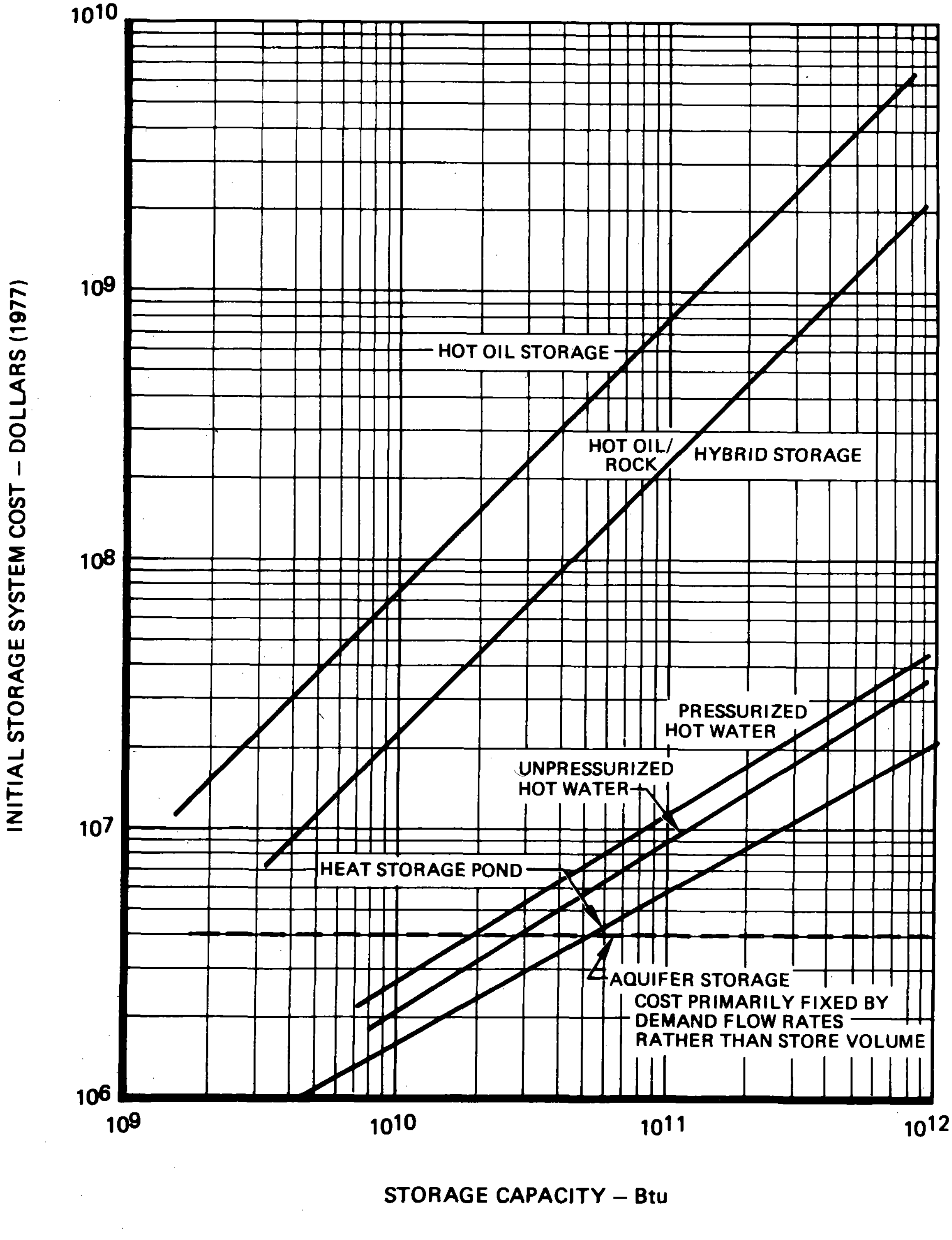


Figure 2

Comparing the three best storage systems (unpressurized hot water in steel tanks, aquifer storage, and heat storage ponds, respectively), the potentially lowest cost storage system is aquifer storage. The limited number of proven applicable sites and the fact that aquifer storage technology has not been reduced to engineering practice, resulted in a decision to base the remainder of this study upon the available technology of unpressurized steel tanks, recognizing that more favorable (economically) systems may result when aquifer technology becomes proven. ORNL is initiating a companion effort to investigate the possibility of developing an aquifer storage system for the Bellingham waste heat system.

Extensive design tradeoff studies have been performed for the example site, Intalco Aluminum Corporation and the surrounding communities of Ferndale and Bellingham, Washington. These tradeoff studies indicate that a heating demand equivalent to 12,000 single-family residences can be supplied by the energy from the Intalco site. Using a 30-year payback criterion (consistent with utility planning practice), the average cost of energy supplied over the system useful life is predicted at one-third the average cost of fossil fuel. The exact distribution of this difference between savings to the customers and profit to the utility is not within the scope of this engineering study; however, the study clearly shows that the utilization of waste energy from aluminum plants is both technically and economically attractive. Figure 3 shows the cost to the user for projected conventional fuels vs. heat from the proposed district heat system. Other economic indices for the 12,000 user case are:

Net capital outlay	\$6.33 x 10^7 (1977 dollars)
Net present value	\$2.56 x 10^8 (1985 dollars)
Average return on investment	62.8%
Internal rate of return	17.1%
Net displaced energy	1.37 x 10^{12} Btu/year

USER ENERGY COST AS A FUNCTION OF TIME

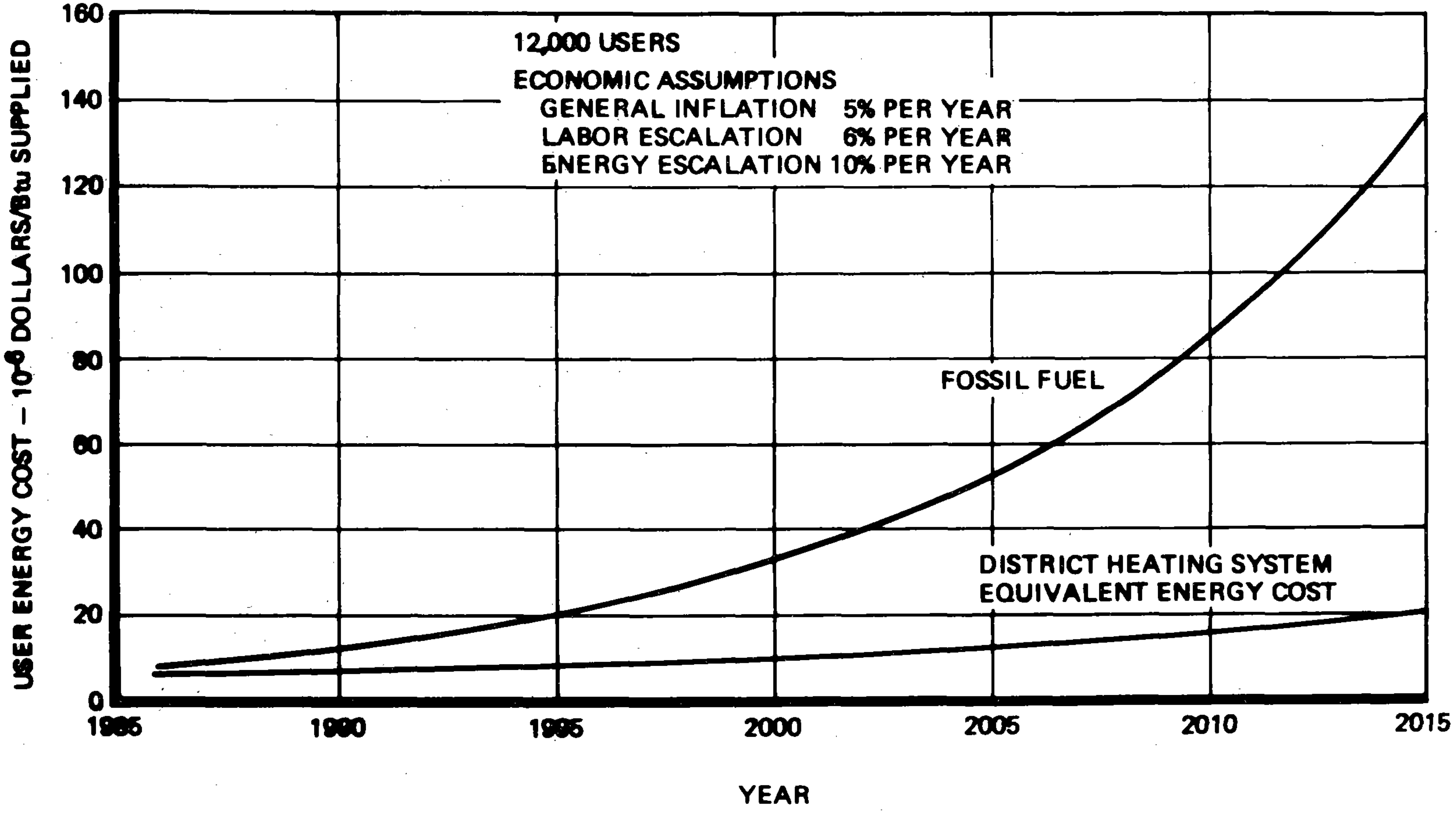


Figure 3

U. S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Low Temperature Thermal Storage in Aquifers: Environmental Assessment

Principal Investigator: Elly K. Triegel

Organization: Environmental Impact Section, Energy Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830
Telephone: (615) 483-8611, ext. 3-1423

Project Objectives: To determine the environmental research and documentation needs of the thermal storage in aquifers project, including preparation of the necessary programmatic environmental impact document.

Project Status: The goals of this environmental evaluation are to:

(1) determine the scope of the individual projects involved,
(2) identify the hydrologic, ecological, aesthetic, societal, economic, and health and safety issues to be addressed and the research needs of those issues,
(3) identify the documents required by the NEPA process,
(4) identify actions to reduce or mitigate environmental impacts, and
(5) promote adequate discussion and interchange of environmental information among industry, government, and public groups.

The project status is as follows:

(1) current projects funded by DOE and European programs have been reviewed with respect to their possible environmental impacts,
(2) concerns which may require additional characterization or research have been identified,
(3) a document describing the environmental requirements of the project has been prepared,
(4) expected results in FY 1979 will be the preparation of the necessary programmatic environmental impact document.

Contract Number:

Contract Period: FY 1978, continuing

Funding Level: $75,000

Funding Source: Department of Energy, Division of Energy Storage Systems

Environmental Aspects of the LTTES Thermal Storage in Aquifers Project

INTRODUCTION

The environmental responsibilities of the LTTES aquifer storage project are centered in the NEPA (National Environmental Policy Act) requirements for full consideration of environmental impacts in the decision-making process. Specific documents (environmental impact statements and assessments), research by DOE or its contractors and environmental reports (ER) by the applicant are needed to fully delineate potential impacts. Other requisite environmental reviews as outlined in Federal laws and regulations are generally coordinated with the NEPA procedures.

ENVIRONMENTAL RESEARCH

The research requirements inherent in the consideration of environmental impacts may occur at any point in the NEPA process where unresolved issues arise. In general, consideration of such requirements should begin early in the project since the results may be needed for completion of the Environmental Impact Statement (EIS) or Assessment (EA). Further work may be necessary later if the resolution of the issue is found incomplete or if new, unanticipated problems develop. Usually, it is only possible to plan the first stages of the research program, particularly in exploratory area where the underlying cause and effect relationships are not known. The need for further work would then depend on the outcome of the initial research.

Environmental concerns which are likely to be of particular importance in the aquifer storage project are summarized in Table 1 and discussed below. It is the responsibility of the funding office in DOE, in conjunction with the DOE environmental branch, to identify, fund, and oversee the required research work.

The areas of potential environmental concern in aquifer storage cover a wide range of fields, but are primarily centered in water quality and hydrologic impacts. Consideration of those issues is necessary to ensure acceptable environmental design and conformance with existing regulations, and to reduce the impacts on the environment.

Water Quality

Water quality in the aquifer is currently protected by Federal drinking water standards and the EPA regulations on underground injections. Quality may be affected by drilling or alterations due to temperature changes. Interactions among the various chemical components may produce unanticipated results, even when only one parameter is altered. Introduction of oxygen could encourage bacteria growth in the aquifer, which may in turn affect the pH and sulfide content of the groundwater. Chemical additives have the potential to react with clays in the formation, altering the balance of cations in the water or the hydraulic properties of the aquifer. Temperature changes affect solubilities of the aquifer's minerals, introducting new species of dissolved solids into the groundwater. Secondary effects from these and other reactions may also occur.

Characterizations of these reactions may be approached by several means. Past research and experience in the fields of geohydrology, petroleum engineering and geothermal resources has produced a great deal of information which may be of use in the aquifer storage project. However, some of the chemical conditions may not have been investigated, particularly those of warm water temperatures coupled with shallow depths and low pressures. In such cases, original research may be needed on a laboratory or field experiment basis. Careful monitoring in the initial aquifer storage projects would add to the research results and provide site specific data needed for a complete evaluation.

Hydrology

The hydrologic aspects of thermal storage in aquifers are closely related and interact with the chemical effects. Chemical precipitation and solutioning, bacterial growth and clay:water interactions may radically alter the flow regime in the aquifer. Conversely, the hydrology of the system to a large extent controls the path of contaminant migration and resulting chemical concentrations.

The hydrology of the aquifer must be related to the site specific characteristics of the formation. Generalized information on thermal and hydraulic behavior of aquifers can be developed from past work in reservoir analysis and incorporated in computer models. Coupled with site data from monitor wells, these models may be used to predict general flow patterns, water levels, and temperature distributions. This combination of field monitoring and computer modeling is useful in assessing the potential for subsidence, disturbance of surface water habitats, thermal pollution, and local well yield alterations. Unanticipated impacts, such as leakage through the cap rock or through improperly designed wells, must be detected through frequent monitoring of wells at the site.

Table 1. Possible environmental concerns in the thermal storage in aquifers project.

Physical Environment

Water Quality

- pollution of aquifer by chemical additives or bacterial growth
- contamination of surface water through accidental spills or via groundwater
- leaching of minerals, affecting water quality
- inadvertant contamination of nearby heavily used aquifer through leaky barriers or faulty well design
- thermal pollution of ground and surface waters

Hydrology

- chemical or thermal alteration of aquifer permeability, affecting yields
- interference with nearby users of aquifer
- alteration of groundwater levels, affecting agriculture, river flows, wetlands

Atmospheric

- effect of cooling towers (in cold water storage) or escape of steam to atmosphere (hot water storage)

Geology and Topology

- subsidence of land surface due to pumping
- induced seismicity in faulted areas

Ecological

- effect on aquatic life due to alteration of water levels, water temperatures

Human Environment

Socioeconomic

- public resistance to possible drinking water contamination
- allocation of groundwater, particulary during droughts

Safety

Occupational

- accidental spills of high-temperature fluids or steam under pressure

ENVIRONMENTAL REPORTS AND APPLICANT RESPONSIBILITIES

Environmental reports are generally supplied by the applicant and provide the information necessary for the preparation of assessments and impact statements. The level of detail required is commensurate with the complexity of the problem and the significance of the impact. Other applicant responsibilities in the NEPA process include: (1) site specific studies, primarily in the context of data gathering, to determine the impacts of the proposed action; (2) consultation with Federal, regional, state, and local agencies to ensure that all concerns are identified; (3) notification to DOE of any involvement by other Federal agencies; (4) submission of applications for approvals in time to allow complete environmental review; and (5) postponement of any actions which would cause significant environmental impacts or which would foreclose alternatives prior to the EA/EIS process.

NEPA DOCUMENTATION AND DOE RESPONSIBILITIES

In addition to environmental research, DOE has responsibility for issuing any required NEPA documents for programs or projects it funds. This responsibility entails providing guidance in ER preparation, verifying the information and analyses provided in the ER, determining the NEPA requirements for the project and independently preparing the necessary documents. In general, the NEPA procedures should begin prior to any action which would significantly affect the quality of the environment or narrow the range of alternative actions. The timing should insure that the information gathered will provide a useful contribution to the decision-making process, but still be late enough in the planning to permit adequate and accurate analysis of the impact.

Environmental Assessments may require six to eight months for the entire process, and impact statements from 16 to 18 months. Unless a negative determination has been made by the DOE Assistant Secretary for the Environment, it should be assumed that an EIS will be required prior to any major policy decision or action in the project.

Several major factors may be considered in ranking the urgency of the environmental work for the various aquifer storage projects:

(1) Timing. Detailed consideration should be given to those projects which:

(a) have major decision points, precluding further options, within the next 1.5 years; or

(b) are scheduled for full scale demonsrations within the next three years; or

(c) are expected to be commercialized with five years; or

(d) are expected to have environmental concerns which require resolution times greater than the estimated impact emergence time.

(2) Adverse Effects. If signficant adverse effects are anticipated or if they cannot be ruled out on the basis of current information, and EA at the least is required.

(3) Magnitude. This includes consideration of the commercial potential, anticipated application, cummulative effects, site impacts, and the extent of DOE committment in the project.

(4) Controversy. Assessing the significance of an impact is to some degree dependent on the reaction of the public, industry, and government. Projects which have been challenged in the past, or are similar to those which have, may be more susceptible to NEPA review.

Environmental Assessments

An EA is generally required for proposed DOE actions when it is unclear whether a complete impact statement is required. As such, its main function is to present information only in sufficient detail to allow determination of the necessity of an EIS. It should contain an adequate description of the proposed action and the existing environment, an assessment of the probable impacts, and a brief description of reasonable alternatives. The format is similar to that of the EIS. DOE then evaluates the Environmental Assessment and decides whether to proceed with the EIS or prepare a negative determination (ND).

Environmental Impact Statements (EIS)

If it is determined by the Assistant Secretary for the Environment that the project is a major action, significantly affecting the environment, an EIS will be required (Section 102(2)(c) of NEPA). The impact statement should include the following information:

(1) a summary of the conclusions, any unresolved issues and the relative merits of alternatives;

(2) a description of the proposed action;

(3) characterization of the existing environment to be affected;

(4) environmental impacts of the proposed action, including mitigating actions and risks;

(5) unavoidable adverse environmental effects;

(6) irreversible and irretrievable commitments of resources;

(7) the relationship between short-term uses and long-term productivity; and

(8) alternatives. A more complete description of the contents of an EIS is given in 10 CFR, Section 1021.41.

A programmatic EIS or EA may be required in the thermal storage in aquifers program to assess the environmental impacts generic to this series of DOE projects. Cumulative effects, impacts resulting from the anticipated commercial deployment of the technologies, and any major uncertainties in the impacts should be considered in the programmatic work. Subsequent individual projects may still require NEPA documentation of environmental impacts are thought to be significant and are not covered in the programmatic EIS/EA.

In addition to preparation of the EIS, DOE has the responsibility (usually through the funding office) to inform the public at various stages in the project and to hold public hearings if necessary.

THE DOW CHEMICAL COMPANY
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MACRO-ENCAPSULATION OF HEAT STORAGE PHASE-CHANGE MATERIALS

PRINCIPAL INVESTIGATOR: George A. Lane, Telephone (517) 636-0292

OBJECTIVES: 1) to assess the technical and economic feasibility of encapsulated phase change materials (PCM's) for storing heat in residential solar energy systems, and 2) to develop and evaluate such encapsulated phase change materials.

TASKS:

1. Materials selection, including a limited literature search, selection of candidate phase change materials, and selection and characterization of encapsulating materials.
2. Procurement of phase-change and encapsulating materials, encapsulation studies, and testing of the encapsulated materials.
3. Preliminary design and economic evaluation of a residence-sized heat storage sub-system.

All tasks have been completed.

CONTRACT NO.: EY-76-C-05-5217

CONTRACT PERIOD: 9-29-76 to 9-6-78

CONTRACT AMOUNT: DOE $175,000

PREPARED FOR: Third Annual TES Contractors' Information Exchange Meeting, December 5-6, 1978, Springfield, Virginia.

At the Second Annual TES Contractors' Meeting a report[1] was presented on the initial phases of this project: selection of phase change materials and encapsulant media, encapsulation studies, materials compatibility, and storage unit modelling. The balance of the effort on this program is now complete, and is summarized here.

Table I lists the PCM's and encapsulants which were tested in a sub-scale thermal storage unit. ASHRAE standard 94-77, *Methods of Testing Thermal Storage Devices Based on Thermal Performance*, was used as a guide in the design of this thermal battery. Air was used as the heat transfer fluid. In addition to the four storage units of Table I, a double-zone heat battery containing $CaCl_2 6H_2O$ encapsulated in steel aerosol cans and $Mg(NO_3)_2 6H_2O/NH_4NO_3$ eutectic encapsulated in R-2 Retort Film pouches, was assembled and tested.

TABLE I

Encapsulated Phase Change Materials Tested

Phase Change Material	M.P., °C	ΔH, Cal/g	Cost, ¢/lb	ΔH/Cost, Kcal/¢	Encapsulant
$Mg(NO_3)_2 \cdot 6H_2O$	89	36	15 (est.)	1.09	Drawn Steel Aerosol Can
Urea + NH_4Br	76	36	30	0.54	Polypropylene Bottle
$Mg(NO_3)_2 \cdot 6H_2O$ + NH_4NO_3	52	30	10	1.36	R-2 Retort Film Pouch
$CaCl_2 \cdot 6H_2O$	27	46	5	4.17	High Density Polyethylene Bottle

Thermal battery testing, after aging, involved monitoring the response in the outlet air temperature to a step change, normally 35°C, in the inlet air temperature, bracketing the fusion temperature of the PCM. In analyzing our results, data were not used above (below) an arbitrary cutoff temperature, the "maximum (minimum) charge (discharge) temperature". These temperatures usually were selected halfway between the inlet air temperature and the PCM melting point. Table II shows the upper and lower set points for the inlet air and the cutoff temperatures for each of the thermal batteries tested. The discharge rate at the maximum or minimum discharge temperature was adopted as the "design rate", q_C or q_D, and used in heat storage sub-system design work.

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[1] "Macro-Encapsulation of Heat Storage Phase Change Materials," Second Annual TES Contractors' Information Exchange Meeting, Sept., 29 and 30, 1977, Gatlinburg, Tennessee.

TABLE II

Upper and Lower Air Temperatures for the Five Thermal Batteries Tested

Thermal Battery	Melting Point °C	High Inlet Air Temp. °C	Maximum Charge Temp. °C	Low Inlet Air Temp. °C	Minimum Discharge Temp. °C
$CaCl_2 6H_2O$, HDPE Bottles	27	44.5	35.75	9.5	18.25
$Mg(NO_3)_2 6H_2O$, Aerosol Cans	89	106.5	94.83	71.5	77.33
$Mg(NO_3)_2 6H_2O/NH_4NO_3$, Plastic Film Pouches	50	67.5	58.75	32.5	41.25
Urea/NH_4Br, Polypropylene Bottles	76	95.0	85.5	60.0	68.0
Double-Zone	27/50	61.0	49.75	16.0	21.6

Figures 1 and 2 show charging and discharging data for the tests on $CaCl_2 6H_2O$ in HDPE bottles. Similar curves were obtained for each of the other PCM's studied.

The areas between the inlet and outlet temperature profiles over the test times of charging and discharging were used to determine the charge and discharge capacities, using the following equations:

$$CC = \dot{m}\, C_{tf} \left(\int_o^{\tau_c} (T_{in} - T_{out})\, dt - L \int_o^{\tau_c} \left(\frac{T_{in} + T_{out}}{} - T_a \right) dt \right)$$

$$DC = \dot{m}\, C_{tf} \left(\int_o^{\tau_d} (T_{out} - T_{in})\, dt + L \int_o^{\tau_c} \left(\frac{T_{in} + T_{out}}{2} - T_a \right) dt \right)$$

Where,

CC = Charge capacity, KJ.
DC = Discharge capacity, KJ.
$\dot{m}$ = Air mass flow rate, Kg/hr.
C_{tf} = Air specific heat, KJ/Kg °C.
T_{in} = Inlet air temperature, °C.
T_{out} = Outlet air temperature, °C.
T_a = Ambient temperature, °C.
L = Heat loss coefficient.
τ_c = Charging test time, hr.
τ_d = Discharging test time, hr.

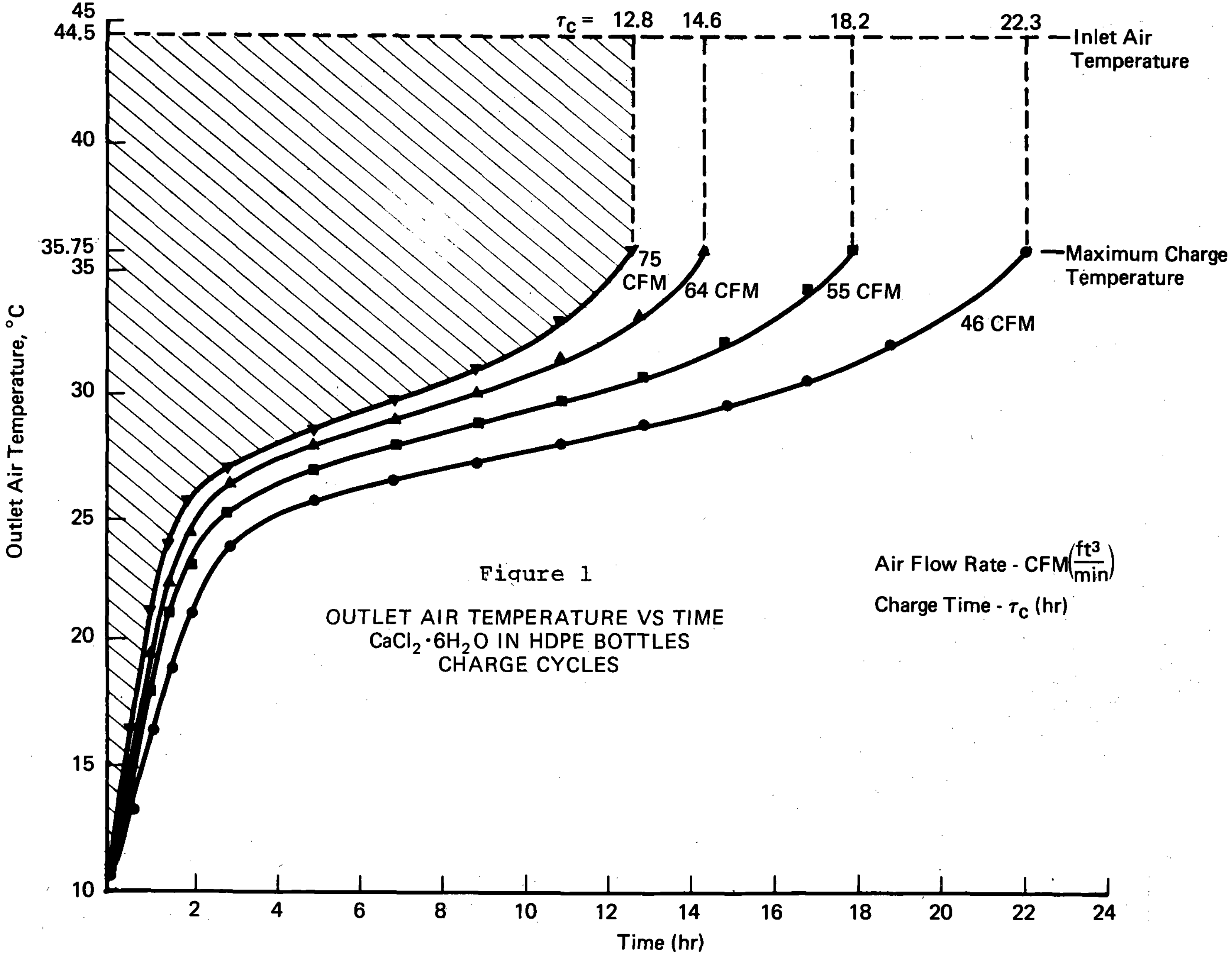
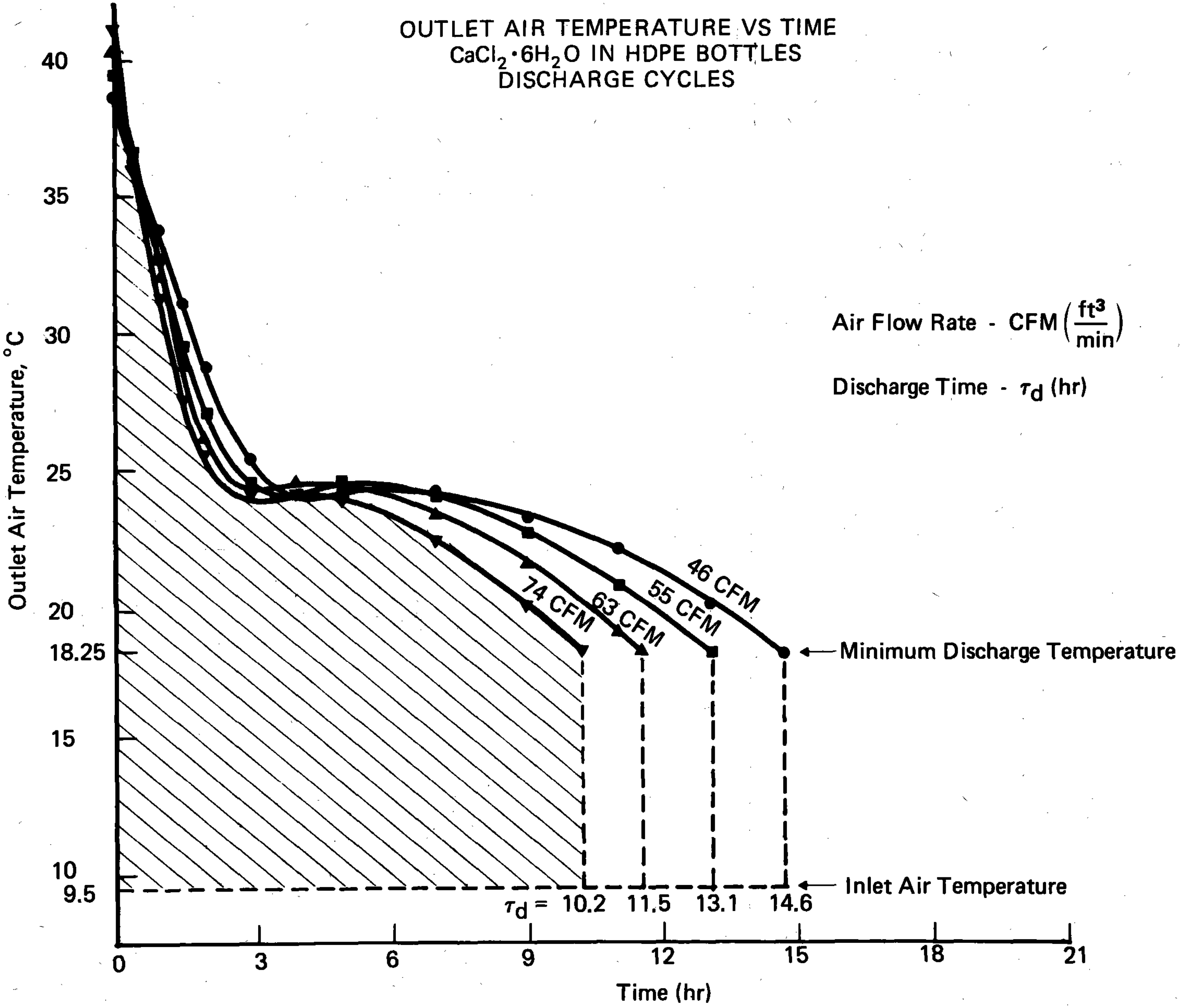


Figure 1

OUTLET AIR TEMPERATURE VS TIME
$CaCl_2 \cdot 6H_2O$ IN HDPE BOTTLES
CHARGE CYCLES

Figure 2

OUTLET AIR TEMPERATURE VS TIME
$CaCl_2 \cdot 6H_2O$ IN HDPE BOTTLES
DISCHARGE CYCLES



This method of calculating capacities differs from that recommended in ASHRAE Standard 94-77, but gives much more realistic values.

Using the latent heat of fusion of the PCM, its solid and liquid heat capacities, and the sensible storage capacity of the storage unit structure, theoretical heat storage capacities were calculated for each of the five thermal batteries tested. Figure 3 gives a comparison for $CaCl_2 \cdot 6H_2O$ of the measured capacities with these theoretical values. Figure 4 shows the percent of the theoretical capacity achieved in our tests. Similar curves were generated for each of the other PCM's tested. For PCM's melting higher than $CaCl_2 6H_2O$, larger heat loss corrections were necessary. In the case of $Mg(NO_3)_2 6H_2O$ (m.p. 89°C), heat loss was so severe that the cutoff temperatures had to be adjusted downward.

Table III compares the results obtained with the different thermal batteries. After correction for heat losses, each test configuration stored and discharged a high percentage of the theoretical amount. An exception is the urea/NH_4Br battery, which was inferior to the other batteries in the number of heat transfer units. This PCM also showed partial segregation of the eutectic at the end of the test.

TABLE III

Storage Test Results for Thermal Batteries

PCM	PCM Weight (Kg)	Air Flow (Ft^3/min)	Capacity CC, DC (MJ)	Capacity Percent of Theory (%)	Design Rate q_C, q_D (MJ/hr)
$CaCl_2 6H_2O$, HDPE Bottles	97 97	46 46	24.4 CC 22.7 DC	101 91	0.73 0.84
$Mg(NO_3)_2 6H_2O$, Aerosol Cans	100 100	61 61	21.7 CC 22.1 DC	98 97	1.09 0.62
$Mg(NO_3)_2 6H_2O$/ NH_4NO_3, R-2 Film Pouches	86 86	59 59	17.1 CC 17.7 DC	98 99	0.91 1.01
Urea/NH_4Br Polypropylene Bottles	93 93	55 54	18.7 CC 14.6 DC	93 72	0.82 0.76
Double Zone[a]	81/29 81/29	91 90	28.6 CC 27.1 DC	90 85	1.80 1.04

[a] $CaCl_2 6H_2O$ in Aerosol Cans (81 Kg) and $Mg(NO_3)_2 6H_2O/NH_4NO_3$ Eutectic in R-2 Retort Film Pouches (29 Kg).

Figure 3

CAPACITY (ENERGY) VS.
AIR FLOW RATE
$CaCl_2 \cdot 6H_2O$ IN HDPE BOTTLES

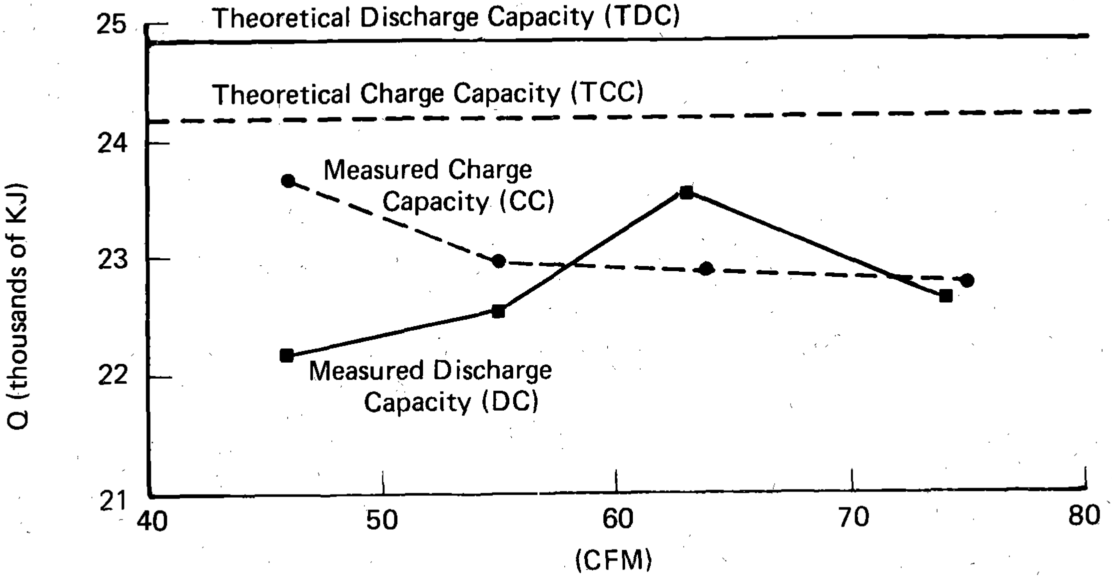
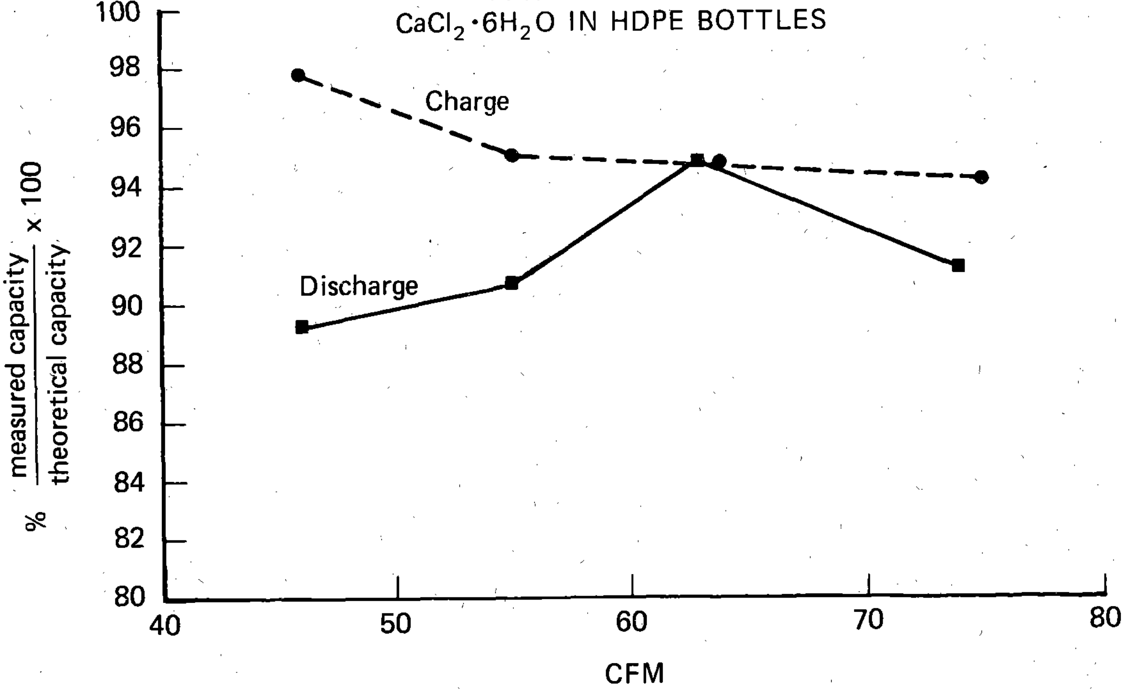


Figure 4

% CAPACITY (ENERGY) VS.
AIR FLOW RATE
$CaCl_2 \cdot 6H_2O$ IN HDPE BOTTLES



The multi-zone heat storage unit has several potential advantages. Higher grade heat can be collected during periods of availability and stored in a higher-melting zone, then lower grade heat can be collected over a wider period in lower-melting zones. The higher grade energy can then be used in applications needing a higher temperature. The low grade storage can be used as a preheat or for uses with less stringent temperature requirements, without degrading the high temperature store. Collection can proceed for a longer period of the day and under more overcast conditions. Heat transfer fluid returns to the collector from the lower temperature storage zone, cooling the collector and increasing the efficiency. Operation of the two-zone unit under test conditions was qualitatively as expected. Under charge, both PCM's began to melt at about the same time and were fully charged in roughly the same time frame. The design rate was higher than for the test unit containing only $Mg(NO_3)_2 6H_2O/NH_4NO_3$ eutectic, and was reached at a lower temperature. On discharge, the high temperature zone was exhausted well before the first bottles of the low temperature PCM. The low temperature zone seems capable of supplying heat at a "set back" level for a considerable time period.

On the basis of our test results and further computer modelling of storage sub-systems, six solar space heating concepts were evaluated for performance and economics in a northern midwest climate:

A) Passive system using encapsulated $CaCl_2 6H_2O$ storage and conservatory collector.

B) Forced air system with $CaCl_2 6H_2O$ storage battery and conservatory collector.

C) Hybrid active/passive system with $CaCl_2 6H_2O$ storage battery and conservatory collector.

D) Forced air system with $CaCl_2 6H_2O$ storage battery and conservatory collector and parallel heat pump.

E) Forced air system with $Mg(NO_3)_2 6H_2O/NH_4NO_3$ storage battery and flat plate collectors.

F) Forced air system with double zone storage battery ($CaCl_2 6H_2O$ and $Mg(NO_3)_2 6H_2O/NH_4NO_3$) and flat plate collectors.

Table IV summarizes projected capital and operating costs of these six concepts, along with comparable values for traditional heating schemes. The solar fraction of the heating load was estimated from available system modelling programs. Though these projections have considerable uncertainty, certain conclusions

TABLE IV

Economics of Various Home Heating Systems

	Heating System	Capital Cost	Fraction of the Heating Load Solar	Utility Costs $/Year A	Yearly Mortgage Insurance and Maintenance $/Year B	Operating Cost $/Year A + B
A.	Passive Solar $CaCl_2 \cdot 6H_2O$ Storage Conservatory Collector	7,606	0.66	479	939	1,418
B.	Forced Air Solar $CaCl_2 \cdot 6H_2O$ Storage Conservatory Collector	6,962	0.50	704	859	1,563
C.	Hybrid Solar $CaCl_2 \cdot 6H_2O$ Storage Conservatory Collector					
D.	Forced Air Solar $CaCl_2 \cdot 6H_2O$ Storage with Parallel Air-to-Air Heat Pump Conservatory Collector	8,762	0.50	493	1,081	1,574
E.	Forced Air Solar $Mg(NO_3)_2 \cdot 6H_2O/NH_4NO_3$ Eutectic Storage Flat Plate Collectors	11,052	0.46	760	1,364	2,124
F.	Forced Air Solar Double Zone Storage with Night Setback Flat Plate Collectors	10,819	0.54	583	1,335	1,918
G.	Forced Air Solar Rock Storage Flat Plate Collectors	9,980	0.51	690	1,232	1,922
H.	Air-to-Air Heat Pump	4,200	0.0	986	518	1,504
I.	Electric Resistance Heat	2,400	0.0	1,408	296	1,704
J.	Oil Fired Forced Air	3,000	0.0	540	370	910
K.	Natural Gas	3,000	0.0	360	370	730

can be drawn. Oil and gas heated homes are less expensive to build and operate than solar homes in this climate, if all costs are considered. Solar homes with conservatory collectors are competitive with resistance electric or heat pump equipped houses. Solar homes with flat plate collectors are considerably more expensive to build and operate.

System B, the forced air heating system with $CaCl_2 6H_2O$ storage battery and conservatory collector, was selected for system design work and solar house planning. The plan chosen incorporates solar collection into the living space, as in a passive system, yet maintains better the comfort level of active solar designs. Heat collected is transferred via an air stream to storage and from there to the rest of the heated space. The vertical glazing system is covered with movable insulation at night and during cloudy periods to minimize heat loss, and may also be used to control overheating when the rate of collection exceeds the storage rate and the load.

Figure 5 shows the storage battery design chosen. High density polyethylene pipe was chosen as encapsulant to withstand the pressure variations caused by freeze-thaw cycling, offer a positive moisture vapor barrier to assure compositional stability of the PCM, and be compatible with $CaCl_2 \cdot 6H_2O$. The storage battery contains 5220 pounds of PCM, storing 360,000 BTU with a design rate of 9,100 BTU/hr. The heating load was assumed to be 527 BTU/hr °F, and the collector area 650 ft^2.

Figure 6 is a floor plan of the solar home. The house is a bi-level design, built ideally on a lot sloping from north to south. The main entrance is at a stair landing midway between the first and second floors. The livingroom, which acts as the second stage of the collector, has a cathedral ceiling design. This is an attractive architectural feature, and also adds height to the hot air collection duct to allow additional thermal stratification in the conservatory. The hot air collection duct is also used as the cold air return for the heating system. The hot air ducts act as the conservatory air supply for heat collection. An outside vent is used to avoid overheating early and late in the heating season. The entire south wall of the house is glazed vertically for solar collection.

Six insulating shades are required, two single story shades in each of the wings, and two double story shades in the livingroom/family room area. To maximize collection efficiency, each shade will be controlled separately. For example, east shades might be open from mid-morning into early afternoon, and west shades from late morning to late afternoon.

This design is intended to demonstrate the best features of both active and passive solar heating systems. It uses a fan to transfer heat to and from storage, while it uses direct

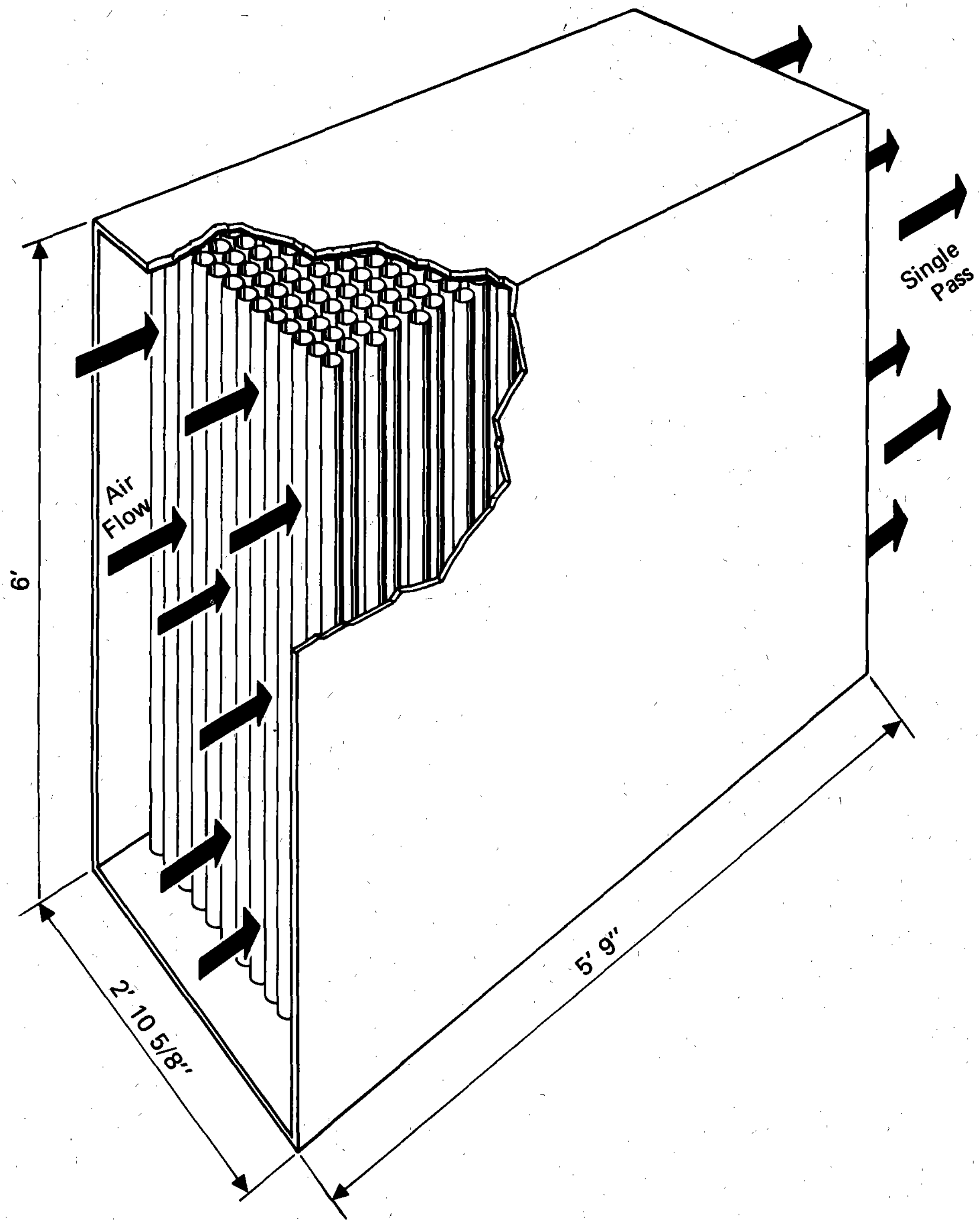


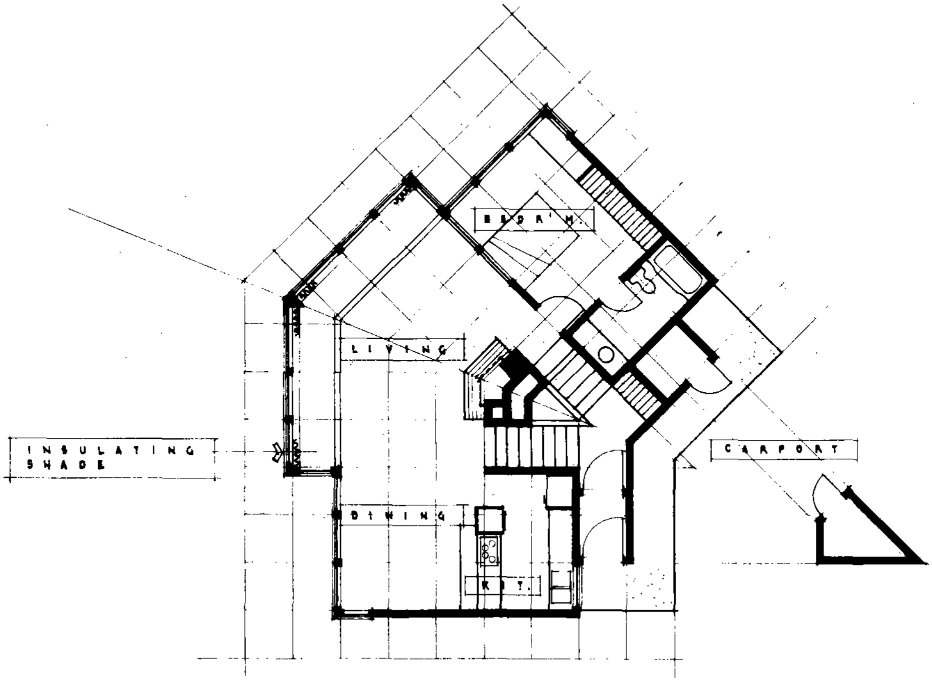
Figure 5

FULL-SCALE STORAGE UNIT
CALCIUM CHLORIDE HEXAHYDRATE
ENCAPSULATED IN HDPE CYLINDERS

Figure 6

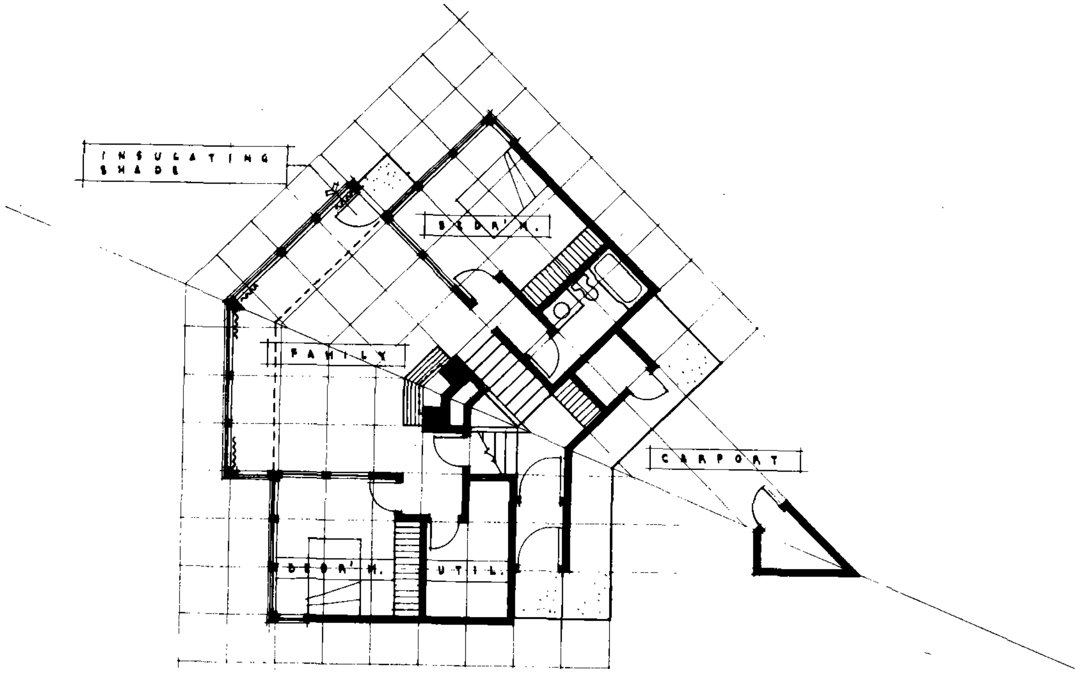
Floor Plan of

Solar Home



UPPER FLOOR PLAN

1/8" = 1'-0"



LOWER FLOOR PLAN

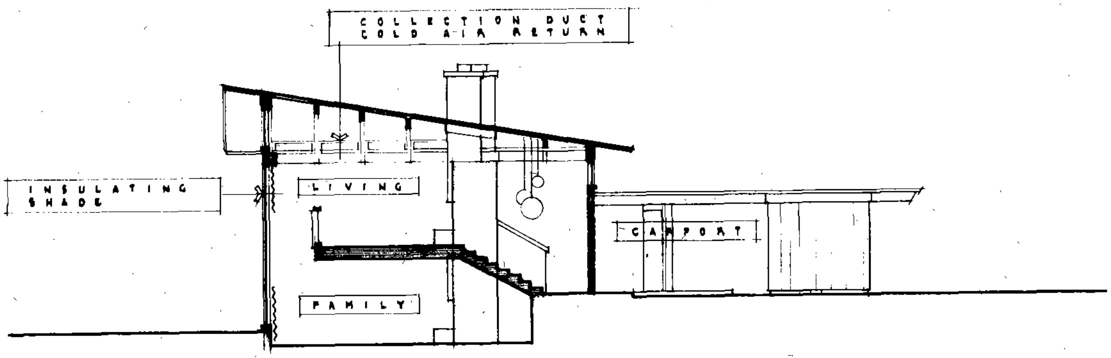
1/8" = 1'-0"

AREAS :

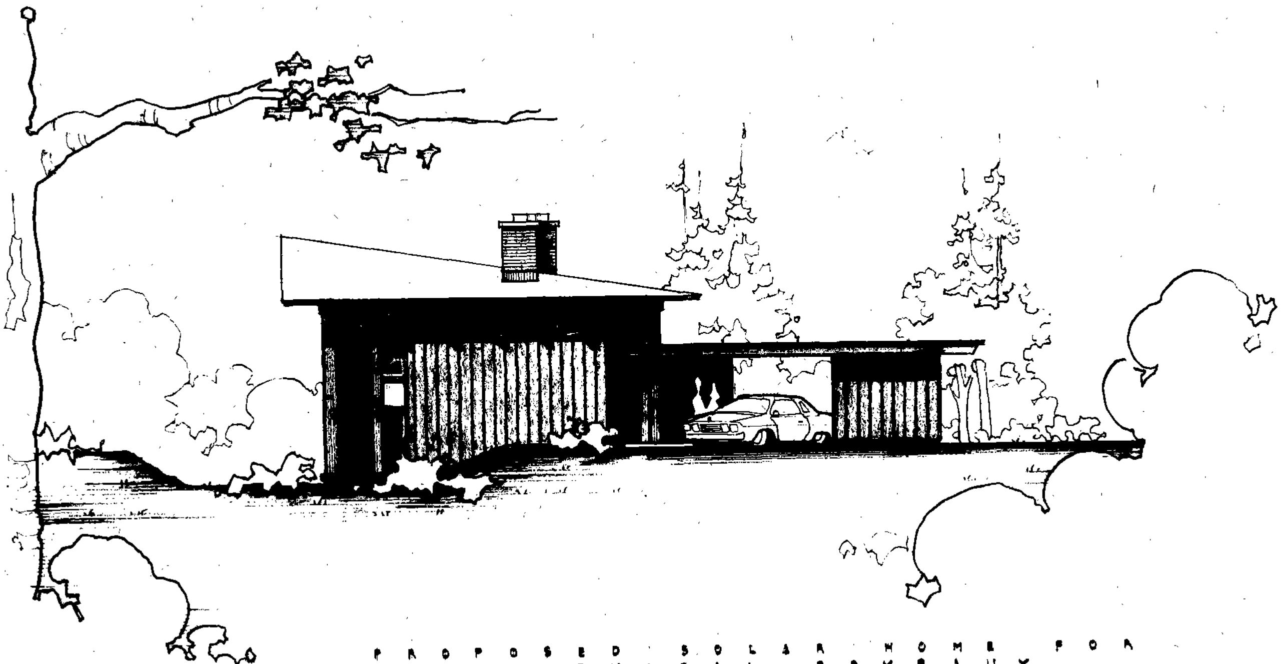
UPPER FLOOR PLAN	:	850 □	
LOWER FLOOR PLAN	:	1000	
		1850	LIVING AREA
		250	CARPORT
TOTAL	:	2100 □	

Figure 6 (Part 2)

Plan of Solar Home



SECTION
1/8" = 1'-0"



PROPOSED SOLAR HOME FOR
DOW CHEMICAL COMPANY
MIDLAND MICHIGAN
FRANCIS E. WARNER ARCHITECT
MIDLAND MICHIGAN
NOV 1978

solar gain to the living area, a feature commonly associated with passive systems. It has the economic advantage of incorporating the collector glazing in the southern wall, coupled with the thermodynamic advantage of low temperature collection. The energy storage material is conveniently located in the utility room, minimizing the architectural constraints of the system.

PROJECT SUMMARY

Project Title: Application of Low-Temperature Thermal Energy Storage in the TVA Region

Principal Investigator: A. M. Manaker

Organization: Tennessee Valley Authority
1360 Commerce Union Bank Building
Chattanooga, Tennessee 37401
Telephone: (615) 755-3345

Project Objectives: The objectives of the study include (1) the identification of potential sources and users of low-temperature thermal energy, such as institutional heating and cooling and industrial processes, in addition to TVA facilities, and (2) the identification of appropriate aquifer sites for storage. Particular emphasis will be given to defining the criteria for storage in aquifers.

Project Status: The project has not yet started. When the project is started, the following five tasks will be performed:

(1) Survey the TVA region for thermal energy producers.

(2) Development of criteria for storing thermal energy in aquifers.

(3) Survey the TVA region for aquifer storage system sites.

(4) Survey potential thermal energy users in the TVA region.

(5) Assess the opportunities for thermal energy storage systems in the TVA region.

Contract Number: EW-78-I-05-6112

Contract Period: December 1978 - September 1979

Funding Level: $90,000

Funding Source: Department of Energy, Division of Energy Storage Systems

I. Purpose

The purpose of the project is to assess the potential low-temperature thermal energy sources, possible aquifer storage sites for the energy, and potential users of this energy in the TVA region. The project work will emphasize the development of storage criteria in an aquifer.

II. Background Information

Low-temperature thermal energy storage (LTTES) systems are receiving considerable attention as a means of utilizing alternative energy sources. Present LTTES concepts, for the most part, address the application of such alternative energy sources as solar, waste heat, and offpeak electricity. These sources are to be applied in the residential, commercial, industrial, and agricultural use sectors through sensible and/or latent heat storage at temperatures generally below 250° C.

One potentially feasible method of storing the low-temperature energy is in aquifers. Some typical cycles for aquifer storage are the following:

A. Hot water daily storage: Hot water is injected during daytime and produced during nighttime.

B. Hot water seasonal storage, semiannual cycle: Hot water is stored in spring, then pumped out and used for air-conditioning in summer. Then hot water is again stored in autumn and finally pumped out to be used for heating in winter.

C. Hot water seasonal storage: Hot water is stored during warm months and used during cold months for heating.

D. Chilled water seasonal storage: Chilled water is stored in cold months and used during warm months for air-conditioning.

E. A two-well system: During the storage period, water is produced from one well, heated, and then injected into the other well. During the utilization period, hot water is retrieved from the latter and the cooled used water is injected back into the former.

III. Project Description

The project consists of identifying, in the TVA region, (1) potential sources of excess low-temperature thermal energy; (2) criteria for storing thermal energy in aquifers; (3) potential aquifer storage sites; and (4) potential users of the thermal energy. In addition, the opportunities for LTTES in the TVA region will be assessed.

The project will be accomplished in the following five tasks:

A. Identification of energy producers: A regional survey will be conducted of the Tennessee Valley Authority service area for low-temperature thermal energy producers in the commercial, industrial, institutional, and utility sectors. Facilities to be considered are: central generating stations, industrial steam plants, chemical processing plants, food processing plants, and smelting operations. In addition, solar collectors will be considered as a heat source and the environmental temperatures as a chill source. The approximate peak, daily, monthly, and seasonal thermal energy production from each facility will be identified and documented, along with sufficient data regarding facility operation to assess the potential availability of energy for storage over an extended period of years.

B. Development of aquifer storage criteria: The criteria for transporting and storing low-temperature thermal energy in aquifers on a seasonal, weekly, or daily basis will be developed. Areas to be addressed in developing the criteria for aquifers are their hydraulic properties, thermal properties, and geochemical properties. Also, the general environmental impacts (e.g., ground water effects) will be addressed. Conceptual storage system designs, siting requirements, thermal transport methods, and interface design conditions will be developed.

C. Storage system site survey: The specific siting requirements for aquifer storage systems identified in the previous task will be used as a basis for determining the availability of TES system siting areas in the TVA service area. Subsurface geology, topographical needs, and environmental impact of the aquifer sites will be determined.

D. Survey of potential thermal energy users: A survey of the potential users of stored low-temperature thermal energy will be made for the TVA service area. The potential users may include: Tennessee Valley Authority; private, municipal, and cooperative utilities; communities (district heating/cooling); schools, hospitals and other institutions; and industries.

Potential users will be grouped by location and type of usage to indicate areas with maximum potential for implementation of thermal energy usage.

E. Assessment of opportunities for thermal energy storage in the TVA region: The results of the previous tasks will be assessed to identify areas where suppliers, sites, and users may be combined to allow the implementation of low-temperature thermal energy storage systems. Technical constraints to actual implementation, such as the problems of system energy imbalances and interconnecting the three system components, will be identified and documented.

The project will be performed by a team of Tennessee Valley Authority participants led by Energy Research and including the Divisions of Water Management and Navigation Development and Regional Studies. Acres American, Incorporated, will provide assistance to TVA on this project.

IV. Results and Future Activities

Project is expected to be started in December 1978.

PROJECT SUMMARY

Project Title: Thermophysical Properties and Behavioral Characteristics of Phase-Change Materials

Principal Investigator: S. Cantor

Organization: Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37830
Telephone: (615)-574-5031

Project Goals: The project goals are (1) ascertain thermal performance of $Na_2SO_4\cdot 10H_2O$ and other incongruently melting salt hydrates by calorimetric investigation of melting and freezing; (2) select compounds and mixtures suitable for isothermal heat storage within the range 90-250°C; selection is to be based on laboratory evaluation as well as on economic and technical screening criteria.

Project Status: Laboratory evaluation and measurements have been completed. Salt Hydrates. By means of differential scanning calorimetry, the ΔH of fusion and of crustallization were determined for six salt hydrates. For $Na_2SO_4\cdot 10H_2O$ (Glauber's salt), ΔH of crystallization near the peritectic temperature is about 50% of the ΔH fusion; at lower temperatures, a second phase transition occurs at the eutectic melting point of mixtures of ice and Glauber's salt. Similar thermal characteristics were observed for $Na_4P_2O_7\cdot 10H_2O$, a higher melting analog of Glauber's salt. Two other incongruently melting compounds, $CuSO_4\cdot 5H_2O$ and $Na_2B_4O_7\cdot 10H_2O$ exhibited marked disparities between ΔH of fusion and of crystallization. For $Mg(NO_3)_2\cdot 6H_2O$ (congruently melting) and $MgCl_2\cdot 6H_2O$, which melts almost congruently, the magnitude of the two enthalpies was equal.

Phase-Change Materials for the Range 90-250°C — Organic Materials. Using economic and technical screening criteria, three compounds (urea, adipic acid, phthalic anhydride) were selected for evaluation by thermal cycling; at the melting point, only phthalic anhydride appeared to be thermally stable. Eutectic mixtures of urea with inorganic salts and with biuret were identified; the urea-biuret mixture was examined experimentally. Polyethylene and (isotactic) polypropylene, in form-stable configurations, may be potentially useful storage materials.

Inorganic Materials. The screening procedures identified $MgCl_2\cdot 6H_2O$ and three congruently melting anhydrous nitrate mixtures. Measurements of $MgCl_2\cdot 6H_2O$ and equimolar $NaNO_3$—KNO_3 indicated generally favorable thermal behavior.

Contract Number: Internal ORNL Account No. 3420-0801

Contract Period: FY 1978

Funding Level: $80,000

Funding Source: Oak Ridge National Laboratory

I. INTRODUCTION

The background information for this project was discussed in last year's proceedings.[1] Since then a slight shift in emphasis has occurred — more intensive investigation of inorganic salt hydrates. The shift was due, in part, to the recognition that the differential scanning calorimeter (DSC) could yield accurate exothermic (i.e., heat discharge) data. For salt hydrates, this instrument was used to determine the apparent differences between ΔH of fusion and ΔH of crystallization and how these enthalpies changed with thermal cycling. In evaluating organic materials melting between 90 and 250°C, DSC measurement of time-and cycle-dependent changes in ΔH of fusion proved to be useful for detecting thermal decomposition. Measurements of exothermic changes also provide information about supercooling. But, the shallow-pan configuration of DSC samples seems to increase the extent of supercooling;[2] it was, therefore, necessary to study supercooling by more conventional thermoanalytic means, i.e., temperature-time plots.

II. SALT HYDRATES

Na_2SO_4 $10H_2O$ (Glauber's Salt)

Preliminary DSC investigation[2] showed that ΔH of solidification was considerably less than ΔH of fusion initially measured. In the present study, three types of samples were measured by DSC: $Na_2SO_4 \cdot 10H_2O$ alone; $Na_2SO_4 \cdot 10H_2O$ with borax, 2-9 wt %; $Na_2SO_4 \cdot 10H_2O$ with 4 wt % borax and additional anhydrous Na_2SO_4. The third type of sample was studied to determine if additional Na_2SO_4 would promote equilibrium (peritectic) solidification of $Na_2SO_4 \cdot 10H_2O$. A summary of experimental results is as follows: (a) The enthalpy release, derived from the initial and subsequent DSC exotherms for all three sample types, was roughly 30 cal/g of $Na_2SO_4 \cdot 10H_2O$ in the sample; this is about half of the enthalpy absorbed on first melting. (b) Continued cooling to temperatures less than -15°C led to the release, with supercooling, of additional energy, often as much as 15 cal/g; immediate reheating showed that this transition occurs just below -1°C, corresponding to the eutectic melting temperature for a mixture of ice and Glauber's salt (and also, where applicable, borax). (c) After the first thermal cycle, a relatively long period (at least three days) at room temperature was necessary to recover the full storage capacity of the 4-10 mg samples of Glauber's salt. (d) Anhydrous Na_2SO_4 added to Glauber's salt did not alter the pattern of enthalpy absorption and release described by (a), (b) and (c). (e) Borax, by greatly decreasing the extent of supercooling, seemed to prevent formation of $Na_2SO_4 \cdot 7H_2O$; the heptahydrate is a metastable phase melting incongruently at 24.3°C, and was detected only in samples that did not contain borax. (f) Storage and discharge of energy at or near the phase transition temperature (32°C) remained essentially constant at 30 cal/g over the first few (daily) thermal cycles between 20 and 36°C; more frequent continuous cycling, up to 400 times, decreased energy storage and discharge of $Na_2SO_4 \cdot 10H_2O$ to a level value of 26-27 cal/g (see Figure 1).

The experimental results indicate that the heat-storage process differs from the heat-discharge process. The reaction for storing heat slightly above the peritectic, can be represented by equation (1):

$$Na_2SO_4 \cdot 10H_2O(c) \xrightarrow{32.4 + \delta t} [1-\frac{10}{z}]Na_2SO_4(c) + \frac{10}{z} Na_2SO_4 \cdot zH_2O(liq) \qquad (1)$$

z, the mole ratio H_2O: Na_2SO_4 in solution, is 15.86, at 32.4°C,[3] the peritectic temperature. Reaction (1) describes the conversion of Glauber's salt to a solution saturated with respect to anhydrous Na_2SO_4. The pattern of energy discharge in the DSC experiments can be interpreted in terms of two reactions:

$$\text{Concd soln } (\sim Na_2SO_4 \cdot zH_2O) \xrightarrow{\text{Borax, } 24°C} Na_2SO_4 \cdot 10H_2O(c) + \text{less concd soln} \qquad (2)$$

$$Na_2SO_4(c) + \text{less concd soln} \rightarrow \text{additional } Na_2SO_4 \cdot 10H_2O \ . \qquad (3)$$

Both (2) and (3) form Glauber's salt but reaction (3) is much slower. The sluggishness of (3) is inferred from the significant transition observed at -1°C, the ice-Glauber's salt eutectic. This sluggish reaction can be attributed to an encapsulating layer which limits reaction of Na_2SO_4 with water to the slow process of solid-state diffusion. The DSC experiments provide information for an order-of-magnitude estimate of the diffusion coefficient. Assuming that the radius or half thickness of the Na_2SO_4 crystals is of the order of 0.01 cm (probably a high estimate) and given that three days were necessary to convert all of the anhydrous Na_2SO_4 to Glauber's salt, we estimate a diffusion coefficient from the expression,[4] $D = {}^4L^2/4\tau = (0.01)^2/4 \cdot 3 \cdot 86{,}400 \sim 10^{-10}$ cm²/sec. Diffusion coefficients in aqueous liquids are about 10^{-5} cm²/sec; for solids, one would expect diffusion constants a few orders of magnitude less which appears to be the case in this instance.

The hypothesis of an encapsulating layer around the anhydrous Na_2SO_4 was put forth by Biswas[5] who suggested that the layer was composed of $Na_2SO_4 \cdot 10H_2O$. Two questions arise from this suggestion: what makes the decahydrate adhere so well to the anhydrate and why doesn't it "seed" Glauber's salt from solution? A possible explanation answering these questions is as follows. When a thin layer of decahydrate forms on the anhydrous salt, heat is evolved (-19.5 kcal/mole for ΔH of hydration of $Na_2SO_4 \cdot 10H_2O$),[6] raising the temperature of the crystal surface and of the adjacent liquid. Two effects would follow from the local temperature increase: the hydrate layer would redissolve and more anhydrate would precipitate out under the driving force of the retrograde solubility. The low diffusion constant suggests that only part of the decahydrate redissolves; indeed, one could imagine the first hydrate layer sandwiched by a layer of Na_2SO_4 which, in turn, forms another hydrate layer and so on. The key property in this mechanism is the negative temperature dependence of solubility of Na_2SO_4.

The prime relevance of these measurements is that, for static latent-heat systems, the energy (26-30 cal per g of $Na_2SO_4 \cdot 10H_2O$) released by crystallization of the aqueous phase will be the only energy that can be reliably retrieved from storage. While this diminishes some of the potential of Glauber's salt, it is of such low cost that it still remains a very attractive and viable candidate even for static systems. In systems with provision for stirring, one can imagine full and unimpeded recovery of the stored energy, provided that the mixture always contains some undecomposed Glauber's salt; if conditions are set so that equilibrium can be maintained between solution and both solid phases (Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$) then reaction (1) can be reversed isothermally by extracting energy from the system.

$Na_4P_2O_7 \cdot 10H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $Na_2B_4O_7 \cdot 10H_2O$

The results obtained for these five hydrates are summarized in Table A; all, except $Mg(NO_3)_2 \cdot 6H_2O$, melt incongruently. $Na_4P_2O_7 \cdot 10H_2O$, whose phase equilibrium behavior is similar to that of Glauber's salt, exhibited similar thermal effects; its higher peritectic temperature seems to permit more rapid reaction between anhydrate and water than is the case for $Na_2SO_4 \cdot 10H_2O$. For $Mg(NO_3)_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ (the latter melts almost congruently) the magnitude of ΔH of crystallization equalled ΔH of fusion; $CuSO_4 \cdot 5H_2O$ and $Na_2B_4O_7 \cdot 10H_2O$ exhibited marked disparity between ΔH of fusion and ΔH of crystallization. Visual observation of the test-tube samples of the incongruently melting hydrates showed that only $MgCl_2 \cdot 6H_2O$ formed enough liquid at its melting point to permit free convection. $Na_4P_2O_7 \cdot 10H_2O$, $CuSO_4 \cdot 5H_2O$, and $Na_2B_4O_7 \cdot 10H_2O$ exhibited small liquid volume fractions upon melting; these 3 hydrates would be very inferior latent-heat storage materials even if their supercooling problems were solved. The results obtained for these five hydrates, as well as those obtained for Glauber's salt suggest that peritectic solidification of hydrates can be viewed as a dual process: crystallization from the liquid solution and reaction of the lower hydrate (or anhydrate) with the solution; where ΔH of crystallization appears to be less in magnitude than the ΔH of fusion, the difference can be attributed to slower reaction rate between solution and the lower hydrate.

III. HEAT-STORAGE MATERIALS THAT MELT BETWEEN 90 AND 250°C

A primary application for these materials is as heat sources for absorption air-conditioning and for heat-engine (Rankine-cycle) driven air-conditioning systems. For both systems, temperatures as high as 204°C can be used, the exact temperature depending on the details of the operating system.[8] A second general area of application involves process heat at intermediate temperatures for industrial (food, textiles, chemicals) usage. In particular, several big volume chemicals are produced catalytically in which the catalyst functions most efficiently over a narrow temperature interval; a latent-heat storage source, at the required temperature could provide process control as well as aid in conserving energy resources.

Organic Materials

Preliminary screening of organic compounds and the criteria used to select candidates for evaluation were outlined in the previous report.[1] Although a very large number have melting points in the desired range, very few organic chemicals are sufficiently inexpensive, hazard-free and chemically stable towards decomposition. Using $1.00/kg for the price of the bulk chemical[9] as the price limitation, a number of materials were selected. The Merck Index[10] was then used to check melting points and decomposition behavior as well as hazardous or toxic attributes. On the basis of this initial screening, three compounds (urea, adipic acid, phthalic anhydride) and two polymers (polyethylene and polypropylene) were selected for further consideration.

Urea, although at first appearing to be very attractive (cost: 15¢/kg; ΔH of fusion: 57.8 cal/g) is unsatisfactory because of supercooling and because it rapidly decomposes at its melting point, 132.7°C.

Table A. Summary of Melting and Freezing Behavior Observed for Five Salt Hydrates

	Results
Sodium pyrophosphate decahydrate, $Na_4P_2O_7 \cdot 10H_2O$. Melts incongruently at 79.5°C to form the anhydrate. Above 79.5°C, anhydrate exhibits retrograde solubility.[7]	ΔH of fusion = 59 cal g^{-1}. ΔH of crystallization, 26-35 cal g^{-1}, occurred in the range, 40-66°C; if cooling scan continued, another transition appears at -0.4°C, the temperature of eutectic melting of ice and $Na_4P_2O_7 \cdot 10H_2O$. Energy storing capacity fully recovered by overnight annealing at 65°C. Test-tube samples showed crystallization first occurring at 72-73°C.
Magnesium nitrate hexahydrate, $Mg(NO_3)_2 \cdot 6H_2O$. Melts congruently at 89.9°C.	ΔH of fusion = 36.2 cal g^{-1}, somewhat less than reported[6] (38.2 cal g^{-1}). ΔH of solid-state transformation = 2.9 cal g^{-1} at 73°C. Experimentally, ΔH of crystallization = $-\Delta H$ of fusion.
Magnesium chloride hexahydrate, $MgCl_2 \cdot 6H_2O$. Melts incongruently at 116.7°C to form tetrahydrate, which, at 120°C, dissolves in the liquid phase.	ΔH of fusion = 39.9 cal g^{-1}, in good agreement with compiled[6] value (40.3 cal g^{-1}). Experimentally, ΔH of crystallization = $-\Delta H$ of fusion. Two-step melting (and freezing) not detected in DSC. Test-tube samples showed two-step melting; on cooling the melt, virtually no supercooling occurred.
Copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$. Melts incongruently at 95.9°C to form the trihydrate.	ΔH of fusion = 32 cal g^{-1}. ΔH of crystallization = 12-19 cal g^{-1} observed at 30-60°C. Test-tube experiments showed crystallization from the melt first occurring at 82°C; volume fraction occupied by melt is relatively small. $CuSO_4 \cdot 5H_2O$ poor for isothermal heat storage because of supercooling and because small liquid volume will not permit much heat-transfer by free convection.
Sodium tetraborate decahydrate (Borax), $Na_2B_4O_7 \cdot 10H_2O$. Melts incongruently to either the tetrahydrate (at 58.5°C) or to the metastable pentahydrate (at 60.8°C).	ΔH of fusion = 33 cal g^{-1} at 60.8°C. Crystallization detected (by DSC) at -10 to -15°C. Borax, heated in test-tube experiments to 70°C, showed little or no melting; slow cooling to 35°C showed no break in temperature-time curve.

Adipic acid (melting pt: 152°C) has a heat of fusion of 59.6 cal/g (DSC measurement in this study), does not supercool, but is relatively expensive (90¢/kg);[9] the price is governed in part by high-purity (99.7%) requirements from nylon production. A 5-mg sample thermally cycled 77 times in the DSC over the range, 135-160°C, showed no evidence of decomposition; however, the same sample, when kept at 156°C for 25 hours, showed a 2% decrease in ΔH of fusion, indicative of some thermal decomposition. Its high price and the detectable thermal decomposition make adipic acid a very uncertain candidate for any latent-heat-storage applications. If a somewhat lower melting eutectic mixture did not decompose and if a less expensive (and likely, less pure) grade was otherwise acceptable, then adipic acid could be considered a more attractive material.

Phthalic anhydride (melting pt: 131°C, ΔH of fusion: 36.3 cal/g[11]) would be expected to be thermally stable because of its fused ring structure. The excellent stability was verified by the absence of changes in the DSC spectrum of a sample that was thermally cycled through its melting point 96 times. Supercooling of 5-mg DSC samples appeared to be about 20°; however, conventional thermal-halt measurements carried out for 10-g samples showed virtually no supercooling. Because its price is 60¢/kg[9], it cannot be considered as attractive as other materials ($MgCl_2 \cdot 6H_2O$, form-stable polyethylene) that melt at nearly the same temperature.

Polyethylene, M. Pt., 125-135°C and Polypropylene (Isotactic), M. Pt., 155-165°C

Both polymers are relatively costly (70¢/kg), but good possibilities exist for very low containment costs. By partially crosslinking the more crystalline high-density form of polyethylene, it has been demonstrated[12] that small cylindrical (about 3 mm long, 1.5 mm diam) pellets retained their form upon melting, i.e., the material acted as its own container. A packed bed of these pellets in a large tank could be the basic storage configuration. A 114-kg lot was cycled through 632 freeze-thaw cycles, 105-145°C, with practically no sintering, and with little or no change in the heat of fusion (45 kcal/kg for this particular material).[12] In this instance, silane crosslinked material was used but less expensive means of crosslinking is probably available by using radiation.[13] Polypropylene, in its highly crystalline (isotactic) form, has a ΔH of fusion of 44 cal/g.[14] Assuming that a form-stable product can be made cheaply, then this polymer would be a potentially useful storage material for a melting range 30° higher than that of polyethylene.

Urea-Containing Mixtures

The observation of fairly extensive decomposition at 133°C does not preclude using urea at lower temperature in a congruently melting mixture. The only urea mixture whose stability was checked experimentally in this study was the eutectic with biuret; the eutectic composition contains 30 wt % biuret and reportedly melts at 111°C.[15] Biuret was chosen as the 2nd component because it is the principal condensed-state decomposition product from urea; the reaction for its formation can be written:

$$\underset{\text{Urea}}{2CO(NH_2)_2} \xrightarrow{t<135^\circ C} \underset{\text{Biuret}}{NH_2CONHCONH_2} + \underset{\text{Ammonia}}{NH_3(gas)}$$

It was reasoned that urea in an encapsulated mixture, when heated to about 115°C would produce a small but sufficient amount of ammonia to halt the reaction from proceeding further to the right. Samples of the eutectic mixture were thermally cycled (range: 65-115°C) as many as 15 times in the DSC as well as maintained in the molten state at 114°C for several hours. Our results showed that the melting point was 104°C, the mixture supercooled, and the extent of decomposition was slight. The results obtained, although mildly encouraging for the utilization of urea, should be viewed cautiously. First, the testing of thermal decomposition was of a preliminary nature and if precautions had not been taken to keep the temperature from getting too high, more decomposition might have occurred; Rollet and Cohen-Adad[15] reported that at 130°C and above, urea-rich mixtures became richer in biuret. Secondly, the problems of supercooling and of hydrolysis persist. There is little doubt that inleakage of moist air would readily decompose a urea-biuret mixture at about 100°C.

Urea forms congruently melting mixtures with several inexpensive inorganic salts. Four are listed in Table B. Several nitrates also form eutectics but these could be hazardous; dry molten nitrates are strong oxidants, and although urea cannot be considered a strong reductant, a dry molten mixture might react violently. None of the mixtures given in Table B were examined experimentally in this investigation. For any urea mixture to function as a latent-heat storage medium, it would be necessary to: (a) maintain NH_3 cover gas to limit thermal decomposition, (b) find a reliable means of preventing supercooling, (c) curtail the extent of hydrolysis, should there be inleakage of water or moisture.

Table B. Urea-inorganic salt eutectic mixtures

Composition	Melting point	Reference
NaCl — Urea 9.8 — 90.2 wt %	112°C	a
KCl — Urea 10.9 — 89.1 wt %	115°C	a
KBr — Urea 20.5 — 79.5 wt %	109°C	a
K_2CO_3 — Urea 14.8 — 85.2 wt %	102°C	b

[a] K. Nogaev, A. G. Bergman, and K. Sularmankulav, Studies of the Interaction of Urea with Inorganic Compounds (Russian), B. Imarakunov, editor (1964), pp. 71-9. Cited in Chemical Abstracts 62, 9851b (1965).

[b] A. G. Bergman and L. V. Velikanova, Russ. J. Inorg. Chem. 12, 1038 (1967).

Inorganic Phase-Change Materials

Perusal of bulk prices[9] established that, with rare exception, only compounds of sodium, potassium, calcium, magnesium, barium, iron, ammonium and aluminum, were inexpensive enough (<$1/kg) to warrant consideration. Barium compounds were deleted on account of toxicity. Ammonium compounds and salts of organic acids (e.g. acetates) were not pursued further because of probable thermal decomposition. When melting points were considered, the number of candidates was reduced to nitrate mixtures, alkaline hydroxides, $AlCl_3$-containing mixtures and inorganic-salt hydrates.

Only hydrates melting between 90 and 120°C were considered because, at higher temperatures, higher vapor (H_2O) pressures would almost certainly require thicker-walled (and, therefore, more expensive) containment. All of the inexpensive salt hydrates that melt above 90°C, melt incongruently. As noted in the previous section, incongruent melting tends to be difficult to reverse in a controlled manner. However, when $MgCl_2 \cdot 6H_2O$ melts at 116.7°C only a relatively small amount of tetrahydrate is formed, and at 120°C, the tetrahydrate dissolves in the liquid phase; thus, $MgCl_2 \cdot 6H_2O$ can be considered as melting completely over a narrow temperature range. This hydrate appears very favorable for isothermal heat storage: it freezes with little or no supercooling; it costs about 15¢/kg; it is not hazardous, nor does it appear to hydrolyze at or near its melting range. A possibly unsatisfactory characteristic could be a tendency to cause stress-corrosion cracking; if this did occur with inexpensive metals of construction, protective coatings, such as fluorocarbons, might be applied to solve the problem.

Among anhydrous inorganic materials, only congruently melting mixtures[16] were considered. Several eutectic mixtures containing $AlCl_3$ have attractive thermophysical and chemical properties; however, in case of leaks (air or water), stable solids [Al_2O_3, $Al(OH)_3$, etc.] would form very readily. Hydroxides, especially the NaOH-KOH eutectic composition (50-50 mole %, m. pt. 172°C) are inexpensive and possess favorable thermal properties; unfortunately, hydroxides are likely to be corrosive to inexpensive metals of construction. Owing to these considerations, neither $AlCl_3$ mixtures nor hydroxides were experimentally examined in this investigation.

Several relatively inexpensive, congruently melting, nitrate mixtures can be constituted from the components: $NaNO_3$, KNO_3, and $Ca(NO_3)_2$. The only such mixture evaluated by DSC in this study was $NaNO_3$-KNO_3, 46-54 wt %; ΔH of fusion was found to be 24 cal/g; the mixture did not appear to supercool; its cost is 19¢/kg estimated from prices for $NaNO_3$ (7¢/lb) and KNO_3 (10¢/lb).[9] At its melting point, it should have a low decomposition vapor pressure; although the vapor is predominantly oxygen, the mixture should be compatible with mild steel because of a protective oxide coating.[17] $NaNO_3$-KNO_3 mixtures, as well as most inorganic nitrates, are strong oxidizing agents. Hence, interaction of nitrates with organics or other reducing agents would have to be prevented; it would be inordinately risky to use a nitrate in conjunction with an organic working fluid. In addition to $NaNO_3$-KNO_3, two other binary nitrate mixtures (not experimentally checked in this study) may have isothermal heat storage application at other temperatures of interest; these are listed in Table C.

Table C. Melting points of congruently melting binary nitrate mixtures

Composition	Melting point	Reference[a]
$NaNO_3$ — KNO_3 50 — 50 mol %	222°C	Fig. 1047
$NaNO_3$ — $Ca(NO_3)_2$ 71 — 29 mol %	232°C	Fig. 1050
KNO_3 — $Ca(NO_3)_2$ 66 — 34 mol %	146°C	Fig. 1050

[a] E. M. Levin, C. R. Robbins, and H. F. McMurdie Phase Diagram for Ceramists, American Ceramic Soc., Columbus, Ohio, 1964.

Acknowledgement. The author thanks Dr. Jerry Braunstein, ORNL, and Dr. John Ricci, Professor Emeritus, NYU, for their very helpful discussion of this work.

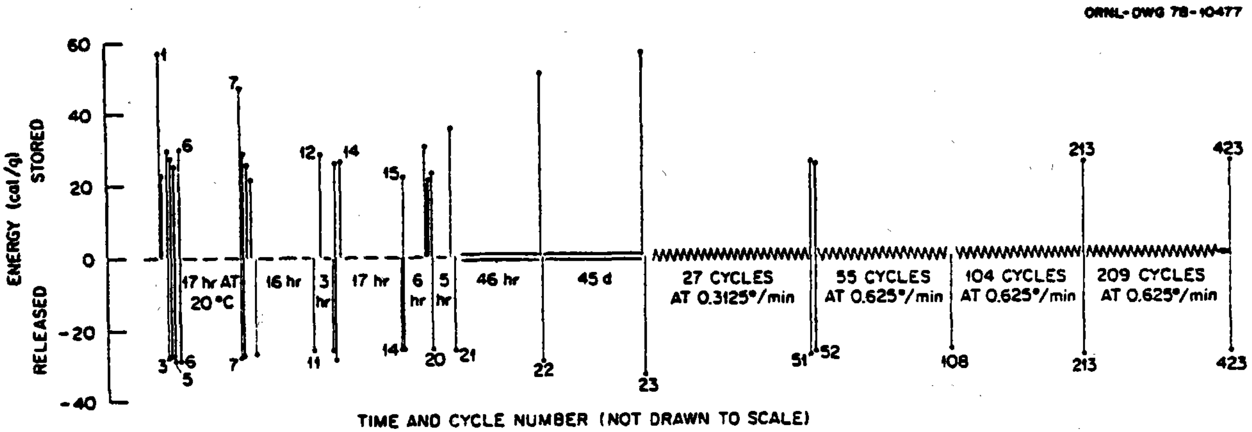


Figure 1. Effect of thermal cycling on energy storage at 32°C and on energy release at ∿25°C in a sample: 3.435 mg $Na_2SO_4 \cdot 10H_2O$, 0.172 mg borax. The length of the vertical lines from zero cal/g is proportional to energy absorbed or released. The cycle number for which DSC measurement was obtained is given at the ends of the lines. After the 23rd cycle, cycling between 19° and 36°C was almost continuous.

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Third Annual Thermal Energy Storage Contractor's Information Exchange Meeting

PROJECT SUMMARY

Project Title: Low-Temperature Thermal Energy Storage (LTTES) Program - ORNL, Bellingham Subsurface Heat Storage Project.

Principal Investigator: Denzel R. Cline

Organization: U.S. Geological Survey, Water Resources Division
1201 Pacific Avenue, Suite 600
Tacoma, Washington 98402
Telephone: (206) 593-6510

Project Objectives: Investigate the geology and hydrology of the Bellingham area to determine the occurrence, yield, and water-quality of any deep, undeveloped, confined aquifers that may be used for storing and withdrawing waste heat from aluminum processing.

Project Status: This project has four phases as follows:

1. Examine pertinent geologic and hydrologic data existing in USGS and state agency files.
2. Review the sites and performance criteria specifications for test-drilling and data-collection programs of project consultants.
3. Collect geologic, hydrologic, and water-quality data on any existing permanent wells and during test drilling, and perform tests on any major aquifers encountered.
4. Write a report describing the geology and hydrology of the area.

The project status is as follows:

(1) Some of the existing data have been assembled and examined.

(2, 3, and 4) Work pending selection of prime contractor by the Department of Energy.

Interagency Agreement No.: EW-78-I-05-6109
Contract Period: FY 1979
Funding Level: $37,000
Funding Source: Department of Energy, Oak Ridge National Laboratory

THIRD ANNUAL THERMAL ENERGY STORAGE CONTRACTOR'S

INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Mathematical modeling of moving boundary problems

Principal Investigator: A. Solomon

Organization: Oak Ridge National Laboratory
Bldg. 9704-1
P.O. Box Y
Oak Ridge, Tennessee 37830
Telephone: (615) 483-8611, X35048

Project Objectives: A) The further development of a computer model of the moving boundary phase change process in the context of a latent heat TES mechanism.

B) The derivation and analysis of analytical tools for validating the computer model, and in support of other aspects of the TES program.

Project Status: The project is divided into two phases as follows:

1) Determine those aspects of the computer program and of the analytical support work that must be done in support of the program.
2) Validate the program by a combination of analytical tools and experimental comparisons.

The project status is as follows:

1) The computer program has been used and compared with a variety of known analytical solutions and approximations and has been found to be valid for all of the cases tested.
2) Comparisons with experimental results and calibration of the program are now being carried out in cooperation with the parallel work of R. Deal.
3) Analytical approximation methods are continuing to be developed for a variety of problems of relevance to the TES program.

Contract Period: FY 1978

Funding Level: $50,000

Funding Source: Department of Energy, Division of Energy Storage Systems

PROGRAM PROGRESS DURING FY 1978

During the 1978 fiscal year the following results were obtained:

1. Computer modeling. The weak solution [1] Stefan problem computer program was applied to a number of test problems and debugged. Among problems run were those with flux and convection type boundary conditions including strongly varying conditions. Particularly important results included temperature profiles and heat balances for periodic heat input at the boundary. Changes made included a boundary condition discretization guaranteeing energy conservation in the system. Parallel runs and debugging was carried out for the multi-component computer program. Both programs are one-dimensional allowing for slab, cylinder and spherical geometries. Documentation, publication and distribution are awaiting the results of experiments being carried out for the testing and calibration of the model.

2. Analytical modeling-melting time of a simple body [2]. The formula

   $$t_f = \frac{L^2}{2\alpha(1+\omega)St}\ [1+(.25+.17\omega^{.7})St]$$

   for the total melting time of a PCM body subject to constant boundary temperature in any geometry was obtained. Comparison with numerical simulations and other data indicates a small relative error over the range of LHTES applications.

3. Numerical simulation of a PCM wall [3],[4]. The thermal behavior of a PCM wall subject to an external periodic input was simulated. It was found that the least inner surface temperature variation is obtained when the phase boundary is maintained within the wall. Conditions guaranteeing this were found, and lead to trade-off criteria between objectives of heat storage and building comfort.

4. Analytical rules of thumb [5]. Simple closed form approximations to the solution of the Stefan problem of phase change in the 2-phase case were obtained for a semi-infinite slab. These can be calculated on a pocket calculator of the HP-45 class and have a small relative error over the range of LHTES applications.

5. Derivation of upper and lower bounds. Using a variety of techniques of mathematical analysis, upper and lower bounds on the phase boundary location, heat storage and temperature have been found for a variety of problems. The bounds are useful both in direct applications and for computer model calibration.

6. A three dimensional computer program. A three dimensional computer model based on pure conduction and using the method of [1] has been prepared. The model is currently undergoing calibration and debugging, and will be compared with results of the experimental program underway.

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NOTATION

c	PCM specific heat	cal/gm-°C
H	PCM latent heat	cal/gm
L	slab length, cylinder or spherical radius	cm
t_f	total melt time	sec
T_w	imposed boundary temperature	°C
T_{cr}	melting temperature	°C
$\Delta T = T_w - T_{cr}$		°C
$St = c \Delta T/H$		Stefan number (dimensionless)
α	thermal diffusivity	cm^2/sec
ω	geometrical parameter (0 for slab, 1 for cylinder, 2 for sphere)	(dimensionless)

U. S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Development of Intermediate Temperature Thermal Energy Storage Systems

Principal Investigator: Jerzy R. Moszynski

Organization: Department of Mechanical and Aerospace Engineering
University of Delaware
Newark, Delaware 19711
Telephone: (302) 738-8141

Project Objectives: Identify suitable materials for thermal storage in the temperature range, 100-300°C. Compile pertinent thermophysical data, as far as possible from existing literature. Determine missing data as required. Build and test a scale model of a storage system using a selected material.

Project Status: Preliminary cost and safety criteria have been formulated. Test cells for thermal cycling, calorimetric measurements and measurements of thermal diffusivity have been designed and built. Scrutiny of materials exhibiting a phase transition in the temperature range of interest has been completed. Through preliminary testing or calculations, energy storage in salt hydrates and in liquid-vapor transitions has been eliminated from consideration for the range of interest. The choice has been narrowed down to four candidate materials which are being submitted for final approval to DOE. These materials are: sodium-aluminum chloride $NaAlCl_4$, zinc chloride $ZnCl_2$, a eutectic mixture of $FeCl_3$ and NaCl and a eutectic mixture of NaOH and Na_2CO_3. In-depth characterization studies of approved materials will proceed during the remainder of the first year of the contract.

Contract Number: EM 78 - S - 05 - 5760

Contract Period: April 1, 1978 - March 31, 1981

Funding Level: $286,200

Funding Source: Department of Energy, Solar Heating and Cooling Division

DEVELOPMENT OF INTERMEDIATE TEMPERATURE THERMAL ENERGY STORAGE SYSTEMS

University of Delaware

Department of Mechanical and Aerospace Engineering

Contract Number: EM-78-S-05-5760

Principal Investigator: J. R. Moszynski

The ultimate objective of this project is the development of optimized thermal energy storage systems in the temperature range from 100°C to 300°C. Special consideration is to be given to the needs of contractors developing absorption, adsorption and Rankine cycle driven air conditioning systems. The first year effort is directed at identification and characterization of suitable storage materials.

Isothermal energy storage has been investigated at the University of Delaware for several years. Low temperature applications aimed at "coolness" storage for air conditioning and slightly higher temperatures up to about 35°C for solar space heating have been focusing around Glauber's salt (sodium sulphate decahydrate) with suitable additives. For high temperature storage, in the range 250°C - 650°C with applications to power generation, eutectic metal alloys are being considered. These efforts are being reported on elsewhere at this conference [1,2].

The present project covers the intermediate range with some overlap at the upper end. Near 100°C prospective applications are to absorption air conditioning and some dessicant systems, although in the latter case stratified rather than isothermal storage is preferable. In one application limited storage capability at temperatures as high as 150°C would be helpful [3]. At the high end, the Rankine cycle operating conditions are somewhat flexible and a useful limit is presented by the performance of a non-concentrating (evacuated tube) collector. Operating temperatures of 175°C have been reported [4]; with 300°C representing perhaps an achievable limit. As a result of these considerations the following preferred (but not exclusive) temperature ranges were chosen: 1) 110-130°C, 2) 150-170°C, 3) ~ 300°C.

The first step in the project was a rather complete literature search for prospective storage materials in the temperature range of interest. To aid in the evaluation of possible candidates a preliminary set of cost and safety criteria have been formulated.

These are: a cost of $2 per 1000 kJ of storage capacity and a requirement that the material or the products of its decomposition or combustion be non-explosive and non-toxic. The first of these criteria may well be relaxed in the light of system evaluation, particularly in comparison with representative collector costs. The safety criteria represents an ideal for household installations. For commercial and particularly industrial applications the requirement is probably much too stringent in that, for example, potential evolution of ammonia may be tolerated in an industrial environment.

The application of the above criteria narrowed down the choice to a surprisingly limited group of materials, except for large numbers of organic substances apparently available in each temperature range of interest. With very few exceptions these organic substances pose questions of stability which would require substantial experimental efforts to answer. For this reason they were excluded from consideration under the present contract.

The next stage in the selection process required the confirmation or determination of the melting temperature and the heat of fusion. To this end two special cells were designed and built. One is designed to allow automatic repetition of heating and cooling cycles, the other rather precise determination of the heat of fusion. In contrast with conventional DTA and DSC instruments, both cells allow measurements of macroscopic samples of up to 200-400 g. The cells are cylindrical. One is inserted in a furnace whose temperature is automatically controlled. The other is provided with an external guard heater, but melting occurs as a result of heating by means of a central heater. Solidification at varying rates occurs by adjusting the output of the guard heater. The accuracy of temperature measurement in the second cell is ±0.1°C and that of the determinations of the heat of fusion is estimated at ±5%.

The cell provides a digital record of readings of four thermocouples located respectively in the center of the internal heater, on the inner cylindrical surface of the cell, in the thin outer wall of the cell and on the inner surface of the guard heater. A plot of a typical record is shown in the figure. The sample, in this case a eutectic mixture of ferric chloride and sodium chloride, is slowly heated to just below the melting temperature. A very small input is provided to the central heater to compensate for losses. When the desired conditions are achieved the power input to the internal heater is increased in a step manner. As the sample melts, the temperatures of both the inner and outer wall increase. When melting is complete the rate of change of the outer wall temperature increases. At this point the outer wall is at the melting temperature. The melting process begins when the inner wall reaches the melting temperature. The power input during the melting interval, after appropriate correction, yields the heat of fusion.

Preliminary experiments using these cells have served to reduce the number of viable candidate materials still further. Thus, for example, $FeSO_4 \cdot 7H_2O$ originally thought to be very promising, was found to melt and dehydrate as expected at respective temperatures of 68°C and 90°C. Upon cooling, however, the heptahydrate did not reform but rather ferric sulphate and ferric oxide were observed with an evolution of SO_2 and SO_3. This occurred even in an inert (argon) atmosphere. Similarly, experiments with $CaSO_4 \cdot 2H_2O$ failed to achieve rehydration upon cooling. These difficulties have led to the conclusions, that at temperatures substantially above 100°C, energy storage in salt hydrates is not very attractive. This conclusion is reinforced by the fact that if the water released is to be retained in the liquid state containment at high pressures would have to be provided for. If the dehydration were to occur at atmospheric pressure large vapor volumes would have to be allowed for. In the latter case storage in the evaporation enthalpy of water would yield very nearly the same storage capacity without the corrosion and rehydration difficulties involved with a salt.

At the time of writing, prospective storage materials in the temperature range of interest have been narrowed down to the following list:

1. A eutectic mixture of $FeCl_3$ and NaCl melting at 152°C and solidifying at 142°C. It has a heat of fusion of 75 kJ/kg. It exhibits some preventable decomposition into Fe_2O_3 and HCl when in contact with atmospheric moisture. Some chlorine evolves.

2. Sodium aluminum chloride, $NaAlCl_4$, with a melting temperature of 159°C and a solidification temperature of 155°C. Repeated cycling (30 complete heating/cooling cycles) shows no detectable change. In particular there appears to be no evolution of chlorine.

3. Zinc chloride, $ZnCl_2$, melting and solidifying at 312°C with a heat of fusion of 155 kJ/kg. Repeated cycling shows no detectable change in composition.

4. Eutectic mixture of NaOH and Na_2CO_3(92.8% molar NaOH) melting and solidifying at 283°C with no detectable change after 20 cycles.

Somewhat inconclusive results were determined with urea, the one organic substance selected for investigation. In one series of tests after some 30 cycles the material, hermetically sealed, was found to have decomposed leaving a white powder (possibly cyanuric acid). At the same time the temperature plateau at about 132°C indicating melting and solidification has disappeared completely. In another series of tests under very similar conditions the plateau is still present after some 40 cycles. Finally during the calorimetric experiments, during which the sample was also hermetically sealed the enthalpy of fusion was observed to decrease from 258 kJ/kg to 40 kJ/kg during the first 20 cycles, suggesting progressive decomposition.

It should be pointed out that the current cost of the above materials in bulk is in each case less than 25 cents per kilogram.

The use of enthalpy of vaporization for energy storage is suggested by the ready availability and containment materials of at least two substances: water and ethylene glycol. Detailed storage capacity comparisons were carried out assuming constant volume and constant pressure storage. At constant volume the storage is not isothermal and comparison with sensible heat storage is in order. Between 100°C and 300°C water has about one half the storage capacity of a typical rock bed of the same volume. The maximum pressure which must be contained is about 8.6 MPa. Between 100°C and 200°C ethylene glycol has only about 1% of the storage capacity of rock but the maximum containment pressure is about 0.1 MPa. As the maximum temperature is lowered, the comparison of capacity with rock storage worsens while the containment requirements become less severe. At constant pressure the demand for isothermal or nearly isothermal storage works in favor of evaporation enthalpy. Thus at 300°C water has five times the storage capacity of rock if the latter is limited to a 20°C temperature fluctuation. Ethylene glycol at 200°C has only one fifth the capacity of similarly limited rock storage on the other hand. These results indicate that in the temperature range of interest, evaporation enthalpy storage does not appear economically feasible.

During the remaining part of the first year of effort it is planned to investigate the long term stability and compatibility with possible containment of the materials approved for such continued study by DOE.

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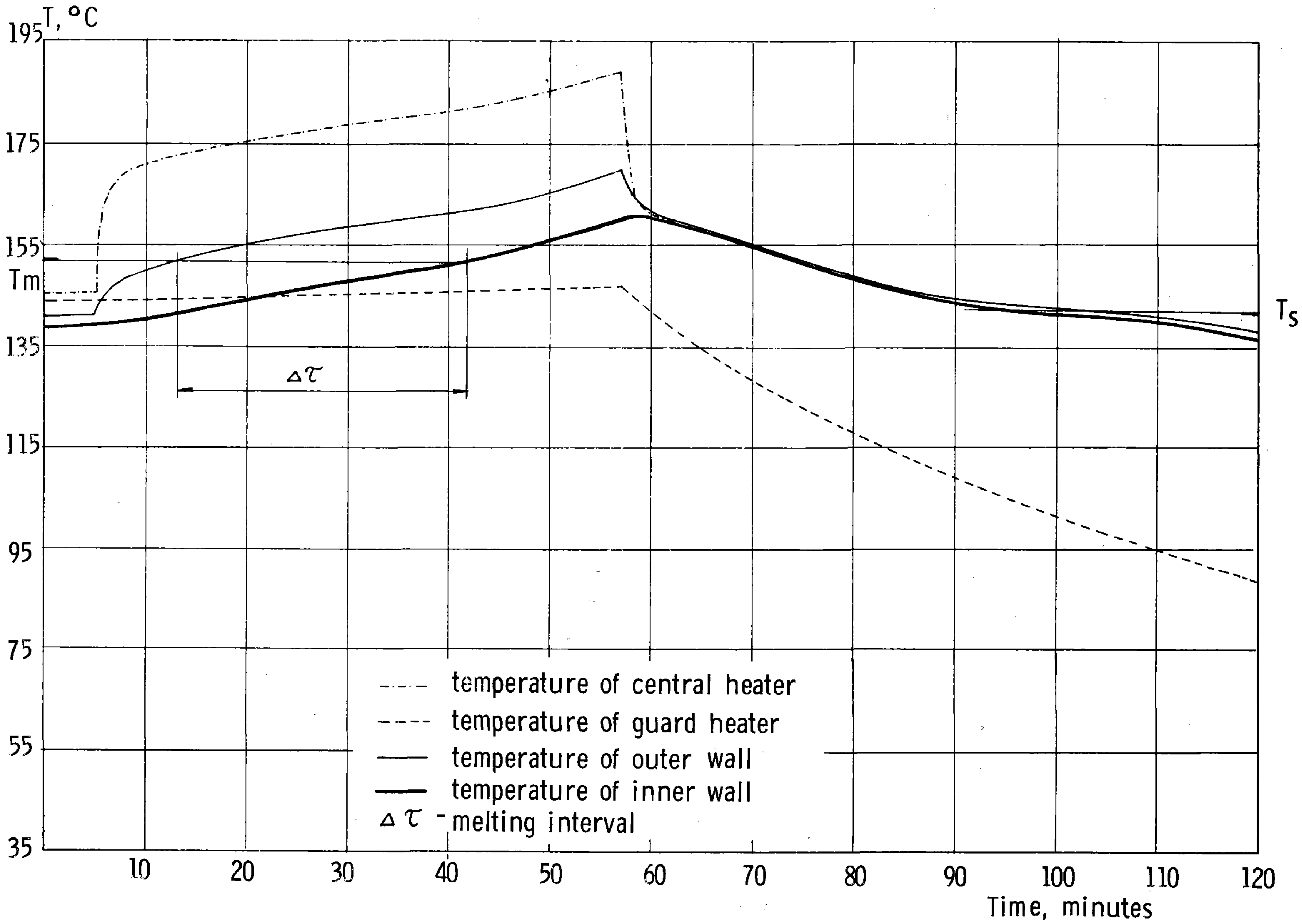
T, °C
195
175
155
Tm
135
115
95
75
55
35
10
20
30
40
50
60
70
80
90
100
110
120
Time, minutes
T_s
$\Delta\tau$
temperature of central heater
temperature of guard heater
temperature of outer wall
temperature of inner wall
$\Delta\tau$ - melting interval

U. S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title:	"Studies of a Salt Hydrate Heat Storage System:
Principal Investigator:	Dr. John Hallett
Organization:	Atmospheric Sciences Center Desert Research Institute University of Nevada System Reno, NV 89507 Phone: (702) 972-1676
Project Objectives:	To investigate salt hydrate storage systems from the viewpoint of attaining optimum power characteristics during crystallization and meltdown.
Project Status:	Completed as of August, 1978. FINAL REPORT to the National Science Foundation - "Studies of a Salt Hydrate Heat Storage System". Being prepared for final publication by U.S.D.E. under new title, "Studies of Nucleation and Growth of Hydrate Crystals with Application to Power Characteristics of Thermal Storage Systems".

Crystallization of a one and two component system for thermal storage by fusion heat of salt hydrates has been investigated for sodium sulfate ($10H_2O$), sodium thiosulfate ($5H_2O$) and sodium acetate ($3H_2O$). A continuous input of small crystals which grew and sedimented from the solution aimed to keep heat transfer surfaces crystal free. The two component system utilized kerosene as the heat transfer fluid, which was circulated as 5 mm drops rising by buoyancy through the salt solution. Both of these systems resulted, under appropriate operating conditions, in the formation of secondary crystals to replace those which grew and sedimented. The one component system proved unreliable as occasional nucleation lead to significant crystals growing on the heat transfer surfaces during cooling. The two component system functioned when crystal concentration was sufficiently low ($1\ cm^{-3}$) to permit growth of crystals of size large enough for sedimentation; otherwise crystals remained in suspension throughout the cycle. The operating characteristics and thermal efficiency of these systems was investigated for a laboratory and a pilot unit. From a study of the pilot system using sodium acetate, optimum operating conditions for near constant power output were delineated. Detailed studies were made of solution nucleation, secondary crystal production, linear crystal growth velocity and habit. Physical properties of the solutions were measured for both supersaturated and undersaturated solutions. These included viscosity, refractive index and density.

Grant Number:	AER75-19601
Grant Period:	July 1, 1975 - August 31, 1978 (includes 8-month no cost extension)
Funding Level:	$176,000
Funding Source:	RANN, National Science Foundation

PROJECT SUMMARY

Project Title: Immiscible Fluid - Heat of Fusion Heat Storage System

Principal Investigators: D. D. Edie, S. S. Melsheimer and J. C. Mullins

Organization: Clemson University
Department of Chemical Engineering
Earle Hall
Clemson, SC 29631

Project Objectives: The primary objective is to evaluate the feasibility of direct contact heat transfer in phase change energy storage using aqueous salt systems. A secondary objective is to improve knowledge and understanding of heat and mass transfer in direct contact aqueous crystallizing systems.

Project Status: In order to facilitate research into this energy storage device, the project was divided into four major research areas:

(1) crystal growth velocity study on selected salts

(2) selection of salt solutions

(3) selection of immiscible fluids

(4) studies of heat transfer and system geometry.

The project status is as follows:

(1) A crystal growth apparatus has been designed and built. Crystal growth data have been obtained for $Na_2HPO_4 \cdot 7H_2O$, $Na_2HPO_4 \cdot 12H_2O$, $Na_2SO_4 \cdot 10H_2O$ and $Na_2CO_3 \cdot 10H_2O$ using this device. Data on $CaCl_2 \cdot 6H_2O$ and $Na_2S_2O_3 \cdot 5H_2O$ presently are being obtained.

(2) This study is complete. Sodium carbonate and calcium nitrate were found unacceptable for this storage system but sodium thiosulfate, disodium hydrogen phosphate, sodium sulfate and calcium chloride were found to be acceptable.

(3) A list of over 160 potential immiscible fluids has been reduced to 12 promising candidates. The two most promising of these fluids presently are being tested.

(4) This study is complete. It was found that while the number of immiscible fluid diffusers did not change the storage efficiency, increasing the storage container height did increase the storage efficiency.

Contract Number: EY-76-S-05-5190

Contract Period: 6/1/76 - 11/30-78

Funding Level: $139,000

Funding Source: Department of Energy, Division of Energy Storage Systems

Background:

In optimizing the overall efficiency of both conventional and nonconventional energy systems, the storage of thermal energy is required. Heat of fusion systems clearly offer a great potential for high density storage of thermal energy, but this potential has yet to be realized in practice due to phase segregation, slow rates of energy transport, long term degradation, nucleation problems and the corrosive nature of the systems. A novel approach, direct contact heat transfer between the aqueous crystallizing solution and an immiscible heat transfer fluid, has been proposed as a possible solution to these difficulties (1, 2, 3). A feasibility study of this technique has been in progress in the Department of Chemical Engineering at Clemson University since 1975. The technical results of this research show the direct contact technique to be promising. The essence of the technique is that a fluid, (lower in density and immiscible with the aqueous salt solution) is used as the primary heat transfer agent. It is introduced at the bottom of the storage vessel as a dispersed phase, and as bubbles of this fluid rise through the vessel, it transfers heat to or from the salt solution, and also agitates the vessel contents. The heat transfer fluid is then pumped through the remainder of the primary heat transfer loop (e.g., solar collectors or heat pump exchanger and the air heating units of a residential heating system). Figure 1 is a schematic of the immiscible fluid - heat of fusion storage system.

In order to facilitate research into this energy storage device, research was divided into four major areas:

1. crystal growth velocity studies
2. selection of salt solutions
3. selection of immiscible fluids
4. studies of heat transfer and system geometry.

All four of these studies are now nearly complete and work is well underway on an energy storage demonstration unit with a 50 gallon capacity which will be cycled over a significant period of time to study long term degradation effects. Each of the four preliminary studies produced some important results.

Results and Discussion:

1. Crystal Growth Velocity Studies

This investigation was, perhaps, the most fundamental of the four major areas of study. Until this work no one had measured the interfacial growth kinetics (how solid growth rate varies with solution temperature or concentration) for the salt hydrates proposed for energy storage. A crystal growth apparatus was designed and built which provides both reliable growth rate data and is still simple to operate. A schematic of the apparatus, as well as the procedure used, is given in reference 2. The growth kinetics for $Na_2HPO_4 \cdot 7H_2O$, $Na_2HPO_4 \cdot 12H_2O$, $Na_2SO_4 \cdot 10H_2O$ and $Na_2CO_3 \cdot 10H_2O$ have been determined using this apparatus (1, 2). The results are plotted in Figures 2 and 3.

It is interesting to note the high growth velocity of sodium sulfate decahydrate from an "unmodified" solution of sodium sulfate. It is also interesting to observe that at equal undercoolings, disodium hydrogen phosphate dodecahydrate grows faster than the pentahydrate form. The growth kinetics of $Na_2S_2O_3 \cdot 5H_2O$ and $CaCl_2 \cdot 6H_2O$ are presently being determined.

This study is providing basic interfacial growth data on energy storage materials which can be directly used in accurately modeling both the performance of direct contact storage devices as well as containerized systems (4, 5).

2. Selection of Salt Solutions

In order to determine quantitatively the storage potential of the various salt hydrate candidates an apparatus (similar to the schematic shown in Figure 1) was constructed. The cylindrical plexiglass tank held 1.25ℓ of salt melt with a remaining 0.25ℓ reserved for coalescence of the immiscible fluid. A light hydrocarbon (Varsol) was pumped from a storage reservoir, through an auxiliary heat exchanger where heat was absorbed or released, and then was circulated through the salt solution to simulate heating or cooling. The heat flux was calculated as a function of time and an integration of this flux over the duration of the cycle gave the total heat transferred between the Varsol and the phase change material.

Initially the system was calibrated using water as the storage medium and Varsol as the heat transfer fluid. This calibration showed that when a salt system was used a 2 to 5% error could be expected. Disodium phosphate, calcium chloride, sodium sulfate, sodium thiosulfate, sodium carbonate and calcium nitrate were compared over an identical temperature cycle. Table 1 gives a comparison of average storage efficiency of these salts. This efficiency is calculated by dividing the actual heat removed or stored in the phase change material by the amount of energy that could have been removed or stored assuming equilibrium.

Sodium carbonate was found to be unacceptable because of both nucleation difficulty and its inverse solubility in water. Calcium nitrate was also ruled out because of excessive carryover using Varsol.

However, it is significant that four salts were found to be acceptable for use as storage materials. Because of their various crystallization temperatures, each of the four might be preferable depending upon the final application of the storage device. For disodium hydrogen phosphate, the majority of its energy was transferred above 34°C, for calcium chloride 27°C, for sodium sulfate 27°C and for sodium thiosulfate 47°C. Thus, one would expect sodium sulfate and calcium chloride to be useful in heat pump or solar assisted heat pump applications whereas disodium hydrogen phosphate and sodium thiosulfate may be applicable to direct solar energy storage. A rough cost estimate for storage of 420,000 kJ using each of these materials was also made and is given in Table 2. It is interesting to note that a similar sized commercial storage unit using Na_2SO_4 is being test marketed by Solarmatic of Tampa, Florida, for about $2200.

3. Selection of Immiscible Fluids

In this study a table of over 64 different heat transfer fluids was compiled from research on direct contact heat transfer and desalination reported in the literature. To this list over 100 additional fluids were added through fluid manufacturers suggestions and exhaustive search of fluid property tables. This gave a list of over 160 potential immiscible fluids for use in the direct contact storage system.

Excessively high cost, toxicity or high density ruled out many fluids. Also bench scale tests showed that high fluid viscosity (greater than 4-5 cp) could also increase carry-over of salt solution during cycling of the storage system (1). It has been found that properly placed and sized screens within the immiscible fluid can allow fluids with viscosities as high as about 10 cp to be used. This gives the list of 12 remaining fluids that are listed in Table 3. From this list the two most promising fluids (Exxon Marcol 72 and Monsanto Therminol 60) are being tested with a solution of disodium hydrogen phosphate as the phase change material. Each fluid is being analyzed for salt carry-over during a week of continuous cycling.

4. Studies of Heat Transfer and System Geometry

In order to design properly a prototype storage unit, heat transfer and system geometry effects were investigated in a fourth phase of the research. For this study a modular storage tank was constructed with a volume of from 4.7 to 14.3ℓ (depending on the tank height desired). This system operated similar to the smaller unit used to select feasible salt solutions. A detailed schematic is shown in Figure 4.

Calcium chloride, disodium hydrogen phosphate and sodium sulphate were tested in this apparatus. A column height of 30 cm gave average storage efficiencies of 68.2% for disodium hydrogen phosphate, 61.4% for calcium chloride and 47.8% for sodium sulphate. These values agree closely with those found in the smaller unit. Even more significant was the fact that reducing the number of diffusers from four to one did not lower storage efficiency (see Table 4) and increasing the column height from 30 to 50 cm increased storage efficiency by 6 to 17% depending upon the salt used (see Table 5).

The device displayed excellent rates of heat transfer. Table 6 gives typical volumetric heat transfer rate data.

Also, this study has shown that the actual performance of latent heat energy storage differs considerably from that of an ideal phase change. Figure 5 shows the salt solution temperature during a typical cooling run using a $Na_2HPO_4 \cdot 12H_2O$ solution. Reference 6 contains a more detailed discussion of this heat transfer and system geometry study.

Description of Future Work:

The remaining two potential immiscible fluids are to be tested and any salt carry-over measured for final fluid selection. Also in the crystal growth study the growth kinetics of $Na_2S_2O_3 \cdot 5H_2O$ and $CaCl_2 \cdot 6H_2O$ are presently being determined.

These four studies have shown that the direct contact latent heat storage system is feasible and gives excellent storage efficiencies. Using the results of these studies, a 200ℓ (55 gal) prototype unit is under construction. It will have 6 inlet diffusers for the immiscible fluid (comparable to the intermediate scale unit using a single diffuser) and be 95 cm high. The unit will be automatically controlled by a Data General Nova 1220 minicomputer system to cycle over a prolonged period and yield long term performance data. A minicomputer has already been programmed to provide on line system monitoring and data reduction. This unit will provide accurate, large scale, long term performance data on a direct contact - immiscible fluid storage device.

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(6) Costello, V. A., S. S. Melsheimer and D. D. Edie, "Heat Transfer and Calorimetric Studies of a Direct Contact-Latent Heat Energy Storage System," Thermal Storage and Heat Transfer in Solar Energy Systems, Proceedings of the Winter Annual Meeting of the American Society of Mechanical Engineers, Library of Congress Catalogue Card Number 78-68099, pp. 51-60, San Francisco, California, December 10-15, 1978.

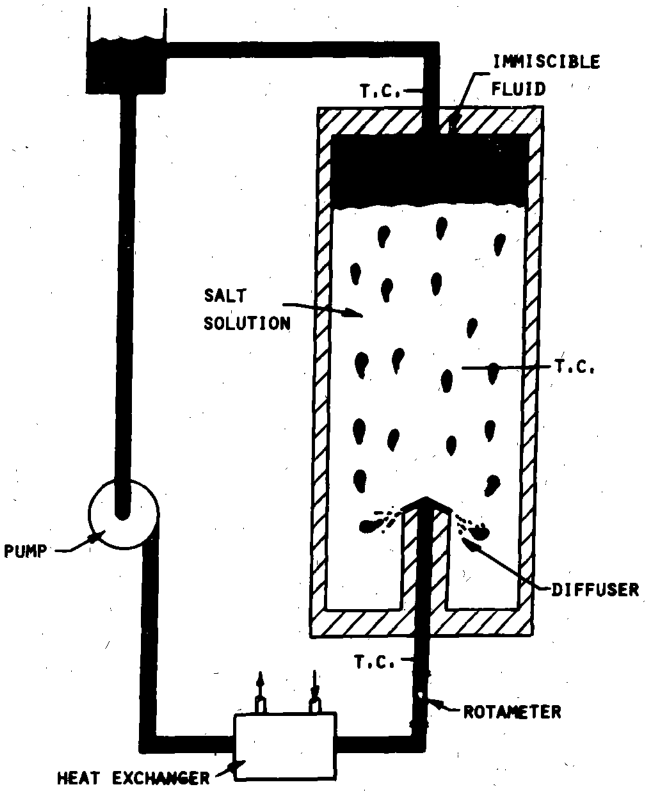


Figure 1. IMMISCIBLE FLUID - HEAT OF FUSION ENERGY STORAGE SYSTEM

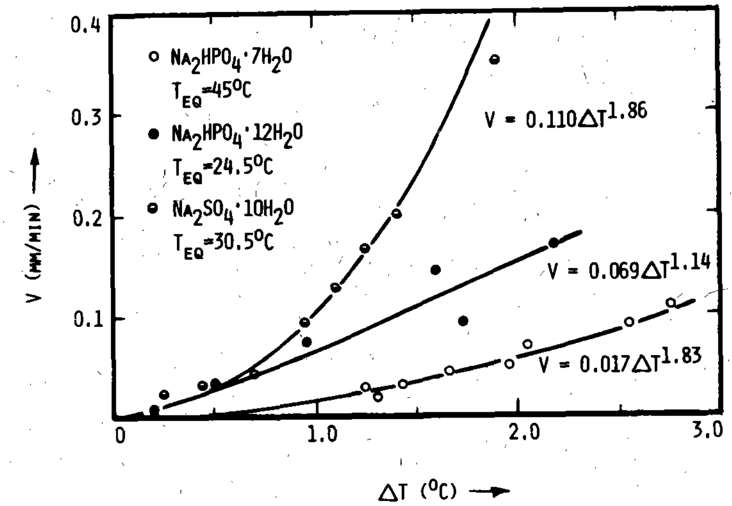


Figure 2. CRYSTAL GROWTH VELOCITY VS. UNDERCOOLING

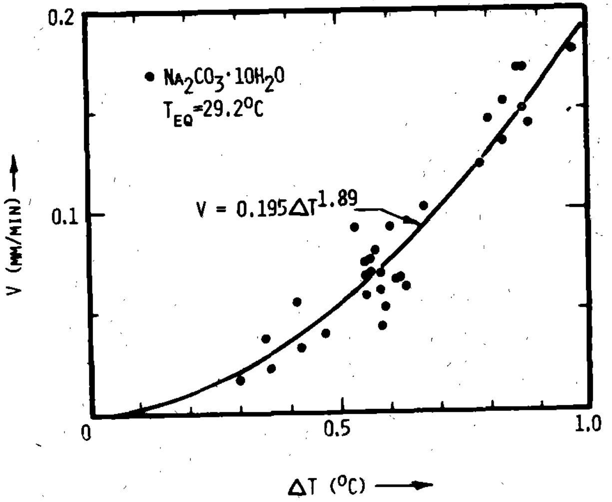
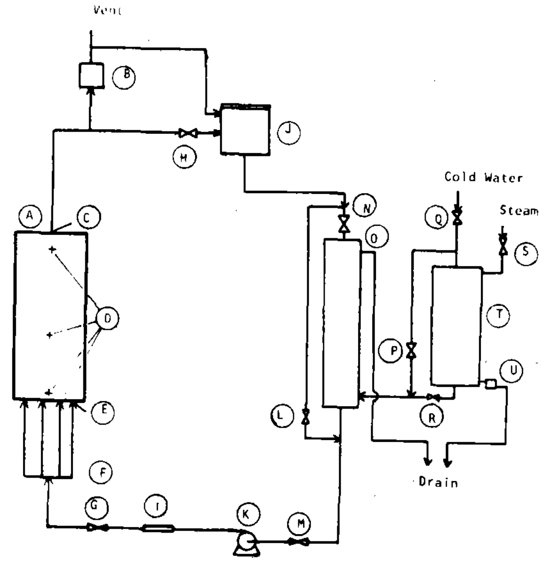


Figure 3. CRYSTAL GROWTH VELOCITY VS. UNDERCOOLING



(A)	Storage Column
(B)	Flow Rate Flask
(C)	Upper Thermopile Junction
(D)	Thermocouple Positions
(E)	Lower Thermopile Junction
(F)	Header
(G)	H, L, M, N, R. Ball Valves
(I)	Filter
(J)	Immiscible Fluid Reservoir
(K)	Positive Displacement Pump
(O)	Primary Heat Exchanger
(P)	Q, S Globe Valves
(T)	Secondary Heat Exchanger
(U)	Steam Trap

Figure 4. SCHEMATIC DIAGRAM OF APPARATUS

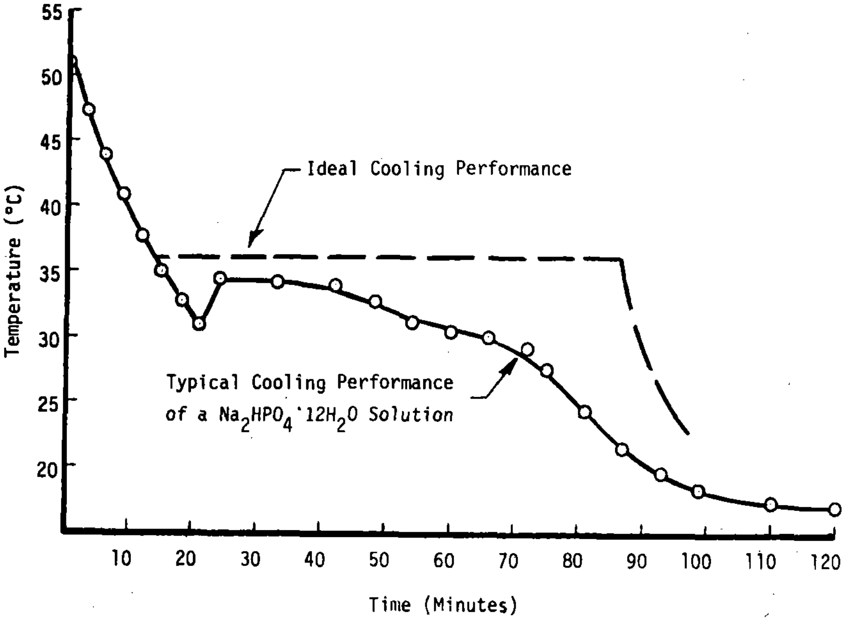


Figure 5. ACTUAL VS. IDEAL PERFORMANCE OF LATENT HEAT - DIRECT CONTACT STORAGE SYSTEM

Table 1. COMPARISON OF THE AVERAGE STORAGE EFFICIENCY OF VARIOUS SALT HYDRATES

Salt	Efficiency (%)
$Na_2HPO_4 \cdot 12H_2O$	76.9
$CaCl_2 \cdot 6H_2O$	62.4
$Na_2SO_4 \cdot 10H_2O$	51.2
$Na_2S_2O_3 \cdot 5H_2O$	95.1

Table 2. COST ESTIMATE FOR STORAGE OF 420,000 kJ

	Na_2HPO_4	$CaCl_2$	Na_2SO_4	$Na_2S_2O_3$
Storage Capability (kJ/kg melt), experimentally based	248	123	159	199
Cost of Storage Material, water and nucleating agents excluded:	$325	$153	$ 77	$415
Container Volume (m^3), based on a 1.83 m height with 0.15 m reserved for immiscible fluid coalescence:	1.27	2.53	2.16	1.39
Container Cost, $0.37/ℓ:	$471	$937	$802	$516
Cost of Immiscible Fluid, Marcol 72	$ 36	$ 71	$ 61	$ 41
Cost of Required House Volume, $27/$m^3$:	$ 34	$ 69	$ 59	$ 38
Miscellaneous, 15%:	$130	$185	$150	$152
Total	$996	$1415	$1149	$1162

Table 3. FEASIBLE IMMISCIBLE FLUIDS

Fluid	Melting PT, °C	Boiling PT, °C	Flash PT, °C	Density gm/cm³	Viscosity cp	Solubility	Cost	MFG's.
Butyl Oleate	-27		180	.865	8.2 @ 20°C	Insoluble	$0.50/ℓ	Ashland Chem., CP Hall, Harwick
Di (2-ethyl hexyl) adipate		214 @ 5mm	199	.921 - .927	8.2 @ 38°C	Insoluble		Ashland Chem., W.R. Grace & Co., Pfizer Chem.
Di (2-ethyl hexyl) azelate		237 @ 5mm	227	.917	10.0	Insoluble		Emery Ind., Pfizer Chem.
Di (n-hexyl) azelate		216 @ 5mm	205	.927 @ 20°C	7.8	Insoluble	$1.81/ℓ	CP Hall, Emery Ind., Pfizer Chem.
Diisobutyl adipate	-38	183 @ 14mm	175	.961	5-6 cp @ 20°C	Insoluble	$1.61/ℓ	CPS Chem., CP Hall, W.R. Grace & Co.
Dow-Corning Silicone Oil Q2-1132	-83	>350	232	.946	18.9 @ 25°C	Insoluble	$5.30/ℓ	Dow-Corning
Exxon Marcol 72	- 9		185	.859	11.4 @ 38°C	Insoluble	$0.32/ℓ	Exxon
Isopropyl-Myristate (EMEREST 2314)	- 5		152		6 (est) @ 38°C	Insoluble	$2.27/ℓ	Emery Ind.
Methyl Oleate (EMEREST 2801)	-16	228	177	.879	5 (est) @ 38°C	Insoluble	$1.14/ℓ	Emery Ind.
Therminol 44	Pour Pt. -62 to -68	10% 337 90% 390	207	.919	8.08 @ 38°C		$2.22/ℓ	Monsanto
Therminol 60	Pour Pt. -67.8	10% 288 90% 394	154	.990	4.09 @ 38°C		$1.93/ℓ	Monsanto
Transcal LT	-46	309 (10P)	160	.864 @ 18°C	6.91 @ 40°C			British Petroleum

Table 4. EFFECT OF NUMBER OF DIFFUSERS ON ENERGY STORAGE EFFICIENCY

Solution Height: 30 cm   Storage Material: $Na_2SO_4 \cdot 10H_2O$

Cycle Number	Number of Diffusers	Superficial Velocity cm/sec	Efficiency percent	
			Cooling	Heating
S1	4	0.11	50.0	44.2
S2		0.15	50.9	45.5
S4	2	0.10	49.5	44.4
S5		0.13	53.2	45.9
S6	1	0.11	49.2	47.0

Table 5. EFFECT OF SOLUTION HEIGHT ON EFFICIENCY OF SALT SYSTEMS

Diffusers: 4

Cycle No.	Solution Height cm	Superficial Velocity cm/sec	Efficiency percent	
			Cooling	Heating
$Na_2HPO_4 \cdot 12H_2O$				
P1	30	0.10	74.4	61.0
P2		0.12	73.2	60.1
P3		0.15	74.3	66.1
P4	50	0.11	84.4	79.6
P5		0.13	76.9	73.1
$CaCl_2 \cdot 6H_2O$				
C1	30	0.11	60.5	62.0
C2		0.15	58.9	64.3
C3	50	0.11	73.9	77.5
C4		0.15	71.4	71.9

Table 6. EFFECT OF SUPERFICIAL VELOCITY ON AVERAGE HEAT TRANSFER COEFFICIENT

Solution Height: 30 cm   Diffusers: 4

Cycle No.	Storage Material	Superficial Velocity cm/sec	Heat Transfer Coefficient watts/ℓ · °C	
			Cooling	Heating
P1	$Na_2HPO_4 \cdot 12H_2O$	0.10	9.7	6.4
P2		0.12	11.1	6.4
P3		0.15	11.8	11.6
C1	$CaCl_2 \cdot 6H_2O$	0.11	8.8	7.8
C2		0.15	11.1	13.2
S1	$Na_2SO_4 \cdot 10H_2O$	0.11	8.5	7.9
S2		0.15	6.9	9.7
S3		0.19	9.8	10.7

U. S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Heat Transfer Salt (HTS) Thermal Storage Peaking Plant

Principal Investigator: D. L. Vrable and R. N. Quade

Organization: General Atomic Company
P. O. Box 81608
San Diego, CA. 92138
Telephone: (714) 455-3693

Project Objectives: Evaluate the use of the General Atomic Company (GA) high-temperature gas-cooled reactor (HTGR) to generate intermediate load and peak power by use of heat-transfer salt (HTS) thermal storage. Investigate the technical and economic aspects of the conceptual design and evaluate the system's viability for this application. Using a reference thermal power level of 2000 MW(t) develop the system configuration, perform preliminary system analysis, and provide design data for the major plant components.

Project Status: This study was done at the request of Oak Ridge National Laboratory (ORNL) in fulfillment of Supplemental Agreement No. 4 to Subcontract 4188, and was completed in December 1976. The information, however, was not presented at the 2nd Annual Contractor's meeting. Because the study information parallels similar concepts discussed at the Third Annual Thermal Energy Storage Contractor's Information Exchange Meeting it is included in these proceedings.

Funding Source: Department of Energy, Division of Energy Storage Systems

Contract Period: 7/1/76 through 12/31/76

Funding Level: $50,000

HIGH EFFICIENCY THERMAL ENERGY STORAGE SYSTEM FOR UTILITY APPLICATIONS

D. L. Vrable and R. N. Quade

General Atomic Company
San Diego, California

ABSTRACT

A concept of coupling a high efficiency base loaded coal or nuclear power plant with a thermal energy storage scheme for efficient and low-cost intermediate and peaking power is presented. A portion of the power plant's thermal output is used directly to generate superheated steam for continuous operation of a conventional turbine-generator to product base-load power. The remaining thermal output is used on a continuous basis to heat a conventional heat transfer salt (such as the eutectic composition of $KaNO_3/NaNO_3/NaNO_2$), which is stored in a high-temperature reservoir [538°C (1000°F)]. During peak demand periods, the salt is circulated from the high-temperature reservoir to a low-temperature reservoir through steam generators in order to provide peaking power from a conventional steam cycle plant.

The period of operation can vary, but may typically be the equivalent of about 4 to 8 full-power hours each day. The system can be tailored to meet the utilities' load demand by varying the base-load level and the period of operation of the peak-load system.

ELECTRIC UTILITIES are keenly interested in making effective use of their installed capacity by charging energy systems with off-peak energy. In addition, it is important for the electric utility industry to relieve the dependency on petroleum-based fuel by shifting to coal and nuclear power plants. Both of these objectives can be met by utilizing thermal energy storage for intermediate and peaking power.

The load demand on an electric utility grid undergoes significant variations on a daily and weekly basis. These demands are broadly categorized as base-load, operating an average of 12 to 24 hours a day; intermediate-load, averaging about 4 to 12 hours a day; and peaking-load, operating up to about 4 hours a day. Since the available generating capacity must equal the peak demands, a significant portion of that capacity is unused during off-peak periods.

Smaller increments of capacity representing lower capital costs and higher operating costs, such as steam plants fired by natural gas, oil, coal (particularly in older units), and, in recent years, gas turbines, usually meet the intermediate and peak power requirements. The newer, larger, fossil-fueled plants and nuclear plants, both of which represent relatively large capital investments and have lower operating costs, usually meet base-load demands. Sharply increased fossil fuel prices have placed a heavy economic penalty on the intermediate- and peaking-load plants and have created an incentive for increased use of base-load plants. Consequently, a means for storing energy when the base-load capacity exceeds the demand and for supplying this energy when the demand exceeds the base-load capacity are high desirable. To date, only hydro-pumped storage has existed for this use.

Recently, a number of different concepts involving thermal energy storage have evolved and conceptual plant design studies have been initiated to prove their feasibility and technical merit. One such concept is to store off-peak power in pressurized hot water in an underground cavity (1).* This stored hot water can be flashed to steam and directed to a peaking turbine facility for generation of additional peaking power. References 2 and 3 discuss a thermal energy storage system using hot oil for off-peak thermal energy storage. In this system, steam extraction from the turbine is increased during off-peak periods resulting in a drop in power output. The steam heats oil through heat exchangers as the oil passes from cold tanks to hot tanks. During the peak demand periods, the oil flow is reversed and the stored heat is used to preheat the boiler feedwater, releasing the extraction steam for expansion work in the turbine and thus raising the power production. While these electrical output changes are taking place, the power plant's boiler runs under constant conditions. A similar scheme is being studied by Electricite de France in conjunction with several companies (4).

Compressed air storage systems have also been considered to meet the utilities' peak energy demands. References 5 and 6 discuss the various studies of this method. In general, the compressed air energy storage (CAES) plant operates in a utility network by using low-cost electrical power (during low-demand periods) to power large electric motors driving air compressors.

The concepts of thermal energy storage presented thus far all have relatively low net plant efficiency or low thermal storage efficiency. Thermal storage efficiency is defined as the ratio of the efficiency of the conversion from heat source to the bus bar via the storage system to the efficiency that can be obtained without the

*Numbers in parentheses designate References at end of paper storage system. In addition, many of the concepts require certain geological considerations that affect the siting of the thermal energy storage system.

In the future, it is expected that an increasing portion of electrical demands will be met by nuclear plants, which can take advantage of the lower fuel costs and the large energy resource represented by domestic supplies of nuclear fuel. The operating characteristics of available nuclear plants make them particularly well suited to base-loaded operation.

The system proposed here utilizes a high-temperature gas-cooled reactor (HTGR) steam power plant coupled with a high-temperature thermal energy storage system to generate peak power. The approach was an outgrowth of a study using nuclear process heat for petroleum refinery applications (7, 8) in which a heat transfer salt was found to transport heat very effectively. A portion of the HTGR thermal output is used directly to generate superheated steam for continuous operation of a conventional turbine generator producing base-load power. The remaining thermal output is used continuously to heat a commercially available heat transfer salt, which is then stored in a high-temperature reservoir [538° to 593°C (1000° to 1100°F)]. During peak demand periods, the salt is circulated from the high-temperature to a low-temperature [204° to 316°C (400° to 600°F)] reservoir through steam generators that power a conventional steam cycle plant. The period of operation can vary, but typically may be the equivalent of about 4 to 8 full-power hours each day. The system can be tailored to the utilities' demand conditions by varying the base-load level and period of operation of the peak-load system. For example, a 2000-MW(t) HTGR could generate approximately a 400-MW(e) base-load continuously and an additional 1000-MW(e) peaking power for an 8-hour period.

The concept has three basic advantages:

1. The overall efficiency of the storage and conversion system is high, approaching that of the base-load plant.

2. The heat source operates continuously at maximum power, taking full advantage of lower fuel cost.

3. The system can utilize a high-technology coal-fired heat source or high-temperature nuclear reactors such as the HTGR, gas-cooled fast breeder reactor (GCFR), and liquid metal fast breeder reactor (LMFBR).

PLANT DESCRIPTION

The basic plant, consisting of the reactor system, the intermediate heat transfer helium system, the base-load steam system, the salt storage system, and the peaking steam system, is shown in Fig. 1. The concept uses the basic reactor design planned for the commercial HTGR steam cycle system.

Several system diagram variations can be considered in coupling the reactor system, the intermediate heat transfer helium system, the base-load steam system, the salt storage system, and the peaking steam system. Since the salt pressure is just slightly above atmospheric pressure, salt leakage in the primary circuit is highly unlikely; however, to eliminate the safety issues resulting from such a postulated accident, an intermediate helium loop is employed. This approach allows placement of the steam generators and salt heaters outside the reactor containment and facilitates access for maintenance or replacement.

The primary helium coolant flows down through the reactor core, transferring heat from the graphite reactor core to the primary helium coolant. The primary helium transfers the absorbed heat to the intermediate heat-transfer loop through four equally sized helium/helium heat exchangers within the prestressed concrete reactor vessel. The intermediate loop is comprised of helium/steam generators, helium/salt heat exchangers, and intermediate loop helium circulators. The thermal energy transferred by the intermediate loop is delivered simultaneously in parallel to the base-load steam plant and the heat transfer salt storage loop. The thermal energy delivered to the helium/steam generator is used directly to supply superheated steam for continuous operation of a conventional turbine generator producing base-load power. The remaining thermal output continuously heats the heat transfer salt, which is stored in large reservoirs. During peak electrical demand periods, the hot salt is circulated from the hot reservoirs through a salt/steam heat exchanger to generate superheated steam used by the turbine/generator conversion equipment of the peaking plant. The cold salt is returned to the cold storage tanks. Cycle diagrams for the base-load portion and the thermal energy storage system peaking portion are shown in Figs. 2 and 3, respectively.

BASE LOAD STEAM SYSTEM-The base load steam system is modeled directly from the steam cycle HTGR, using a reheat cycle but using an intermediate loop. The steam generators produce superheated steam at 513°C (950°F) and 16.6 MPa (2400 psia) and reheat steam at 537.8°C (1000°F) and 3.8 MPa (550 psia).

Steam from the high-pressure turbine exhaust passes through the primary helium circulator turbines before being reheated for admission to the intermediate-pressure turbine. Approximately 19% of the intermediate-pressure turbine exhaust is routed to the condensing drive turbines for the boiler feedpumps and intermediate helium circulators. The exhausts from the condensing turbines flow directly to the surface condenser. The remaining intermediate-pressure turbine exhaust is admitted to the low-pressure turbine. Turbine bleed flows are extracted from the low-pressure turbine for three stages of closed feed water heating and one stage of deaeration.

The low-pressure turbine exhaust is condensed by a surface condenser operating at 57 mm (2.25 in.) of mercury. The heat load imposed on the condenser is rejected through a natural draft evaporative cooling tower. The circulating water system is based on 24°C (75°F) dry bulb temperature, 50% relative humidity, 11°C (20°F) approach temperature, and 13.3°C (24°F) rise in the circulating water temperature across the condenser.

THERMAL ENERGY STORAGE SYSTEM - The candidate heat storage fluids can include several salt

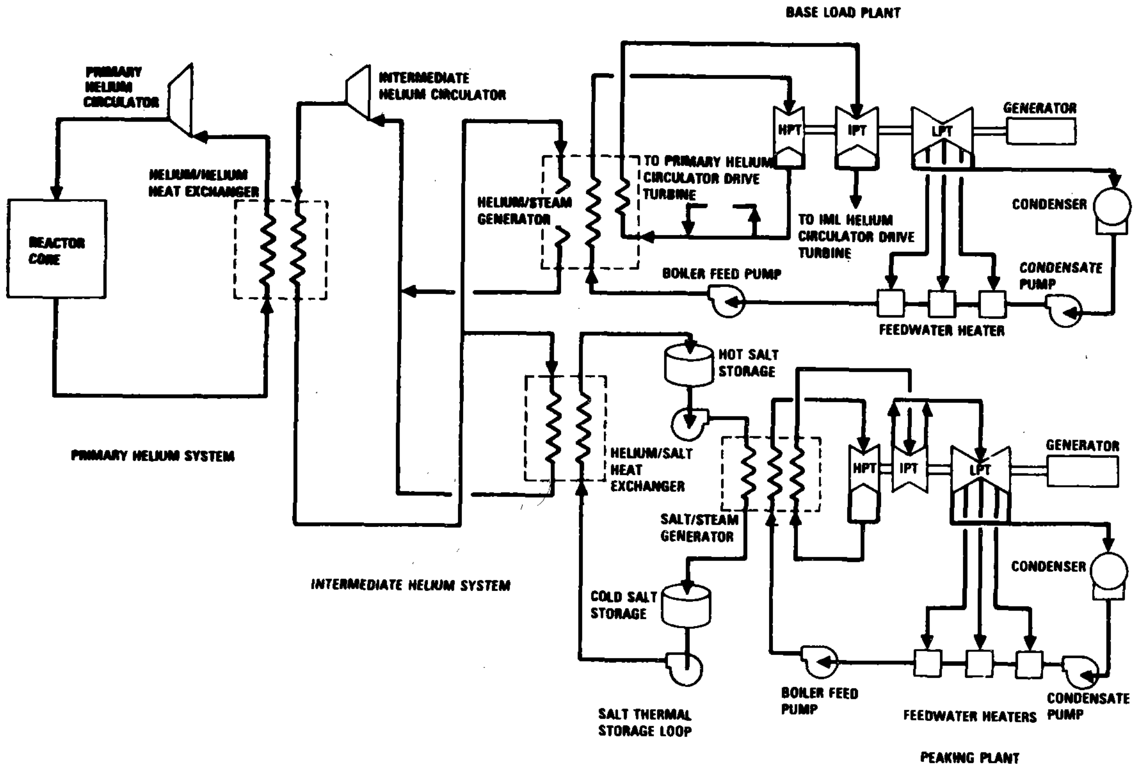


Fig. 1 - HTGR/heat transfer salt thermal peaking plant

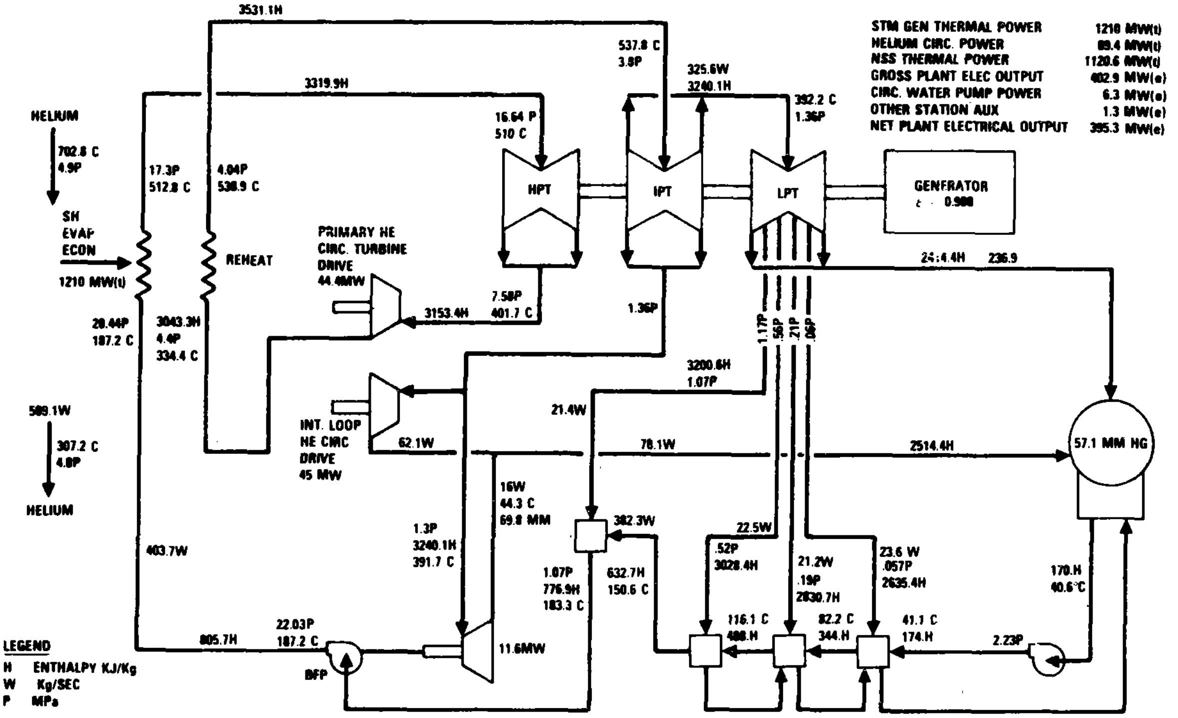


Fig. 2 - Base load system

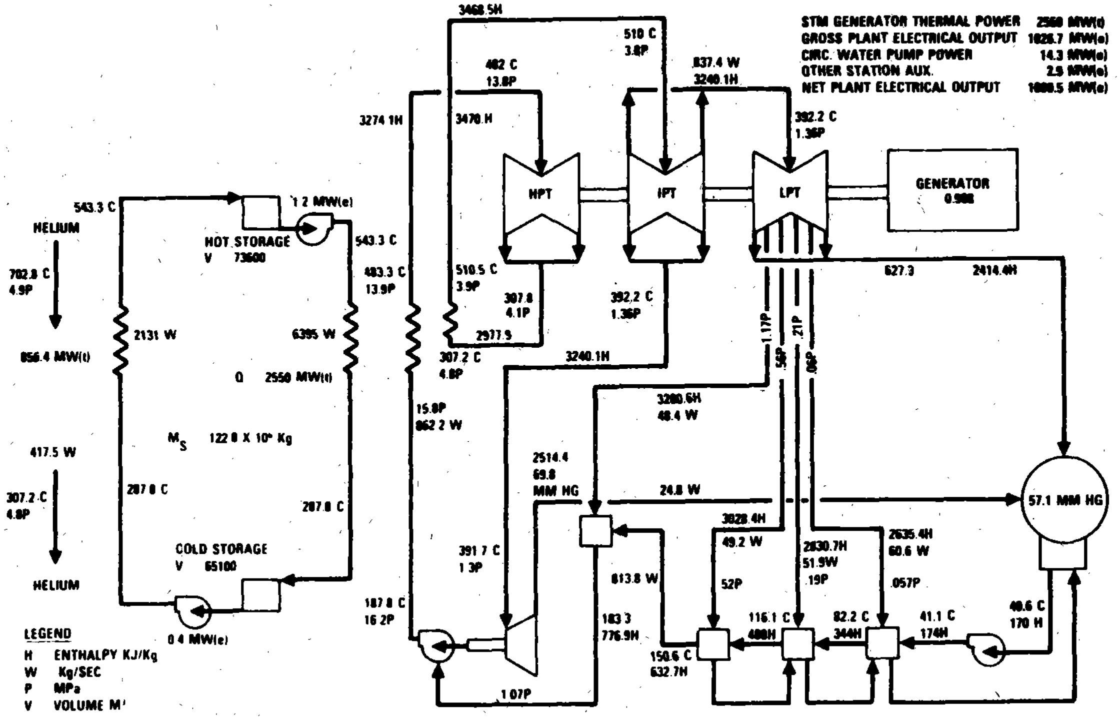


Fig. 3 - Peaking system cycle diagram

mixtures and some liquid metals. From the standpoint of economics, operating experience, and efficiency, only two molten salt mixtures were considered. These were the eutectic mixture of 53 wt % Na NO_2, 40 wt % KNO_3, and 7 wt % Na NO_3, and the eutectic mixture of 54.3 wt % KNO_3 and 45.7 wt % Na NO_3. Both salt mixtures have considerable operating experience (9) and both have similar thermophysical properties except for different melting points. The lower melting point of the ternary mixture was favored for this study.

The heat storage system uses groups of four hot and four cold tanks containing heat transfer salt at 543°C (1010°F) and 288°C (550°F). The top surface of the fluid is covered with nitrogen at slightly above atmospheric pressure.

The fluid is pumped continuously from the cold tank, through twin heat exchangers [where it is heated from 288°C (500°F) to 543°C (1010°F)], to the hot tank at the rate of 2134 kg/s (16.9 x 10^6 lb/hr). During the 8-hour period of each day when peaking power is required, fluid is pumped from the hot tank through twin steam generators [where it is cooled to 288°C (550°F)] to the cold tank at the rate of 6400 kg/s (50.7 x 10^6 lb/hr). The capacities of the hot and cold tanks accommodate these flows are 73,600 m^3 and 65,100 m^3 (2.6 x 10^6 ft^3 and 2.3 x 10^6 ft^3), respectively.

The heat storage system and its relationship to the peaking system are shown in Fig. 3.

The heat transfer salt oxidizes and promotes general corrosion of the ferrous alloys. Studies have shown, however, that corrosion rates are uniform and decrease with time (10-13). These results substantiate the formation of a tenacious, passive, oxide film, which is desirable. Up to temperatures of 454°C (850°F), carbon steels have been successfully used with virtually no corrosion. For higher temperature systems operating near 593°C (1100°F), stainless steels or heat-resistant alloys are recommended by the supplier. They have shown improved resistance to general corrosion over carbon steels, and possess the strength required at the elevated temperatures.

With a large system involving heat transport, the potential for mass transport of chemical species within the heat transfer salt is of concern. If elements are removed from the structural containment materials and redeposited or absorbed at different locations, design integrity could be impaired. This phenomenon would not be anticipated in a heat transfer salt system. The tenacious, passive oxide present on the metal surfaces should act as a very effective barrier to diffusion of interstitial elements such as carbon.

Data indicate that temperatures up to 593°C (1100°F) can be handled satisfactorily from a corrosion standpoint, the salt decomposition becoming the limiting factor at this level. The low-temperature side of the loop thus can utilize carbon steel, but the high-temperature side will require stainless steel or another alloy.

PEAK LOAD STEAM SYSTEM - The peaking steam cycle design is similar to the base-load steam cycle with the following exceptions:

1. High-pressure turbine inlet conditions are

482°C and 13.8 MPa (900°F and 2000 psia).

2. Intermediate-pressure turbine conditions are 510°C and 3.8 MPa (950°F and 550 psia).

3. Helium circulator drive turbines are eliminated.

The lower temperature and pressure inlet conditions of the high-pressure turbine are advantageous since the turbine is operated in a cycling mode. This results in less severe turbine casing design conditions, which reduces the physical mass of the machine. Conventional practice also indicates that lower turbine inlet temperature and pressure are desirable for turbines used in peaking applications.

PLANT OPERATION

Unique to the HTGR/heat transfer salt peaking plant are its two modes of operation: continuous base-load and cyclic peak-load. The reactor system portion of the plant follows the operation pattern of the standard HTGR steam cycle plant. The reactor core operates continuously at full power, supplying thermal energy to both the base-load system and the heat transfer salt thermal storage loop.

The primary helium system, the intermediate helium system, the base-load system, and the thermal storage peaking-load system are each divided into two completely independent loops, allowing one-half of the total plant to operate while the other portion is down for maintenance. In addition, the heat exchangers (helium/heat transfer salt and helium/steam) within one loop can be taken out of service while those in the other continue to function normally. This allows full or partial base-load operation with full or partial peaking system operation. Moreover, operation of the base-load system only can be accommodated. The peaking system cannot be operated alone since the primary and intermediate helium circulator drive turbines are driven by steam from the base-load system.

The steam system portions of the HTGR/heat transfer salt plant are similar in operation to conventional base-load steam and peaking-load steam plants.

ASSESSMENT WITH OTHER THERMAL ENERGY STORAGE TECHNOLOGIES

While hydro-pumped storage has been the only approach to utility storage of energy in widespread use, several other concepts have been proposed. The concepts selected for a relative technical and economic assessment are steam storage, hot oil storage, and molten salt sensible heat storage. Although available data on energy storage are extensive, only cursory cost comparisons are possible. This results from insufficient costing detail and assurance of consistent costing methods used in the various investigations. The economic information presented here is intended only for a preliminary comparison of the various concepts. The Electric Power Research Institute and ERDA addressed an economic comparison between a variety of different energy storage systems (14); however, the HTGR/heat transfer salt systems had not been introduced at the time of their study. The method of comparison introduced in Ref. 14 is based on estimating the capital cost of the energy storage system in two parts: the cost [$/kW(e)] of the power-related equipment and the cost [$/kW-h] of the energy-storage-related equipment. An independent assessment of the HTGR/heat transfer salt system was conducted by the Oak Ridge National Laboratory (15). Using the costs developed by General Atomic for the HTGR/heat transfer salt power peaking plant, the Oak Ridge National Laboratory conducted an economic assessment of other types of thermal storage systems including the hot oil system. Table 1 summarizes a comparison between the HTGR/heat storage salt system and other near-term concepts. The power-related costs for thermal energy storage systems are approximately the same. The storage-related costs, however, favor the heat transfer salt and hot oil system. Based on these comparisons, no clear economic choice can be made without further design studies to refine the cost estimates.

Table 1 - Expected Technical and Cost Characteristics of Energy Storage Systems

	Hydro[a]			Thermal	
Characteristics	Pumped Storage	Compressed[a] Air	Steam[a]	Oil[a]	HTS[b]
Commercial availability	Present	Present	Before 1985	Before 1985	1985 and on
Economic plant size, MW	200-2000	200-2000	50-200	50-200	50-1000
Power-related costs, $/kW[c]	90-160	100-210	150-250	150-250	200-250
Storage-related costs, $/kW-hr[c]	2-12	4-30	30-70	10-15	10-15
Efficiency, %	70-75	---	65-75	65-75	85-95

[a] Information extracted from Ref. 14.

[b] Information extracted from Ref. 15 adjusted to 1975 dollars.

[c] Based on 1975 dollars.

In addition to comparing energy-storage related costs and power-related costs, the storage energy efficiency is also an important criterion. The HTGR/heat transfer salt system has a storage efficiency (defined as the ratio of the efficiency of the conversion from the heat source to the bus bar via the storage system to the efficiency obtained without energy storage) of approximately 90%. This represents a significant increase over the other methods of storage, and has additional merit in terms of fuel conservation. The sizing flexibility associated with the base load to peaking load level also allows the HTGR/heat transfer salt system to be tailored to a particular utility's needs and system load characteristics.

Although further studies will be required to assess the quantitative aspects of the HTGR/heat transfer salt system, qualitative comparisons indicate it is a viable concept and possesses advantages over other near-term energy storage schemes.

CONCLUSIONS

The heat transfer salt thermal storage concept makes highly efficient use of energy generated during off-peak periods to provide electrical generation for daily intermediate and peaking power demands. The coupling of this concept with an HTGR nuclear plant results in peaking power costs that are competitive with fossil-fueled systems for this application. In addition to potential cost savings, the HTGR/heat transfer salt concept provides an important means of conserving fossil fuels by substituting nuclear energy.

The system utilizes existing HTGR technology as incorporated into the Fort St. Vrain plant and the large HTGR design for commercial application. Salt has been used on a smaller scale in commercial applications under similar temperature conditions for many years.

The concept's economic appeal results from high efficiency, low fuel costs, and the economy of large size. Except for very large utilities with geographically concentrated loads, the attractiveness of the concept may depend on the utility's need for additional base-load as well as peaking power. The plant capacity can be adapted to a utility's peaking power requirements by selecting an appropriate base-load/peaking-load power split.

The efficiency of the thermal energy utilization is approximately 90% of that for direct use of the energy (without storage) in a modern steam electric power plant. The thermal storage system developed for this study may also be coupled with other types of high-temperature heat sources such as coal-fired fossil or the LMFBR and GCFR nuclear plants, as well as solar systems having similar high-temperature capability.

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HIGH TEMPERATURE THERMAL ENERGY STORAGE PROJECT OVERVIEW

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Manager, Thermal and Mechanical Energy Storage Project Office
NASA Lewis Research Center

The DOE Division of Energy Storage Systems is responsible for formulating and managing research and development in energy storage technology. Major responsibility for project management in selected areas has been shifted to the DOE national laboratories and other government agencies. As part of DOE's Thermal Energy Storage and Transport Program, the NASA Lewis Research Center (LeRC) was given the primary responsibility for the development of high temperature sensible and latent heat storage technology. Project management responsibility for the DOE High Temperature Thermal Energy Storage Project was formally delegated to NASA under an Interagency Agreement on January 17, 1977. The Project is being managed within the Power Generation and Storage Division at the NASA Lewis Research Center in Cleveland, Ohio.

The general objective of the High Temperature Thermal Energy Storage Project is to develop the technology for cost and performance effective thermal energy storage systems for end-use application sectors. The technologies include all sensible and latent heat storage for temperatures above approximately 250°C. Technologies for selected applications will be developed to the point of acceptance by the private sector or for systems integration and field testing by a DOE end-use Division. The Project's activities are accomplished principally through contracts within the private sector to provide early and effective transfer of technology. Government funds in support of the Project are provided entirely by DOE. Activities are coordinated with complementary projects and tasks being pursued by DOE end-use Divisions and national laboratories, the Solar Energy Research Institute (SERI), the Electric Power Research Institute (EPRI), the Tennessee Valley Authority (TVA), and the Naval Research Laboratory (NRL).

The structure of the High Temperature Thermal Energy Storage Project is shown in Figure 1. The project's current major activities are directed toward electric utility, industrial process and reject heat, and solar thermal power systems applications. The major activities support the DOE Thermal Energy Storage and Transport Program's FY 79 thrust and key technology development areas. A summary of the Project's activities follows.

Electric Utility Applications

Potential applications of high temperature thermal energy storage and transport systems within electric utilities include peaking power generation, process heat for in-plant and industrial use, and advanced power generation systems. Current project activities emphasize thermal energy storage for peaking power generation. Thermal energy storage systems integrated with conventional coal power plants can displace petroleum-fueled peaking power plants and, hence, reduce oil consumption within the utility industry. Thermal energy storage is also attractive because many of its technologies have potential for early commercialization and are not dependent on site geology. The identification, comparative evaluation, conceptual design, and analysis of candidate systems for mid-term applications was initiated in FY 78. This is a cooperative effort involving DOE's Divisions of Energy Storage Systems and Electric Energy Systems, EPRI, and TVA. The effort is being accomplished principally under a system study contract competitively awarded to the General Electric Company. (The status of this contract is summarized in the Proceedings.) The results of this system study will be used to perform a comparative evaluation of thermal energy storage with other storage technologies, coal cycling plants, and load management techniques. If feasible and justified, thermal systems will be selected and required development and a preliminary engineering design of a large scale field test in an operating utility will be initiated.

Industrial Process and Reject Heat Applications

Many industrial applications have been identified where thermal energy storage of process and reject heat for subsequent in-plant or off-site use appears to be economically and technically feasible with significant near-term conservation benefits. Assessment studies of food processing, aluminum, iron and steel, paper and pulp, and cement industrial applications were completed in FY 78. Results are summarized in the Proceedings. Current plans are to continue these activities and proceed with a development and technology demonstration program of selected systems and applications. Request for proposals will be issued in FY 79. Selection criteria will emphasize applications which offer significant potential for near-term oil savings. Multiple awards are anticipated.

Solar Thermal Power Systems Applications

The future impact and penetration of solar thermal power systems are dependent on the development and integration of viable thermal energy storage systems. Plans are being developed with the DOE Division of Central Solar Technology for a comprehensive thermal energy storage technology development program matched to solar thermal power systems requirements and milestone schedules for FY 80-85. Inputs to the plan are being provided by a task force consisting of representatives from SERI, SLL, SLA, NASA-JPL, Aerospace Corporation, PRC Energy Analysis Company, and NASA-LeRC. It is the intent of DOE to provide the draft planning document to the private sector for information and critiquing.

In the proposed program thermal energy storage technologies will be developed that provide either advanced alternatives offering improvement over current baseline subsystems or baseline storage subsystems for those applications which have no storage subsystems under development. A summary of the draft program plan elements is shown in Figure 2. Major program elements are diurnal storage for applications requiring the use of storage on a daily cycle, short-term or buffering storage, long duration storage, and supporting research and development for advanced solar technologies.

Based on the draft planning document, current emphasis with the High Temperature Thermal Energy Storage Project is being directed toward diurnal thermal energy storage for large steam Rankine systems and thermal buffering storage for repowering. Depending on DOE solar thermal FY 79-80 program priorities, development and technology demonstrations of storage subsystems for these two applications will be initiated in FY 79. System definition studies will also be initiated for small power diurnal and buffering storage applications. SERI's Systems Analysis Branch will provide preliminary engineering requirements for these storage subsystems. The requirements include specific hours of storage duration, quantity of heat stored, fluid input and recovery temperatures and pressures, heat transfer rates, heat transfer fluids and value of storage criteria. In addition, a future goal of SERI sponsored studies will be optimization of the value of integrated solar/storage systems.

Laboratory development efforts and engineering evaluations of advanced storage technologies initiated in FY 78 will be continued and focused on solar thermal power systems applications. These include an assessment study of sensible heat storage in deep aquifers and caverns being performed by the University of Houston and the development of advanced latent heat storage concepts by Honeywell, Inc., Grumman Aerospace Corp., NRL, and Comstock and Wescott, Inc. The status of each of these efforts is in the Proceedings.

Supporting Research and Technology

Focused and exploratory research and technology studies will be continued in FY 79. The objective of these activities will be continued in FY 79. The objective of these activities is to establish a technical base enabling the resolution of generic thermal energy storage problems and the identification of new storage concepts and Project application areas. Current emphasis is on thermal energy transport and very high temperature (> 1000°F) storage and advanced power conversion system applications.

A list of Project supporting research and technology activities is shown in Figure 3. An assessment of storage systems using fluidized bed heat exchangers will be performed under a competitively awarded contract now being negotiated. Another activity will define promising high temperature thermal transport applications and identify technology requirements for future research and development efforts. Engineering evaluations of a latent heat NaOH system fabricated by Comstock and Wescott and a storage module using sodium sulfate fabricated by Calmac, Inc. are being performed in-house at NASA-LeRC. The remaining contractor-identified tasks are described in the Proceedings. Currently, 20% of the Project's funding is directed toward supporting research and technology.

This briefly summarizes the structure, activities, and status of the High Temperature Thermal Energy Storage Project. Future activities will be directed toward the identified principal thrusts with technology and supporting research studies being conducted to the extent budgetary constraints permit.

FIGURE 1

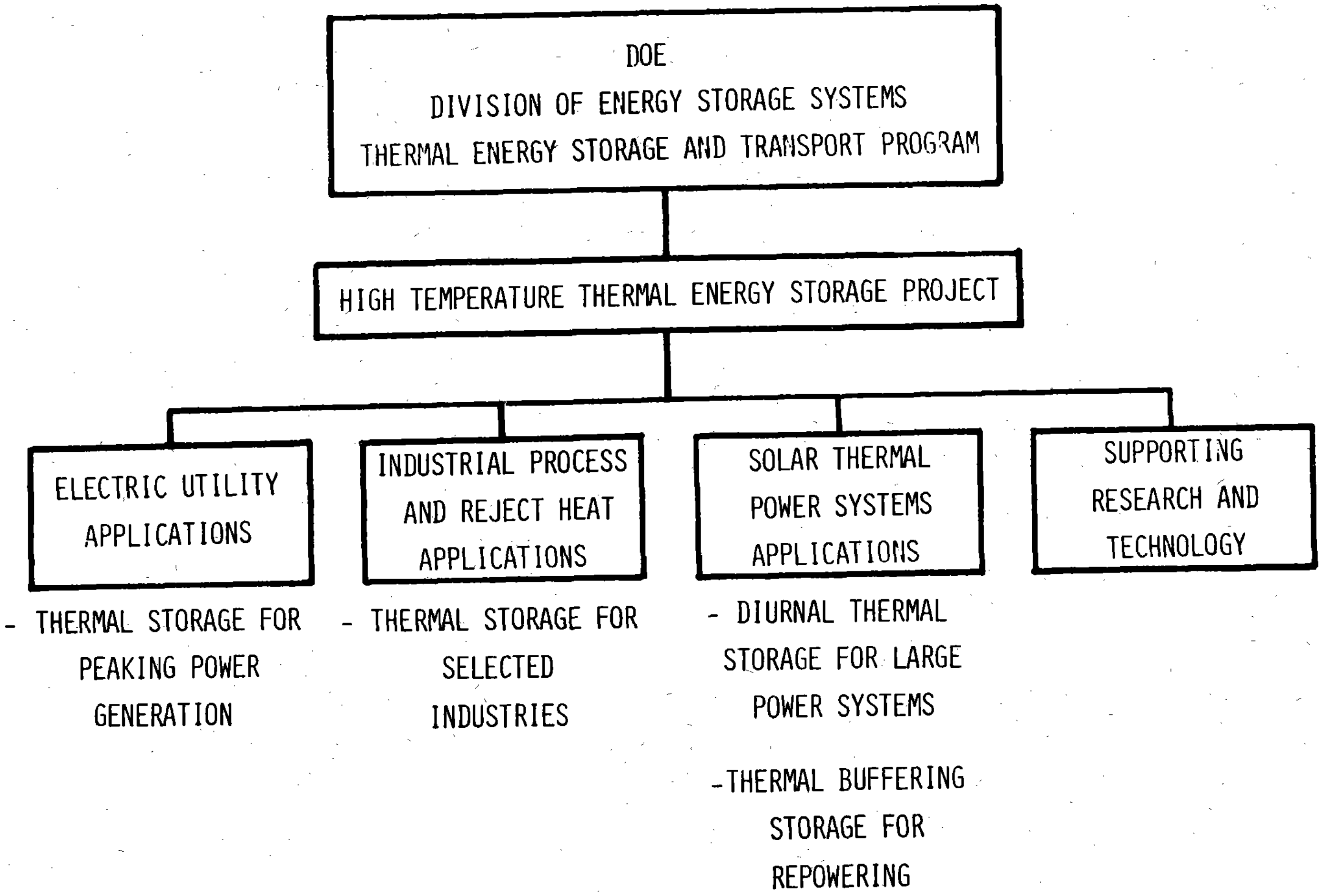

DOE
DIVISION OF ENERGY STORAGE SYSTEMS
THERMAL ENERGY STORAGE AND TRANSPORT PROGRAM
HIGH TEMPERATURE THERMAL ENERGY STORAGE PROJECT
ELECTRIC UTILITY APPLICATIONS
- THERMAL STORAGE FOR PEAKING POWER GENERATION
INDUSTRIAL PROCESS AND REJECT HEAT APPLICATIONS
- THERMAL STORAGE FOR SELECTED INDUSTRIES
SOLAR THERMAL POWER SYSTEMS APPLICATIONS
- DIURNAL THERMAL STORAGE FOR LARGE POWER SYSTEMS
-THERMAL BUFFERING STORAGE FOR REPOWERING
SUPPORTING RESEARCH AND TECHNOLOGY

FIGURE 2

SOLAR THERMAL POWER SYSTEMS APPLICATIONS

SUMMARY OF THERMAL ENERGY STORAGE TECHNOLOGY DEVELOPMENT DRAFT PROGRAM PLAN ELEMENTS

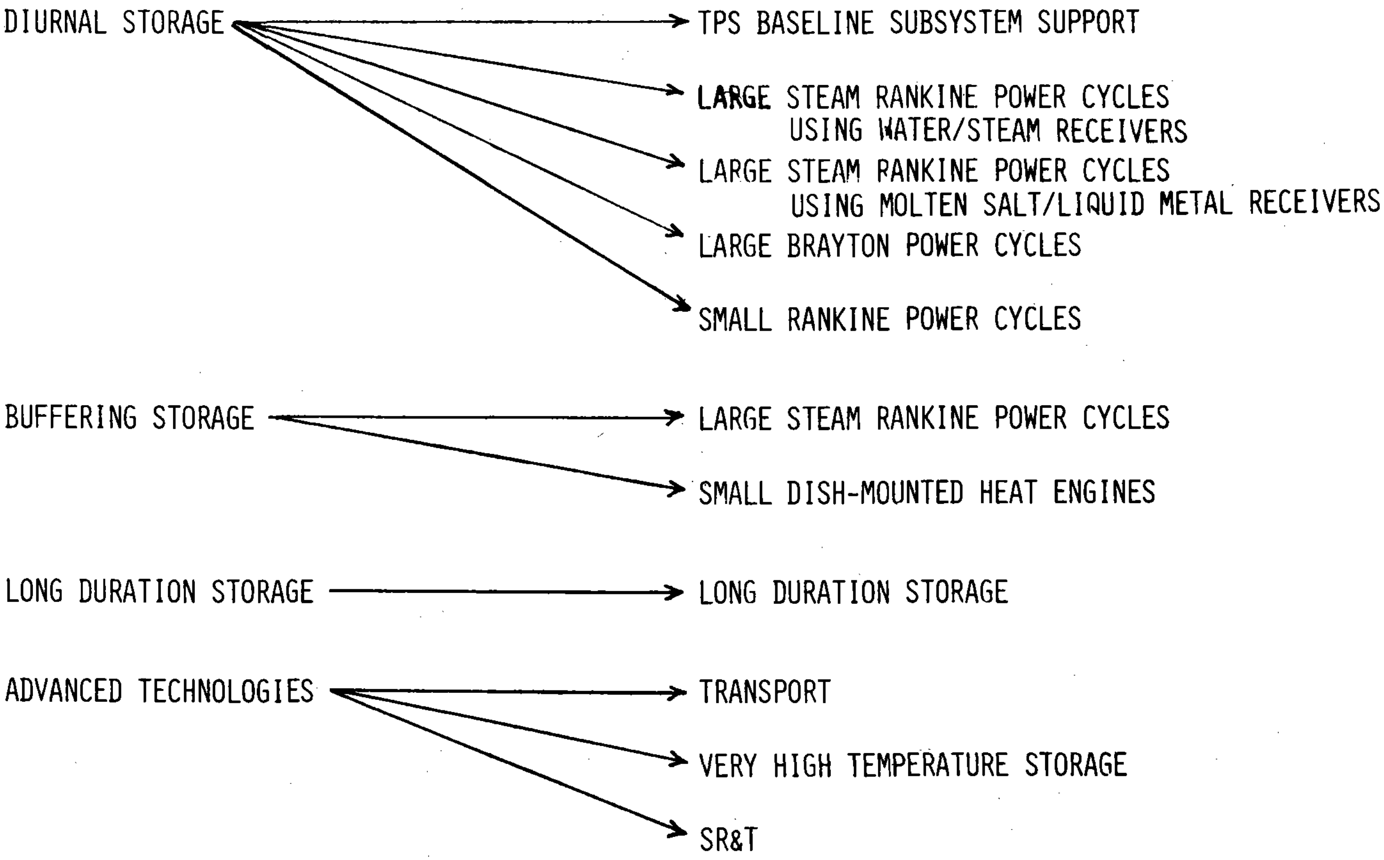


FIGURE 3

SUPPORTING RESEARCH AND TECHNOLOGY

GENERIC ADVANCED TECHNOLOGY AND EXPLORATORY RESEARCH STUDIES

CURRENT PROJECT ACTIVITIES:

- ASSESSMENT STUDY OF STORAGE SYSTEMS USING FLUIDIZED BED HEAT EXCHANGERS (COMPETITIVE AWARD IN NEGOTIATIONS).
- LABORATORY STUDIES FOR ADIABATIC COMPRESSED AIR STORAGE (MIT-LINCOLN LABORATORY).
- DEFINITION OF THERMAL TRANSPORT APPLICATIONS AND IDENTIFICATION OF TECHNOLOGY REQUIREMENTS (NASA-LeRC).
- ASSESSMENT AND CONCEPTUAL DESIGN STUDIES OF LATENT HEAT STORAGE/STIRLING ENGINE SYSTEMS FOR HIGHWAY VEHICLE APPLICATIONS (ANL/SIGMA RESEARCH CORP./THERMO ELECTRON CORP.)
- THERMOPHYSICAL PROPERTY MEASUREMENTS OF METAL ALLOY MEDIA (UNIV. OF DELAWARE).
- ANALYSIS OF PHASE CHANGE HEAT TRANSFER (UNIV. OF HOUSTON).
- LABORATORY STUDIES OF HIGH TEMPERATURE LATENT HEAT STORAGE SYSTEMS (INST. OF GAS TECHNOLOGY).
- NASA-LEWIS IN-HOUSE EXPERIMENTS.

PROJECT SUMMARY

Project Title: Conceptual Design of Thermal Energy Storage (TES) Systems for Near-Term Electric Utility Applications

Principal Investigator: Eldon W. Hall

Organization: General Electric Company
Energy Technology Operation
1 River Road
Schenectady, NY 12345

Project Goals: The project objective is to examine the field of proposed concepts for thermal energy storage (TES) systems and select, conceptually design, and analyze the most promising for near term electric utility applications.

Project Status: The technical effort is divided into the following four tasks:

Task I: System Selection
Task II: Conceptual System Designs
Task III: Benefit Analysis
Task IV: Development and Field Test Program Recommendations

The project status is as follows: Tasks I and II have been completed and Task III is nearing completion.

In Task I over forty TES concepts gleaned from the literature and personal contacts were examined for possible application on two reference plants, an 800 $\mathrm{MW_e}$ high-sulfur coal plant, and an 1140 $\mathrm{MW_e}$ light water nuclear plant. A preliminary screening on near term availability and applicability reduced the set to twelve selections, some of which combined the elements of several concepts.

Of the twelve, four options were selected and further analyses made to improve the performance.

Conceptual designs of the four options have been completed with heat and mass balances and plant layouts.

Analyses have been made of the benefits to utilities, including the cost of electricity, and recommendations will be made for further developments and tests.

Contract Number: NASA DEN3-12 and EPRI RP-1082-1

Contract Period: January, 1978 - January, 1979

Funding Level: $350,000 plus EPRI - $125,000

Funding Source: NASA/LeRC and EPRI

I. PURPOSE

Thermal energy storage (TES) is one of several ways that an electric utility could use to help meet peak load demands. Excess thermal energy is stored during low demand periods for use during peak periods. The thermal energy can be stored as hot water in pressurized containers, as sensible heat in oil, molten salt, rocks or other materials, or as latent heat in phase changes materials.

Many concepts have been proposed both for storing thermal energy and for combining the storage system with a utility plant. It is the purpose of this project to examine the proposed concepts, evaluate them on a consistent basis, select those that appear most promising, make a more detailed evaluation through a conceptual design and analysis of performance and cost, and then make recommendations for further developments and tests.

II. BACKGROUND INFORMATION

There is a need in electric utility operation for an economic means of supplying the varying demand for electric power. While there are seasonal and weekly demand patterns, the daily load pattern is of primary concern in this project. Load-following with conventional base load generating capacity may not be the most economic way since its high capital cost and low fuel cost per unit of energy delivered favor continuous operation.

One method for meeting peak load demands is the use of energy storage. Energy storage has long been used in pumped-hydro form where off-peak power moves water from a lower to an upper reservoir, and electricity is generated during peak demand hours as the water returns to the lower reservoir through a hydraulic turbine.

The final reports prepared by the Public Service Electric and Gas Company of New Jersey (PSE&G), reference 1, identified and compared a number of energy storage concepts including above- and below-ground pumped hydro, compressed air storage, thermal energy storage, battery storage, and flywheel storage. Thermal energy storage was identified as a potentially viable contender because of its technical and economic features and potential for early commercialization.

A topical report summarizing the results of Task I of this project, reference 2, has been completed. This document discusses the results in more detail than reported herein and lists the references and sources of data used in the project.

III. PROJECT DESCRIPTION

To be efficient, the thermal energy must be stored and used prior to conversion to electricity. The TES system must therefore be tied closely to the power plant. When used with steam generating equipment the TES utilizes steam produced in the boiler (usually coal fired or boiling water reactor) or from saturated water in a pressurized water reactor. The use of thermal energy storage following the steam generator permits operating the steam generator at nearly constant load; however, the turbine and generator must be sized for the peak load. This is in contrast to those storage systems which store energy converted from electricity and operate the turbine generator at a constant power level.

While there are several ways that thermal energy could be converted to electricity (e.g., gas turbines), the only one considered in this project is the use of steam turbines.

Storage Media

The materials considered for storage are listed in Table I.

TABLE I

MATERIALS FOR THERMAL ENERGY STORAGE

- Hot water
- Oil
- Rock, iron, or other solids
- Molten salt, sulfur, etc.
- Phase change materials (PCM)

All systems are considered as high temperature systems since they must operate near or above 500°F. In some cases combinations can be used, such as oil and rock, where the oil is used as the transfer medium. Except for hot water, heat exchangers are required to transfer the energy between the material and the steam.

Hot water can, of course, be stored directly and used either as hot water or as a source of steam. Steam as such is seldom stored because of its low density. When the energy of steam is to be stored and steam is required as output, it is first condensed to hot water by mixing with water, stored, and then flashed to steam for reuse.

Phase change materials (PCM) depend mainly on the latent heat of fusion between the solid and liquid phase for energy storage. Liquid to gaseous phase change has not been used because of the large gaseous storage volume requirements.

Molten salts, sulfur, PCM, etc. still require considerable R&D effort before they can be utilized in commercial or utility applications.

Hot Water Containment

Hot water containment is of two major categories: underground and aboveground. Underground containment is based on geologic features that absorb most of the containment stresses. The necessary geologic features, however, are not available everywhere so that this category of containment is site specific and not suitable for all locations. Aboveground containment, on the other hand, can be located in many more places. Table II shows several different concepts for storing high temperature pressurized water.

TABLE II

HOT WATER CONTAINMENT VESSELS

- Aboveground
  - Steel Tanks
  - Prestressed Cast Iron Vessels (PCIV)
  - Prestressed Concrete Pressure Vessels (PCPV)
- Underground (UG)
  - Hard Rock Cavities
    - Concrete Supported Liners
    - Compressed Air Supported Liners
  - Lined Salt Domes
  - Aquifers

Aboveground steel tanks, when used for storing hot pressurized water, are limited in size for individual tanks because as the size increases the tank wall thickness quickly goes beyond that which can be fabricated and used safely. Prestressed cast iron vessels (PCIV) use modular sections that are shipped, then field assembled using high strength cables to sustain the loads. The cables are thermally insulated to avoid the high storage temperatures and thermal cycling either by placing insulation between the vessel and the cables or within the entire vessel. An alternative to the PCIV is the prestressed concrete pressure vessel (PCPV) where high strength cables are used to prestress concrete walls.

Sensible Heat Containment

For sensible heat storage in solids (e.g., packed beds of rock) and heat transfer liquids (e.g., oils and molten salts) at atmospheric pressure, steel tanks are adequate. Very large storage volumes are required so multiple tanks in modular sizes can be selected for cost and convenience. Most tanks are cylindrical with a height under 15m (50 ft) and diameters from 6m to 90m (20-300 ft).

Conversion to Electricity

Two ways are being considered for using steam (either stored or generated from the storage) to produce peaking electricity. In the simplest case a separate peaking turbine is used to generate the peaking power and is shut down during low power demand. In the other case, the main turbines are designed to handle the peak load either with increased flow or reduced extraction for feedwater heating and the reduced load is achieved either with reduced flow or by increasing extraction with the excess energy transferred to storage. In the first case of a separate peaking turbine, a higher ratio of peak to minimum power can be achieved.

The conversion of the stored thermal energy in pressurized HTW to steam may be done in several ways. The following three were considered in this study. In all cases the storage volume is nearly full of hot water at the beginning of the discharge cycle.

(1) Variable pressure, (2) Expansion, and (3) Displacement.

In the variable pressure mode steam is drawn from the top and water in the vessel boils to replace the steam as the pressure drops. Only a portion of the water can be boiled off this way before the pressure drops to unacceptably low levels.

In the expansion mode hot water is drawn from the bottom and water in the vessel flashes to steam to replace the volume of water withdrawn. All the water can be withdrawn in this mode but an external flash evaporator must be used to obtain steam and only a small portion of the water produces steam and the rest must be stored in a separate containment vessel.

In the displacement mode the vessel is maintained completely filled with water. Hot water is drawn from the top and replaced with cold water injected at the bottom. As with the expansion mode the hot water is externally flashed to steam. A sharp temperature gradient called a thermocline separates the hot and cold water and can be the cause of the large stresses in the tank walls.

Concepts

A list of the concepts that were considered and the institution(s) and the individuals associated with the concept are given in Table III. The concepts are listed in the table according to the storage medium.

IV. RESULTS

Preliminary Screening

The purpose of the preliminary screening was to reduce the number of concepts to twelve which could then be applied to reference coal and nuclear plants for further evaluation and selection. The criteria used in this selection were:

- Be compatible with near-term application
- Be economically viable in the mid-term
- Meet utility operational requirements
- Be diverse in type
- Be environmentally sound
- Have conservation potential
- Be broadly applicable
- Have potential for future growth/improvement

Primary emphasis was given to the first four of these criteria in the first screening and resulted in the twelve concepts shown in Table IV.

TABLE III

CONCEPTS CONSIDERED

HTW Concepts

1. Graz University (Austria) Waagner Biro (Austria) Siempelkamp GmbH (FRG) Deutsche Babcock (FRG)	Paul V. Gilli Georg Beckmann F. Schilling, L. Gülicher E. Bitterlich	PCIV
2. R&D Associates	J. Dooley, S. Ridgway	Concrete Stress Supported Hard Rock Cavern
3. Ontario Hydro Atomenergi (Sweden)	A.G. Barnstaple, J.J. Kirby Peter Margen	Air Supported Hard Rock Cavern
4. University of Houston Subsurface, Inc.	R.E. Collins K.E. Davis	Aquifers
5. General Electric-TEMPO	C.F. Meyer	Aquifers

Other Sensible Heat Concepts

21. EXXON Corp.	R.P. Cahn, E.W. Nicholson	Hot Oil/Feedwater
22. McDonnell Douglas Rocketdyne	G. Coleman J. Friefeld	Hot Oil/Packed Bed
23. Martin Marietta	F. Blake	Oil/HITEC and All HITEC
24. Honeywell, Inc.	J.C. Powell, R.T. LeFrois	Oil/HITEC
25. Bechtel Corp.	William Stevens	Oil/Retrofit
26. General Atomic ORNL	R.N. Quade, D. Vrable E. Fox, M. Silverman	HITEC/HTGR
27. General Electric-Space Div.	E. Mehalick	Oil/Drained Bed
28. University of Minnesota	M. Riaz, P. Blackshear	UG Rock Beds/Hot Air
30. Jet Propulsion Laboratory	R.H. Turner	Steel Plates
31. Energy Conversion Engrg.	Allen Selz	Molten Sulfur
32. Boeing Company	J. Gintz	Refractory Brick/H_e
33. University of Houston Subsurface, Inc.	R.E. Collins K.E. Davis	Oil in Salt Domes

Phase-Change Materials Concepts

41. Xerox Corp.	J.A. Carlson	HX Subsystem
42. Naval Research Laboratory	T.A. Chubb	Salt/Terphenyl/Steam
43. Comstock & Westcott, Inc.	B.M. Cohen	NaOH
44. Inst. of Gas Technology	J. Dullea, H. Maru	Carbonates
45. Clemson University	D.D. Edie	Immiscible Fluids HX
46. Honeywell, Inc.	R.T. LeFrois	$NaNO_3$ Slurry/Scrapers
47. Boeing Company	J. Gintz	Fluorides/Helium
48. Grumman Corp.	A. Ferrara	HX Concepts
49. General Electric-CR&D	H. Vakil, F. Bundy	Immiscible Fluids HX
50. Rocket Research Corp.	E.C. Clark	H_2SO_4
51. Swiss Federal Inst. for Reactor Research	M. Taube	Immiscible Fluids HX

TABLE IV

TWELVE CANDIDATE CONCEPTS

Selection Number	Feature(s)	Other Data
1	PCIV	Expansion Accumulator, 1 Evaporator
2	PCPV	Variable Pressure Accumulator, etc.
3	Steel Tanks	Displacement Accumulator, etc.
4	UG - Concrete Stress Transfer	Variable Pressure Accumulator
5	UG - Comp. Air Stress Trans.	Displacement/Feedwater Storage
6	UG - Comp. Air Stress Trans.	Displacement/3 Evaporators
7	Aquifer	Feedwater Storage
8	Oil/Feedwater Storage	Hot and Cold Tanks
9	Oil/Packed Rock Bed/Thermocline	Steam Generator, Peaking Turbine
10	Oil and Salt Loops	Steam Generator, Peaking Turbine
11	All Molten Salt	Steam Generator, Peaking Turbine
12	PCM Materials	Various Heat Exchanger Concepts

As it turned out, most of the concepts shown in Table III are contained in Table IV as variations to one or another of the selected twelve or as future growth potential. Others are either not applicable or are not near-term available.

Economic Comparison

An analysis of these concepts was then made to determine their capital cost and the cost of electricity. Two reference plants were selected to which the TES systems could be added for comparison - an 800 MW_e high-sulfur coal (HSC) plant and an 1140 MW_e light water nuclear plant. To avoid problems in the boiler and additional costs of the HSC plant when varying the steam flow between charging and discharging, the reheater was eliminated from the boiler in the reference HSC plant. This elimination resulted in a three percent increase in heat rate and seven percent loss in net power in the base case HSC plant to which the TES systems could be added.

Various factors such as acceptable size, suitable temperatures, and unique storage characteristics resulted in the selection of the following combinations of base plants and TES systems. The results are shown in Table V.

TABLE V

ECONOMIC COMPARISON

Selection	Feature	Base Plant	TES Cost $/kw	Rank		Cost of Electricity $/MWh
				Economic	Availability	
* 1	PCIV-FWS	NUC	923	6	4	130
2	PCPV-FWS	NUC	1019	8	4	142
3	Steel-FWS	NUC	1624	9	1	213
* 4	UG-C-VARP	HSC	649	1	3	99
5	UG-A-FWS	NUC	775	5	6	114
6	UG-A-EVAP	NUC	667	2	4	101
* 8	Oil-FWS	NUC	670	3	5	103
* 9	Oil/Rock	HSC	729	4	3	109
11	Salt/Rock	HSC	927	7	4	132

The TES costs shown in column 4 are the incremental costs of the total plant over the cost of the base plant divided by the incremental increase in net power out over the base plant power. The economic ranking orders these costs sequentially.

The availability ranking is partly subjective and indicates groups that are comparable on a scale of one (most near term) to ten (worst). Of the selections in Table IV, selection number 10 is treated as all oil in number 9 and all salt in number 11 and selection number 12 is ranked ten in availability. Selections 10 and 12 were not considered further.

The last column in Table V shows the cost of electricity for six hours of peaking assuming that during charging the electricity is replaced by a coal fired plant assumed to have a levelized cost of coal of 2.07 $\$/10^6$ BTU based on a 30 year period and 1976 dollars.

Because it is very difficult and not intended here to make simple comparisons of the TES systems with other type storage or peaking systems and many assumptions were necessary to determine the values in Table V, the costs shown in Table V should be used only for a rough ranking of the TES systems and not for comparison with other systems.

Selection Options

Based on the economic analysis and the desire to cover a diversity of concepts, the four selections indicated by an asterisk in Table V were selected for a more detailed analysis and conceptual designs.

Preliminary capital cost estimates and a breakdown of the costs for the TES systems are indicated in Figure 1 for the four selected options. These costs are reflected in the cost of electricity shown in Table V. In all cases the largest part of the TES system cost is in the turbine island for supplying the peak power. The lowest cost system, option A, and the one that has the lowest cost of electricity uses an underground tank for storage of hot pressurized water in combination with a HSC plant and separate peaking turbines. By using peaking turbines the power can be varied by ± 50% from the normal baseload power. This system, however, is site specific and not applicable to all locations.

Option B uses oil and rock in aboveground tanks and heat exchangers and is also based on a HSC plant and separate peaking turbines. While not site specific long-term materials stability and compatibility are not yet fully proven.

Options C and D are both based on nuclear plants with feedwater storage so that the power swing is limited to about ± 20% from baseload normal power. Option C stores hot water in a PCIV and Option D again utilizes an oil/rock system with heat exchangers.

V. FUTURE ACTIVITIES

Conceptual designs of the four selected options will be completed and an assessment will be made of the technical, economic, and operational characteristics and potential benefit to the electric utility industry. Based on this assessment, the market potential of TES will be estimated.

TES system components will be reviewed to determine the need for additional tests or developments and recommendations will be made for programs that will lead to early commercialization of thermal energy storage for electric utility applications.

VI. REFERENCES

1. (PSE&G) Public Service Electric and Gas Company, *An Assessment of Energy Storage Systems Suitable for Use by Electric Utilities*, Volumes 1, 2, and 3, EPRI EM-264 ERDA E(11-1)-2501; Prepared for Electric Power Research Institute and Energy Research and Development Administration; Newark, New Jersey, July 1976.

2. (GE) General Electric Company—TEMPO, *Conceptual Design of Thermal Energy Storage Systems for Near Term Electric Utility Applications*, Volumes 1 and 2, GE78TMP-60; Prepared for National Aeronautics and Space Administration, U.S. Department of Energy, and Electric Power Research Institute; Santa Barbara, California, October 1978.

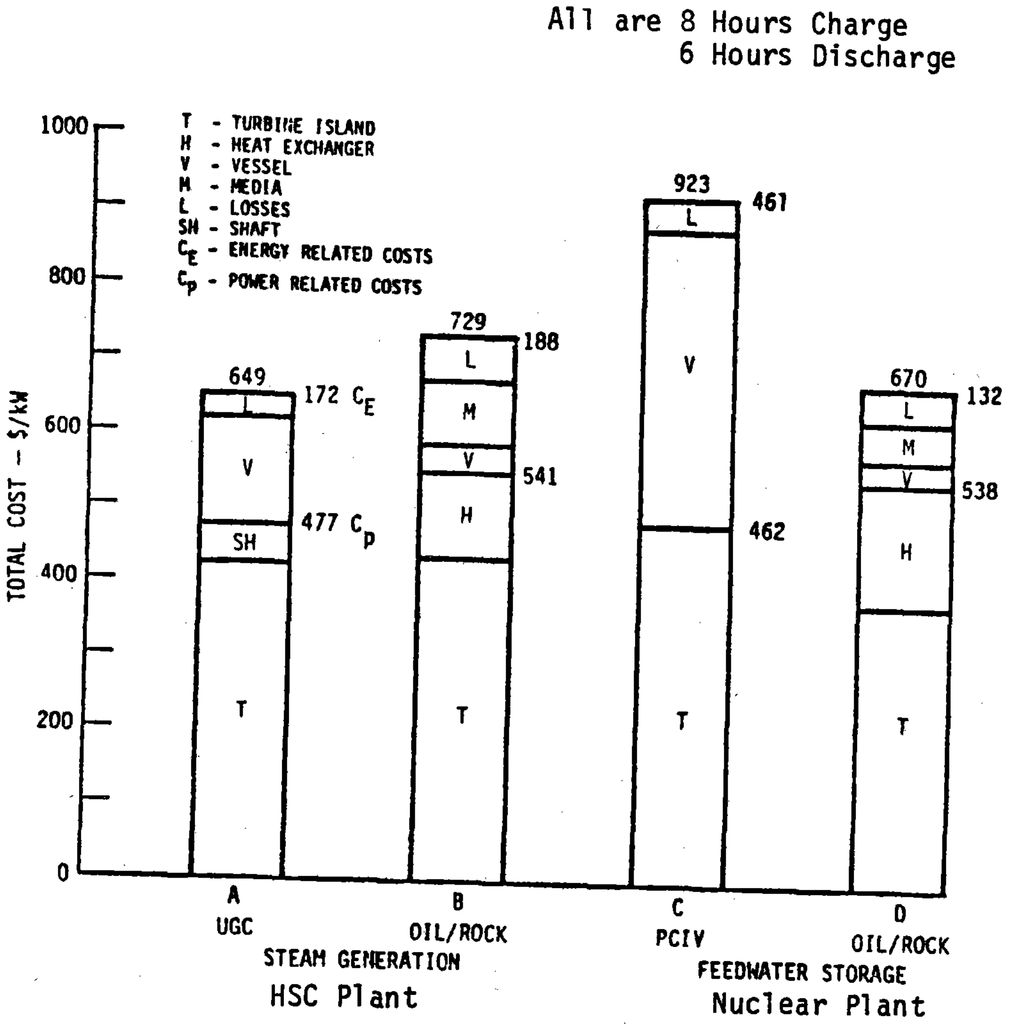


Figure 1. Breakdown of Capital Cost of Selected Options

PROJECT SUMMARY

Project Title: High Temperature Underground Storage of Solar Energy

Principal Investigator: R. E. Collins

Organization: Energy Foundation of Texas
University of Houston
Houston, Texas 77004
(713) 749-3887

Project Goals: The objective of this project is to establish the feasibility of high temperature underground thermal storage of energy and arrive at a practical system design.

Project Status: The project status is as follows:

(1) Numerical analyses of aquifer and cavern storage systems are proceeding according to the program plan.

(2) Geological feasibility survey has been completed.

(3) The math model for cavern stability studies is in the debugging stage.

(4) Well design is underway and calculations to establish sizing criteria to interface the well to heat exchangers are being made.

(5) Preliminary design of heat exchangers has been completed

(6) Final overall design and economic evaluation will be completed when component designs and operating parameters are determined.

Contract Number: EG-77-C-01-3974

Contract Period: September 1978 - August 1979

Funding Level: $377,245.00

Funding Source: Department of Energy, Division of Central Solar Technology

HIGH TEMPERATURE UNDERGROUND THERMAL ENERGY STORAGE

INTRODUCTION

The development of an efficient method for storage of large quantities of heat for use during future demand periods could provide a significant impact on the utilization of energy sources. Underground storage of sensible heat by hot fluid injection for subsequent electric power production is under investigation in this study. The basic requirement is to be able to inject and store large volumes of fluid heated to a high temperature because large scale systems have lower relative thermal losses and high storage temperatures yield more efficient electric power production. The two storage systems under study are deep aquifer storage of high temperature, high pressure water and cavern storage of hot oil within solution caverns in massive salt deposits. Aquifer storage efficiency is reduced because downhole pumping is required for recovery. Also silica solubility and deposition present a major problem at the temperatures considered. For near term application hot oil storage in a gravel filled salt cavern with a nitrogen gas cap appears most feasible.

RESEARCH TASKS

The overall objective of this study is to evaluate the technological and economic feasibility and to determine the best total system design for underground storage systems. The primary application being considered is the production of peaking or baseline electric power from a solar power tower. Alternative uses are storage of waste heat for power generation, district heating or process heat. The major topics for study have been identified as:

(1) Geological feasibility analysis - identification of potential sites.

(2) Computer simulator studies - evaluation of thermal and pressure histories, conduction-losses, operational procedures.

(3) Engineering problems - studies of mineral solubility and scale formation, thermo-mechanical stresses, corrosion, etc.

(4) Economic evaluation.

(5) Total system design - integration of storage system with surface facilities.

COMPLETED STUDIES AND RESULTS TO DATE:

(1) Geological Feasibility

On the basis of a preliminary geological study using published data it has been found that underground storage of high temperature and high pressure fluid is geologically feasible in approximately 80% of the United States, with the exception of the West Coast and areas of mountain intrusion. These geological feasibility assessments considered deep and shallow sedimentary aquifers, solution cavities in massive salt deposits and excavation cavities in crystalline and massive rocks. Many of the areas considered suitable for underground storage coincide with regions of good solar insolation or sites of significant heat supply from industries or nuclear power plants.

(2) Preliminary Study of Cavern Storage Operations

A simple mathematical model has been used to study the operation of a cavity heat storage system. The system considered consisted of two caverns, one hot and one cold, each cavern being partially filled with a gas (nitrogen) which is compressed during injection. Expansion of the compressed gas forces the fluid out during retrieval. The hot cavern was approximated as a spherically symmetric heat source embedded in an infinite earth of uniform thermal diffusivity. The contents of the cavern were assumed to be completely and uniformly mixed at all times. Numerical integration of the heat conduction equation and a coupled heat balance equation for the cavern is used to compute the temperature, the heat loss rate, and the pressure as functions of time.

At the end of one year of cyclic operation consisting of injection during the day and withdrawal at night the heat lost per cycle was less than 4% of the heat input per cycle for any cavern radius less than 100 ft. at an injection flow rate of 2000 gpm which corresponds to a transfer rate of about 25 Mw (thermal). The asymptotic value of the ratio of the heat lost per cycle to the heat input per cycle goes approximately as the radius divided by the flow rate. Therefore, the minimum cavern size consistent with desired storage performance should be used in order to minimize heat losses and provide for maximum power production.

A study of the pressure history and pumping requirements using this simple model showed that the compressed gas cap would not provide adequate flow rates during prolonged retrieval periods as might be called for in cloudy weather with a solar system. Injection of more nitrogen during withdrawal operations in order to maintain the pressure is possible but the pumping requirements are exorbitant due to the work of compression of the gas. Cavern pressure could be more easily maintained by returning oil to the cavern. This suggests that the optimum configuration for cavern storage might consist of a single cavern operating in a thermocline mode. The thermocline mode would require two wells, one hot and one cold, into the cavern with "hot" oil injected and retrieved through one well to the upper portion of the cavern and "cold" oil injected and retrieved from the lower portion of the cavern through the other well. This is illustrated in Figure 1.

Such a cavern would be filled with gravel, or coarse sand, to reduce the required oil volume while maintaining adequate heat capacity, to reduce convection effects in any upset and to provide some mechanical support and stability to the cavern in the massive salt body.

Further study of the cavern storage will address such a system in more realistic fashion as will be described below.

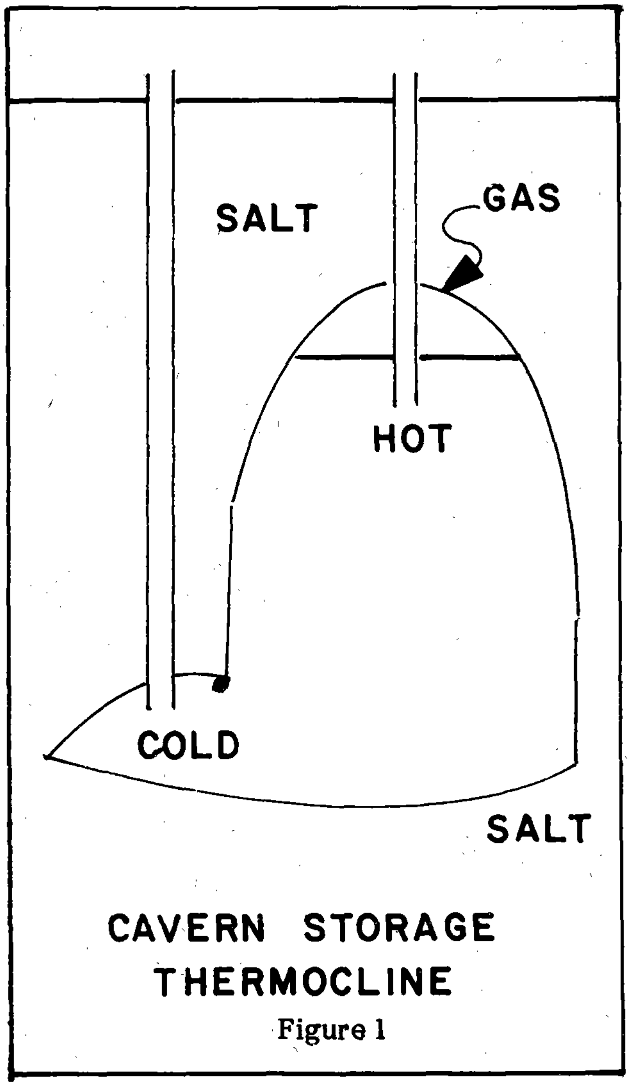


Figure 1

(3) Study of Aquifer Storage Depth Constraints and Pumping Requirements

Simple analytical calculations have been performed to provide a preliminary evaluation of the back-flow capability of an aquifer storage well. These calculations show that for a single storage well artesian backflow is only possible from small, totally enclosed aquifers. Downhole pumps could be installed to achieve fluid retrieval. This technology is currently being developed in the geothermal industry. Even with downhole pumps, the problem of mineral solubility and scale formation, particularly silicate minerals, appears to be a major problem confronting aquifer storage systems. Silica solubility in the vapor phase is much less than in the liquid phase, therefore, scale problems in the aquifer formation and wellbore could be minimized if the pressure of the fluid is not permitted to drop below the vapor pressure of water at the storage temperature. This requirement determines a minimum depth below which the fluid will remain single phase. This depth depends upon the storage temperature, flow rates, flow periods, and aquifer properties.

Once a storage temperature and maximum flow rate have been selected the most important variables are the permeability and thickness of the formation and the value of the skin factor, S. The value of S will in general depend upon drilling and completion techniques used to install the well since it is determined primarily by the reduced value of the permeability near the wellbore. Any silica deposition near the wellbore will further reduce the permeability which increases the skin factor and increases the well depth required (or reduces the allowable flow rate).

Power requirements of the downhole pump depend upon the depth, flow rate and storage temperature. For example at 300° C and a flow rate of 2000 gpm using typical aquifer properties the minimum depth required is 5000 ft. and the pumping power is more than 25% of the net electric power which can be generated from the retrieved hot water. An aquifer with zero skin factor and very large permeability would still have to be at least 2800 ft. deep and the pump would need about 9% of the available power.

At lower temperatures the minimum depth and power required are reduced but the dependence upon the variables is much stronger. At 150° C and a flow rate of 500 gpm the minimum depth ranges from a few hundred feet to a few thousand feet depending upon the aquifer properites. Power requirements could be very small or as much as 15% or more.

Aquifer storage at high temperatures requires the use of downhole pumps with large power requirements. Therefore it appears that aquifer storage will not be competitive for heat storage for subsequent electric power generation.

(4) Cavern Leaching Plan

A preliminary cavern leaching plan has been developed for constructing solution cavities in massive salt deposits based upon existing technology. The three most important criteria necessary for leaching a cavern are 1) a thick deposit of salt, 2) plenty of fresh water, 3) a good way of disposing of brine (underground injection, ocean dumping). Sale of the recovered brine is also a possibility.

For a cavern with 8 million gallons storage capacity, 48 million gallons of fresh water would be required creating 55 million gallons of brine. Total leaching time depends upon the fresh water flow rate. At 500 gpm the leaching operation would require approximately three months depending upon how well the full flow rate could be maintained. Elevated water temperature could be used to accelerate the process.

Control of cavern dimensions and shape is achieved by control of injection level through a moveable pipe and a floating blanket of diesel oil on top of the fresh water layer.

(5) Preliminary Well Design

A preliminary well design for cavern storage has been completed. Thermal expansion is accomodated with expansion joints. Steels and cements able to withstand the thermal stresses as temperature is increased after completion are available. The storage wells can be constructed with off the shelf equipment. Some details of design remain to be worked out.

(6) Preliminary Study of Equipment for Storage/Power System Interface

Preliminary studies of a thermal storage system have been directed toward a hot oil storage fluid coupled with a solar power tower heat source. In most cases the steam conditions from the central receiver tower were fixed at 130,500 lbs/hr, 650° F and 1465 PSIA as shown in McDonnell Douglas Phase I Preliminary Report. The conceptual design parameters for the thermal storage heater (TSH) have been defined and the TSH heat exchanger working surface area and estimated costs have been calculated for several operating conditions. A charging rate of 33.48 Mw thermal with a flow rate of 2000 gpm at 600° F can be obtained with two counterflow heat exchangers of 6000 sq. ft. each installed in parallel at a cost of approximately $125,000.

Study of the conceptual design parameters for the thermal storage steam generator (TSSG) has been initiated. To properly optimize the TSH and TSSG design parameters, the impact on the overall power cycle output capacity must be addressed.

(7) Cost of Cavern Storage Operating in Thermocline Mode

At this time, hot oil storage in a gravel filled salt cavern with a nitrogen gas cap appears to be the best system for near term utilization. The preliminary cost of such a system using 2×10^6 gal of oil is estimated at $4.6 million as shown in Table I. The total heat stored in the cavern would be about 1.5×10^6 kwh thermal with 28% of this in the oil and the remainder stored in the sand. Optimum storage size, primarily dependent upon charging and discharging rates, and periods, has not yet been determined as the computer simulator for this storage system is still being debugged.

TABLE I.
Cost of Cavern Storage Operating in Thermocline Mode

	$ Millions
Wells (1 hot, 1 cold)	1.4
Cavern Leaching	.3
Brine Disposal Well	.4
Heat Transfer Oil (2×10^6 gal)	2.0
Sand/Gravel Filling	.1
Nitrogen Gas Cap	.1
Surface Equipment	.3
Total	$4.6

SUMMARY OF WORK IN PROGRESS

Currently several efforts are underway to finalize the overall design of a thermal storage system. A computer simulator for studies of thermal and pressure history in the gravel filled cavern system is being developed in order to define the design parameters and optimum operational procedures. The design of surface equipment for a pilot plant storage system is continuing. Also the major effects of larger scale operation are being evaluated. An economic study of the complete storage system is underway.

In addition to the above design effort, a computer simulator is being developed to investigate the stability of salt caverns at high temperature. This simulator treats the salt and the cavern contents as two visco-elastic fluids. There is an extensive body of literature on the plastic flow and creep of salt at high temperatures and the cavern deformation question has been studied for other storage operations but none at the temperatures contemplated here. It is hoped that maintenance of adequate cavern pressure and gravel filling will provide a stable cavern storage system.

TOPICS FOR FUTURE STUDY

In the investigation of high temperature underground thermal energy storage it has become evident that several new technologies should be investigated for their impact on thermal storage feasibility. The geothermal industry has been investigating non-steam power cycles using binary fluids and dual cycles in order to extract energy more efficiently from hot geothermal fluids. These techniques could also be used to increase the usable energy contained in a thermal storage system. A major problem in the exploitation of geothermal and hot dry rock resources has been the uncertainty of reservoir lifetimes. It may be economically feasible in the future to combine underground thermal storage (from a solar or nuclear source) with geothermal or hot dry rock systems. This could provide higher temperature operation in some cases and might extend the lifetimes of the reservoirs. Another possible application of storage is in combination with a solar power/district heating cogeneration system.

Direct heat exchange is being investigated as a means of economic heat recovery from geothermal fluids. The main attraction of this approach is the avoidance of scaling problems in heat exchangers. Direct heat exchange in the wellbore has been proposed as a method of stimulating the production of geothermal wells. The heat exchange fluid is injected at the bottom of the well. Upon vaporization the less dense vapor carries the geothermal fluid out of the well. If adequate flow rates could be obtained, such a system might prove feasible for aquifer storage of high temperature water.

PROJECT SUMMARY

Project Title: Active Heat Exchanger System Development for Latent Heat Thermal Energy Storage System

Principal Investigator: Richard T. LeFrois

Organization: Honeywell, Inc.
Energy Resources Center
2600 Ridgway Parkway
Minneapolis, MN 55413

Project Goals: Develop an active heat exchanger system, utilizing a phase change thermal storage medium, where operating characteristics are compatible with a 250° to 350°C steam power cycle.

Project Status: This project is divided into five tasks as follows:

(I) Sodium nitrate was selected for the medium and two heat exchanger concepts, i.e., a modified shell and tube and a direct contract reflux boiler were recommended and approved.

(II) The TES Modules have been designed to test the critical elements of the heat exchanger.

(III) Detailed designs are complete and bids are in process for the construction of the heat exchangers.

(IV) The test phase will commence early in 1979.

(V) The draft version of topical report was delivered, reviewed, and the final version is in process.

Contract Number: DEN 3-38

Contract Period: May 1978 to May 1979

Funding Level: $235,541.00

Funding Source: NASA/LeRC

ABSTRACT

This paper summarizes the program objectives and progress to date for Active Heat Exchanger System Development for a Latent Thermal Energy Storage System. The tasks required under this program include selection of a thermal storage medium for large steam cycle power generation and the design and testing of two active heat exchangers utilizing this medium. Sodium nitrate has been selected from over 200 candidates for the storage medium, and two heat exchanger concepts have been formulated from among eight considered. Small-scale experimental models have been designed to test the critical elements of the heat exchanger concepts. Testing will commence in the first quarter of 1979.

DESCRIPTION OF VIEWGRAPHS

The objective of this program is to design a phase change heat exchange system compatible with a steam power generation system operating in the 250° to 350°C temperature range. To accomplish this, properties of a wide range of molten salts were obtained from the literature and evaluated. Heat exchanger systems from the chemical process industry were evaluated for applicability and performance, together with several new concepts that were generated in house. Experimental data obtained during the program will lead to better quantitative heat transfer predictions upon which an improved heat exchanger system can be designed.

Viewgraph 1 lists the tasks and the scheduled completion date for each. The first two tasks have been completed and reports submitted to NASA/LeRC detailing this work. A topical report covering Task I has been prepared and is awaiting final approval.

Viewgraph 2 is a summary table of the most attractive molten salt thermal storage media. Over 200 candidate materials and mixtures melting in the 250° to

400°C range were screened. Those materials that were chemically active, unstable, or hazardous, either through liberation of toxic fumes or having an unproven safety record, were rejected. Several of the materials were determined to be prohibitively expensive or do not exist in sufficient quantities to meet consideration for large-scale thermal storage system applications. Of the phase change media candidates remaining, system performance estimates were made considering the effects of latent heat, thermal conductivity and media cost upon the total system cost. This resulted in the selection of a sodium-nitrate-based medium as the most promosing candidate.

Viewgraph 3 lists eight different heat exchanger concepts proposed to deal with the problems associated with recovering the latent heat of fusion from molten salts. The configurations used for making system cost comparisions was a large storage system capable of delivering 1000 MW(t) for six hours. System cost estimates were based upon Honeywell experience in building laboratory equipment, the Solar Pilot Plant System Research Experiment and the designs for the solar pilot plant.

Each of the systems was designed to utilize a different technique of removing the solids from the heat exchange surfaces, either through hydrodynamic forces, shell-and-tube and jet impingement, abrasion or scraping. Aggressive removal of solids from heat transfer surfaces tends to increase the size and complexity of the exchangers, resulting in increased costs. The passive tube intensive system was also analyzed to provide a bench mark against which the other systems could be compared.

Viewgraph 4 illustrates one of two heat exchanger concepts recommended under Task I for experimental study. The application of a plated coating to a polished surface shows promise of reducing the salt-to-heat-exchanger adhesion to the point where hydrodynamic forces can remove the solids. A small portion of a shell-and-tube exchanger is being built to evaluate the parameters listed.

Viewgraph 5 is a schematic diagram of the reflux boiler concept wherein water is injected directly into the molten salt, which flashes to steam and condenses on the outside of tubes in a shell-and-tube heat exchanger. This system segregates the salt solidifcation from the heat exchanger surface and utilizes the very effective direct contact boiling and condensing heat transfer coefficients. A laboratory experimental model is being constructed to test these processes. The model will operate in a batch mode rather than in a continuous flow to avoid the high pressure, high temperature, low capacity pump requirements for the experiment.

VIEWGRAPH 1

PROJECT WORK PLAN

TASK	DESCRIPTION	SCHEDULED COMPLETION
I	STORAGE MEDIA SELECTION	1ST MONTH
	HEAT EXCHANGER CONCEPTS	2ND MONTH
II	LABORATORY MODULES DESIGN AND TEST PLAN	3RD MONTH
III	FABRICATION AND TESTING	6TH MONTH THROUGH 10TH MONTH
IV	DATA ANALYSIS AND RECOMMENDATIONS	10TH MONTH
V	FINAL REPORT	12TH MONTH

VIEWGRAPH 2

STORAGE MEDIA SELECTION

SALT NO.	MAJOR COMPONENT (99 WT %)	MELTING POINT (°C)	HEAT OF FUSION (kJ/kg)	SALT COST ($/kg)	TES SYSTEM COST ($/kWh (t))	COMMENTS
1	$LiNO_3$	254	372	3.51 (2.51)	49 (39)	MELTING POINT TOO CLOSE TO LIMIT OF RANGE OF INTEREST -- ELIMINATE.
2	$NaNO_2$	282	212	0.53	26	FITS 8.6 MPa CHARGE/4.1 MPa DISCHARGE (1250/600 PSI).
3	$ZnCl_2$	283	74	3.06	170	VERY HIGH SYSTEM COST -- ELIMINATE.
4	$NaNO_3$	310	174	0.17	22	FITS 12.4 MPa CHARGE AND 6.9 MPa DISCHARGE CYCLE (1800/1000 PSI).
5	NaOH	318	158	0.33	26	FITS 16.5 MPa CHARGE/12.4 MPa DISCHARGE CYCLE (2400/1800 PSI).
6	NaOH	318 299	158 158 (HEAT OF TRANSITION)	0.33	19	IF SYSTEM COULD BE DESIGNED TO UTILIZE THE HEAT OF TRANSITION.
7	KNO_3	337	116	0.33	30	FITS 22 MPa CHARGE/DISCHARGE CYCLE (3200 PSI).
8	KOH	360	167	0.55	29	FITS SUPERCRITICAL CYCLE

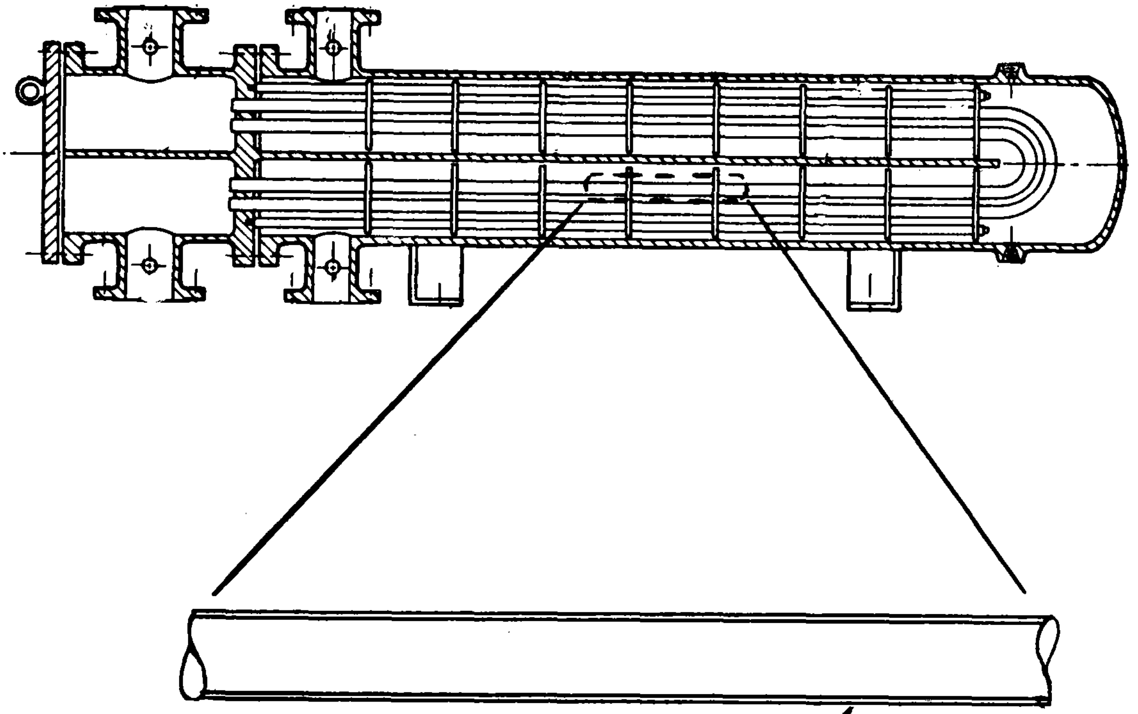
VIEWGRAPH 3

HEAT EXCHANGER CONCEPTS EVALUATION

CONFIGURATION	TEMPERATURE LOSS (° C)	COSTS			
		EXCHANGER ($/kWh)	RATE ($/kW)	CAPACITY ($/kWh)	SYSTEM ($/kWh)
DIRECT CONTACT OPEN SYSTEM	4	1.92	46.0	13.4	20.5
SHELL AND TUBE	18	1.52	44.7	13.4	20.9
REFLUX BOILER (CONTINUOUS FLOW)	15	1.84	45.5	13.4	20.9
JET IMPINGEMENT	18	1.90	47.0	15.4	21.2
REFLUX BOILER (SELF-PRESSURIZING)	15	2.58	50.2	13.4	21.7
TUMBLING ABRASIVE (SHELL AND TUBE)	18	3.60	57.7	13.4	23.0
EXTERNAL SURFACE SCRAPER	18	3.13	54.9	15.5	24.6
INTERNAL SURFACE SCRAPER	18	27.50	20.1	13.4	46.9
PASSIVE TUBE INTENSIVE	18	8.63	94.1	11.5	27.2

VIEWGRAPH 4

LABORATORY EXPERIMENT SHELL AND TUBE EXCHANGER



TEST PARAMETERS

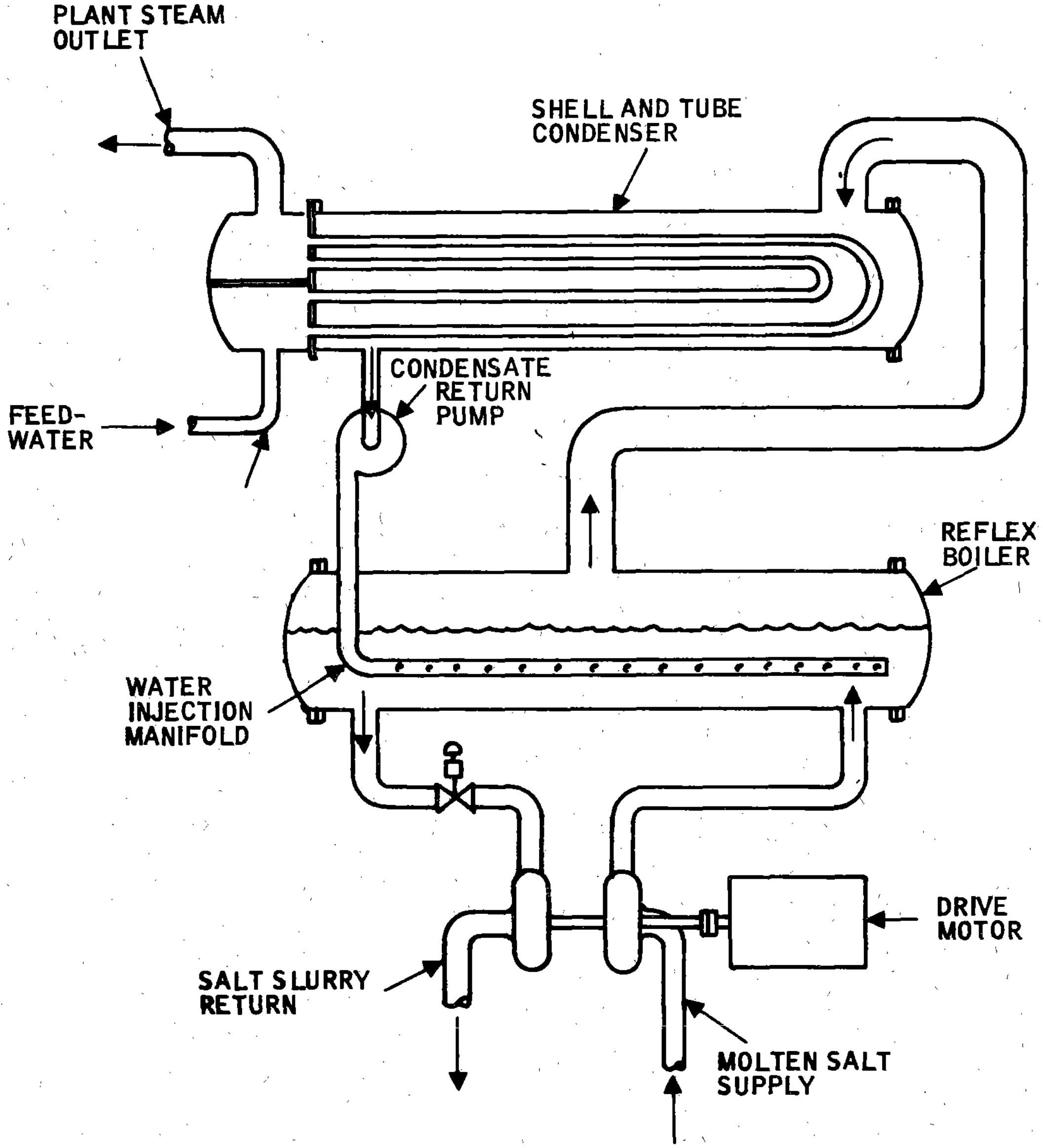
- POLISHED AND PLATED SURFACES
- METAL-TO-SALT COMPATIBILITY
- METAL-TO-SALT TEMPERATURE EFFECT
- FLUID VELOCITY EFFECTS

EXCHANGER TUBING

GROUND
POLISHED
PLATED OR COATED

VIEWGRAPH 5

LABORATORY EXPERIMENT
CONTINUOUS FLOW REFLUX BOILER



TEST PARAMETERS

- **DIRECT CONTACT HEAT TRANSFER**
- **SALT CARRY OVER**
- **SOLUBILITY OF WATER IN MOLTEN SALT**
- **FLUID FLOW PROPERTIES OF SALT SLURRY**

PROJECT SUMMARY

Project Title: Active Heat Exchanger System Development for Latent Heat Thermal Energy Storage System

Principal Investigator: R. Haslett, J. Alario, G. Yenetchi

Organization: Grumman Aerospace Corporation
Bethpage, NY 11714
Telephone: (516) 575-3924/2433

Project Goals: Design, build and test two active heat exchanger concepts which are best suited for latent heat thermal energy storage systems for the utility industry.

Project Status: This project is comprised of five tasks as follows:

(1) Select suitable TES media and make one primary recommendation. Identify candidate HX concepts, evaluate their performance and recommend two for lab testing.

(2) Prepare detailed designs and test plans for two HX concepts.

(3) Fabricate the test hardware and perform laboratory tests.

(4) Analyze the test data and make recommendations for implementation.

(5) Issue scheduled monthly reports, a topical and a final report.

Status is as follows:

(1) The primary TES media has been selected (chloride salt eutectic, mp = 725°F)

(2) Heat exchanger design concepts have been identified and evaluated; three are candidates for detailed design but two will be selected pending results of element adhesion tests.

(3) Element adhesion test apparatus is being assembled and tests will begin soon.

(4) The liquid metal carrier direct contact HX concept is entering detailed design.

Contract Number: DEN 3-39

Contract Period: June 13, 1978 to September 13, 1979

Funding Level: $225,000.00

Funding Source: NASA/LeRC

ACTIVE HEAT EXCHANGER SYSTEM DEVELOPMENT FOR LATENT HEAT THERMAL ENERGY STORAGE SYSTEM

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. The concept is to store excess thermal energy available from the steam boiler (or concentrating solar collector) during off-peak demand periods and then use this stored energy to increase steam capacity during peak load periods. In the case of a solar application this stored energy could be substituted for the primary energy source during non-sunlight periods.

There are two primary means of thermal energy storage which do not involve chemical reactions. It can either be stored in sensible form by a temperature rise in a suitable medium (e.g., water, oil, rock, etc.) or in the latent heat of phase transformation from solid to liquid. The latent heat approach is attractive since the heat absorbed per pound of storage material is much greater, which can result in a more compact system. However, to obtain melting points and high heats of fusion suitable for potential power plant applications, molten salts and salt eutectics are the likely storage media and these can be troublesome.

A preceeding study for NASA-Lewis showed that a latent thermal energy storage system which utilized a conventional tube and shell heat exchanger for salt containment was both technically and economically feasible. The study highlighted the fact that suitable latent heat media are inexpensive and that the major portion of the cost is the passive heat exchanger system, whose size (and cost) is directly influenced by the required heat transfer area. In a passive design, this heat transfer area in turn is adversely affected by the high thermal resistence of the solid PCM media. Large areas are needed to effect efficient heat exchange.

Recognizing this shortcoming, significant performance and cost benefits should be realized if active heat exchanger concepts can be developed which prevent the buildup of a solid layer of salt on the heat transfer surfaces. The overall objective of this program is to design and demonstrate two active heat exchanger concepts which are best suited for latent heat thermal energy storage systems for the utility industry. Test modules will be designed for a storage capacity of 10 Kw_t - hr and a heat transfer rate of 10 Kw.

TES Media Selection

Fossil fueled electric utility plants can use low temperature stored energy for feedwater heating as discussed in our previous study. Solar plants will require stored energy to boil and superheat the steam used to generate electricity during evening hours. To achieve acceptable plant efficiency requires high pressure steam (2400-3600 psi) which means boiling temperatures above 343°C (650°F) with superheating up to 1050°F.

To cover these utility requirements phase charge materials (i.e., salts) with melting points from about 550°F to 1200°F were considered. Table 1 lists the salt media which were judged reasonable candidates since they also possessed other important qualities such as: availability in quantity, low cost, good corrosion characteristics and few handling problems.

The PCM recommended as the primary one for this study is 14.5 KCl-22.3NaCl 63.2 $MgCl_2$ which melts at 385°C (725°F). This salt was chosen since its behavior should be representative of chloride systems which are expected to be important in moderate to high temperature TES applications. Unusually detailed containment information is available indicating low corrosion and specifying purification techniques. The thermal properties of the salt are very good, much better than for hydroxides or nitrates, and it is neither toxic, caustic, or oxidizing. The required constituent salts are inexpensive and readily available in large quantities. Some possible drawbacks are that this salt does have relatively large volume change on fusion and that $MgCl_2$ tends to form a hydrate $MgCl_2 \cdot 6H_2O$ if the anhydrous salt is exposed to moist air. However, it is not felt that these are serious from a point of view of overall system operation. Proper container design can accommodate the density change and demonstrated purification techniques can remove all significant traces of water.

The other salts which are recommended as alternatives for this test program are KOH and $NaNO_3$. Although they melt at distinctly lower temperatures (680°F for KOH and 585°F for $NaNO_3$), these salts could be used in combination with a chloride eutectic to extend the temperature range of interest to feedwater heating or they could service lower temperature boilers. Hydroxides and nitrates are already in use as heat transfer and storage media. While neither of these salts has thermal properties that compare with chloride salts, both do have certain advantages which recommend them to continued study, particularly for the temperature range of interest. Specifically the ability of $NaNO_3$ to passivate steels could be important in active designs where slight atmospheric contamination of the salt is possible.

No problems regarding long-term stability or kinetics of transformation are expected with any of these salts. Vapor pressures for all the salts are low at the temperatures of interest, which simplifies containment vessel construction. Supercooling does occur with some chloride salts (particularly $ZnCl_2$), however, it is not expected to occur with the specific eutectic chosen.

Active Heat Exchanger Concepts

The types of active heat exchangers considered could be grouped under three generic categories: (1) mechanical scrappers, (2) vibrators and (3) slurries. The scraper concepts consisted of translating blades, internal tube rotating blades, external tube rotating blades and rotating drum with a fixed scraper blade. Vibrator concepts dealt with either mechanical or ultrasonic vibration of the heat transfer surfaces or the heat transfer fluids. The slurry design consisted of a direct contact heat exchange between a liquid metal carrier fluid and the molten salt storage media.

Of the concepts considered, the following three offered the most advantages over a completely passive design alternative, including lower cost per Kwhr of storage.

- o Direct contact heat exchanger
- o Nitrogen bubble tubulator
- o Rotating drum scraper

A final choice between the last two concepts will be made after coupon adhesion tests are run between several tube materials and the chloride salt eutectic. The high operating temperatures preclude the use of available non-stick coatings, which have service temperatures below 500°F, and the bubble turbulator relies on low adhesion forces to be effective.

Direct Contract Heat Exchanger

A preliminary design of the test module for a liquid metal/molten salt direct contact heat exchanger has been completed and the detailed design is proceeding. The concept for the demonstration test module is shown in Figure 1. Heat is stored in the chloride salt eutectic by electric heaters in the bottom of the tank, which are used to simulate a fluid heat source. Natural convection facilitates melting. During the usage cycle heat is removed from the salt by direct contact heat transfer with a liquid metal carrier fluid (Pb Bi eutectic) within the heat exchange reservoir. The molten salt is pumped into the bottom of the liquid metal reservoir where because of its lower density (102 lb/ft^3 vs 624 lb/ft^3) it rises through the metal giving up its heat. At the same time the heated liquid metal is pumped from the heat exchanger reservoir to an external heat exchanger. Here the metal is cooled by a flowing water heat sink and then returned to the reservoir. As the solid salt agglomeration rises in the contact heat exchanger reservoir, it is directed over the edges and falls back into the salt mass at the bottom. A separate holding tank for the molten salt could be provided to permit sensible heat extraction from the solid salt if desired.

The demonstration module requires 270 lbs. of the chloride salt eutectic at a flow rate of .34 GPM. The specified carrier fluid is 44.5% Pb 55.5% Bi eutectic (mp = 257°F) with a flow rate of 3.9 GPM. The quantity of liquid metal is determined by the height of the reservoir required to insure solidification of the salt (1.5 ft) and the associated plumbing. It would not significantly be impacted by the increased thermal energy storage capacity needed for larger systems since only the mass flow rate is important. About 340 lbs. of metal are required for the demo module. As with all of the molten salt heat exchanger concepts, a dry nitrogen gas blanket is provided to minimize atmospheric contamination.

Gas Bubble Turbulated Heat Exchanger

This concept, shown in Figure 2, relies upon relatively week adhesion between the solidifying salt and the heat exchanger tubes. At temperatures below about 500°F standard non-stick coatings such as Teflon can be used. The higher temperatures of this application, however, (725°F) require highly polished metal surfaces (nickel or possibly stainless steel tubes) and a clean, dry environment. The tubes at the top of the unit are always submerged in a molten salt slurry and contain the fluid to be heated. As the salt solidifies, the turbulating action of the nitrogen gas bubbles, help to break up and dislodge the solid pieces. The solids fall to the bottom of the tank where they can then be remelted during the charging cycle. Electrical heaters are again used to simulate the fluid heat source and flowing water is the heat sink for this demonstration unit.

The detailed design effort is being delayed pending the results of element tests which are being run to determine adhesion characteristics of certain tube materials with the specified chloride salt eutectic. Based on published results with floride salts, highly polished nickel is the primary choice. Various stainless steels will also be evaluated. The backup to this concept is the rotating drum scraper described below.

Rotating Drum Scraper

The rotating drum scraper concept is shown in Figure 3. The fluid to be heated passes through the order annulus while the molten salt is sprayed onto the surface of the rotating drum where it solidifies. Salt which still adheres to the drum after 180° of rotation is removed when it contacts a fixed scraper blade. Thus, a clean heat transfer surface is continually available for the salt spray. The solidification rate depends strongly upon the overall heat transfer coefficients inside the drum and the angular rotation. High values of each are desired. In this case, adhesion of the salt to the drum surface will maximize the total heat extraction from the salt by also permitting sensible heat removal.

A major mechanical design consideration is the requirement of two leak tight seals for each rotating drum. To avoid contamination of the salt, these seals would be of the gas pressurized type. The gas would be the same as that used for the inert gas blanket above the salt and any leakage would be out of the system. Standard rotating fluid couplings could then be used in the heat sink fluid system away from the salt container.

The major advantage of the rotating drum scraper compared with other scrapers is the capability of discharging subcooled solid rather than partially solidified slurry, hence increasing the specific heat storage capacity of the salt.

Future Effort

The following tasks are scheduled over the next ten months:

- Finalize all detailed designs
- Fabricate and assemble all hardware for the two test modules
- Evaluate performance
- Report results

SALT ELEMENT A•B•C	MELT POINT °C (°F)	COMPOSITION WEIGHT %			HEAT OF FUSION, ΔH_{fs} CAL/GM (BTU/LB)	SPECIFIC HEAT CAL/GM°C		THERMAL CONDUCTIVITY 10^3 X CAL/SEC °C CM (BTU/HR FT °F)		DENSITY GM/CC (LB/FT^3)		HEAT STORAGE KW-HR/FT^3
		A	B	C		SOLID (C_{ps})	LIQUID (C_{pl})	SOLID (k_s)	LIQUID (k_l)	SOLID (ρs)	LIQUID (ρ_l)	
$NaNO_3$	307 (585)	100	–	–	43.5 (78.1)	.45	.44	1.35 (.33)	1.45 (.35)	2.26 (141)	1.90 (119)	3.23
$NaOH$	318 (605)	100	–	–	76 (136)	.48	.50	2.20 (.53)	2.20 (.53)	2.83 (180)	1.76 (108)	7.05
$KCl \cdot KNO_3$	320 (608)	4.5	95.5	–	26.21 (47)	.28	.29	1.15 (.278)	1.15 (.278)	2.11 (132)	1.85 (116)	1.82
KOH	360 (680)	100	–	–	32.1 (57.6)	.32	.36	2.20 (.53)	2.20 (.53)	2.04 (127)	1.73 (108)	2.14
$KCl \cdot NaCl \cdot MgCl_2$	385 (725)	14.5	22.3	63.2	70.4(126)	.23	.248	3.6–3.8 (.87–.92)	1.9–2.4 (.47–.59)	2.25 (140)	1.63 (102)	8.08
$NaCl \cdot BaCl_2 \cdot MgCl_2$	418 (784)	28.4	31.8	39.8	81.6 (146)	.19	.21	3.6–3.8 (.87–.92)	1.9–2.4 (.47–.59)	2.76 (172)	2.12 (132)	7.36
$NaCl \cdot MgCl_2$	450 (842)	60	40	–	111 (199)	.22	.24	3.6–3.8 (.87–.92)	2.27 (.55)	2.23 (139.1)	1.61 (100)	8.11
$CaCl_2 \cdot KCl \cdot NaCl$	465 (869)	64.5	6.5	29	77.6 (139)	.21	.23	3.6–3.8 (.87–.92)	1.9–2.4 (.47–.59)	2.15 (134)	1.85 (115)	5.46
$NaCl \cdot CaCl_2$	500 (928)	33	67	–	67 (121)	.20	.24	3.6–3.8 (.87–.92)	2.44 (.59)	2.16 (134)	1.89 (118)	4.75
$KCl \cdot NaCl \cdot CaCl_2$	504 (939)	5	29	66	67 (120)	.26	.24	3.6–3.8 (.87–.92)	2.39 (.58)	2.15 (134)	1.90 (119)	4.71
$KCl \cdot CaCl_2$	600 (1112)	66.8	33.2	–	77.7 (139)	.19	.21	3.6-3.8 (.87-.92)	1.9-2.4 (.47-.59)	2.10 (131)	1.69 (106)	4.32
$KCl \cdot CaCl_2$	640 (1184)	29.2	70.8	–	68.3 (123)	.19	.21	3.6-3.8 (.87-.92)	1.9-2.4 (.47-.59)	2.13 (132)	1.90 (118)	4.25
$KCl \cdot NaCl$	658 (1216)	56.1	43.9	–	98.9 (177)	.23	.24	3.6-3.8 (.87-.92)	1.9-2.4 (.47-.59)	2.06 (129)	1.53 (95)	4.93

TABLE 1

Candidate PCM Salts With Property Data

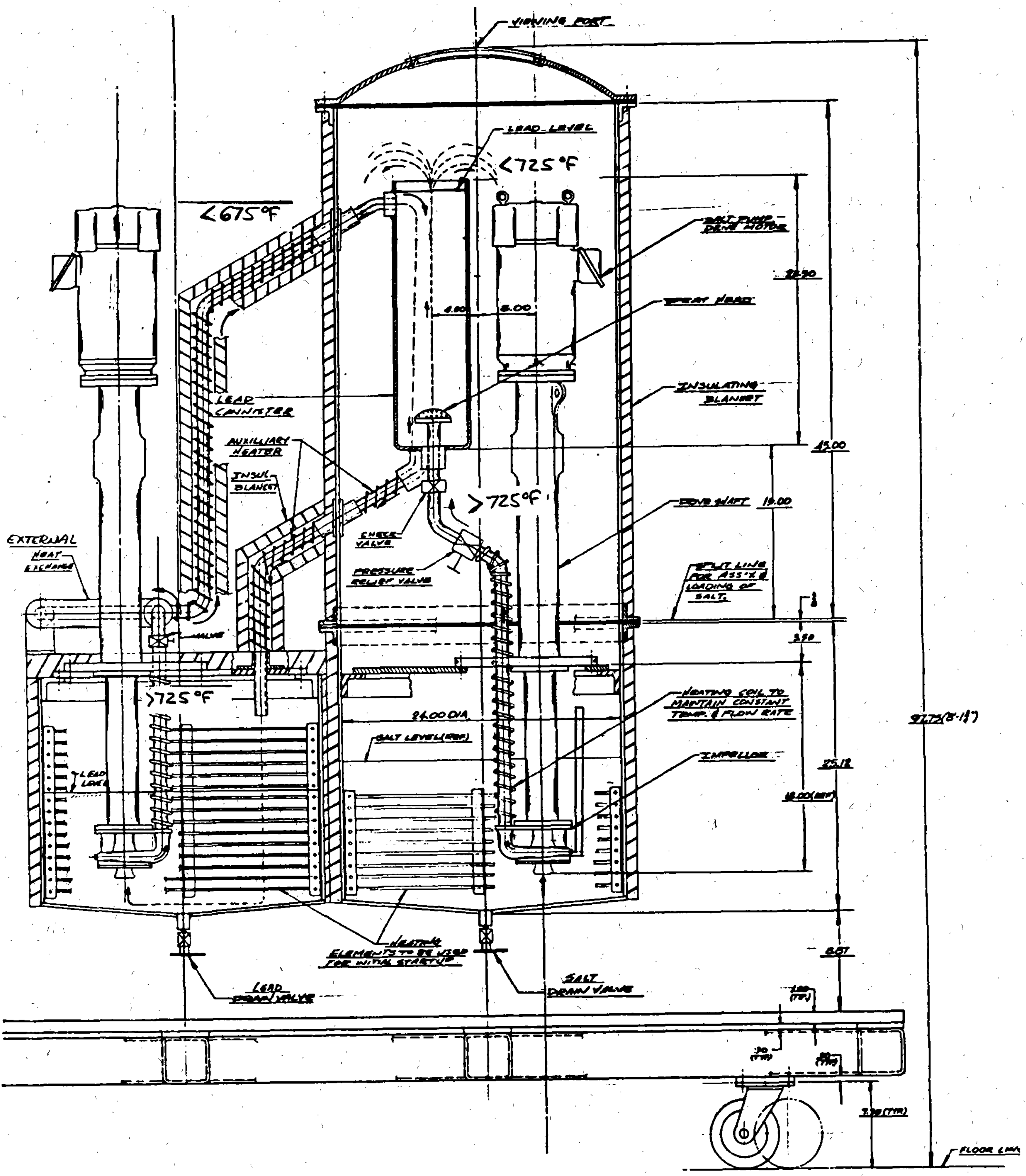


FIG 1.- DIRECT CONTACT HEAT EXCHANGER CONCEPT

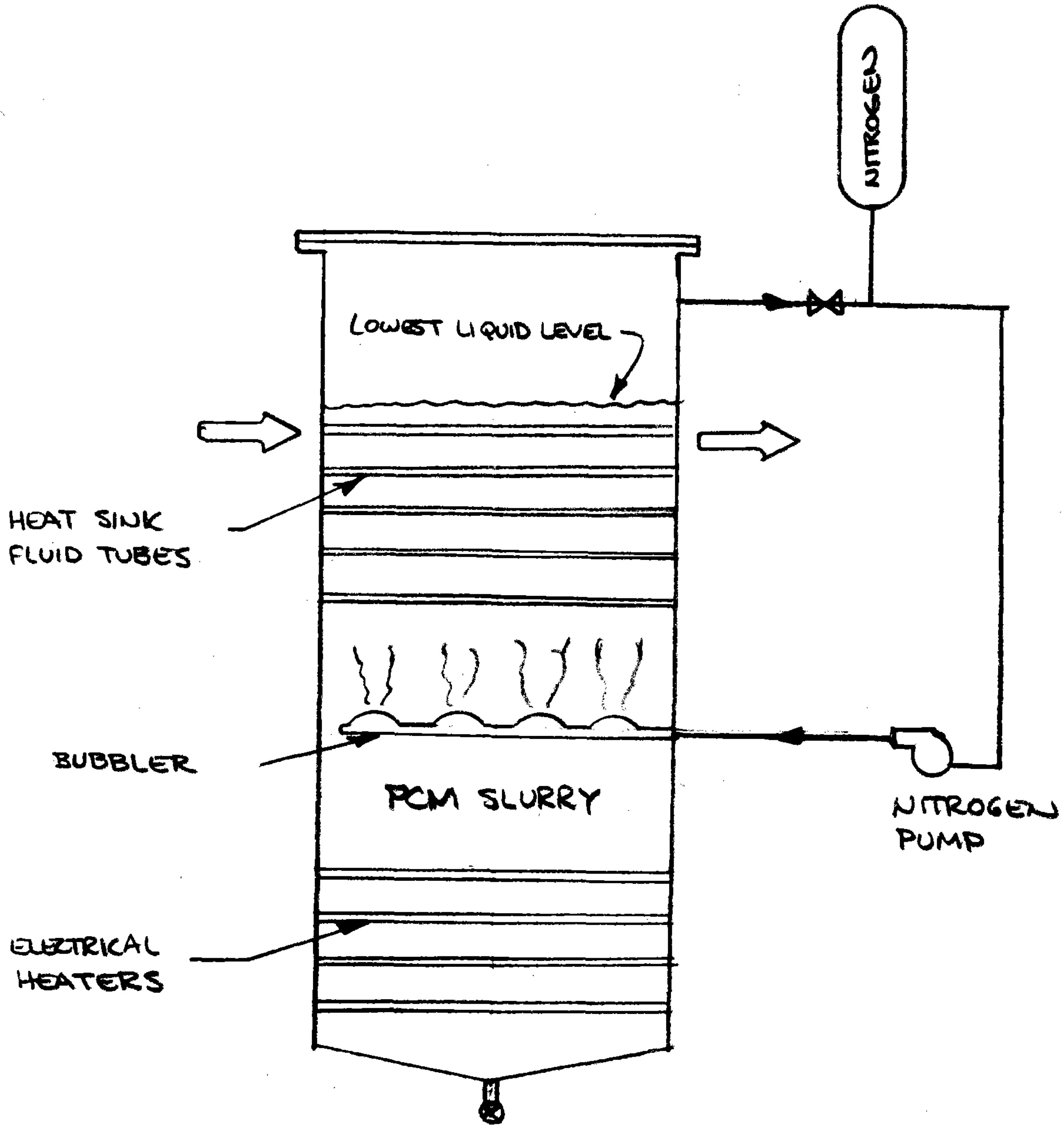


FIG 2 - BUBBLE TURBULATOR HX CONCEPT

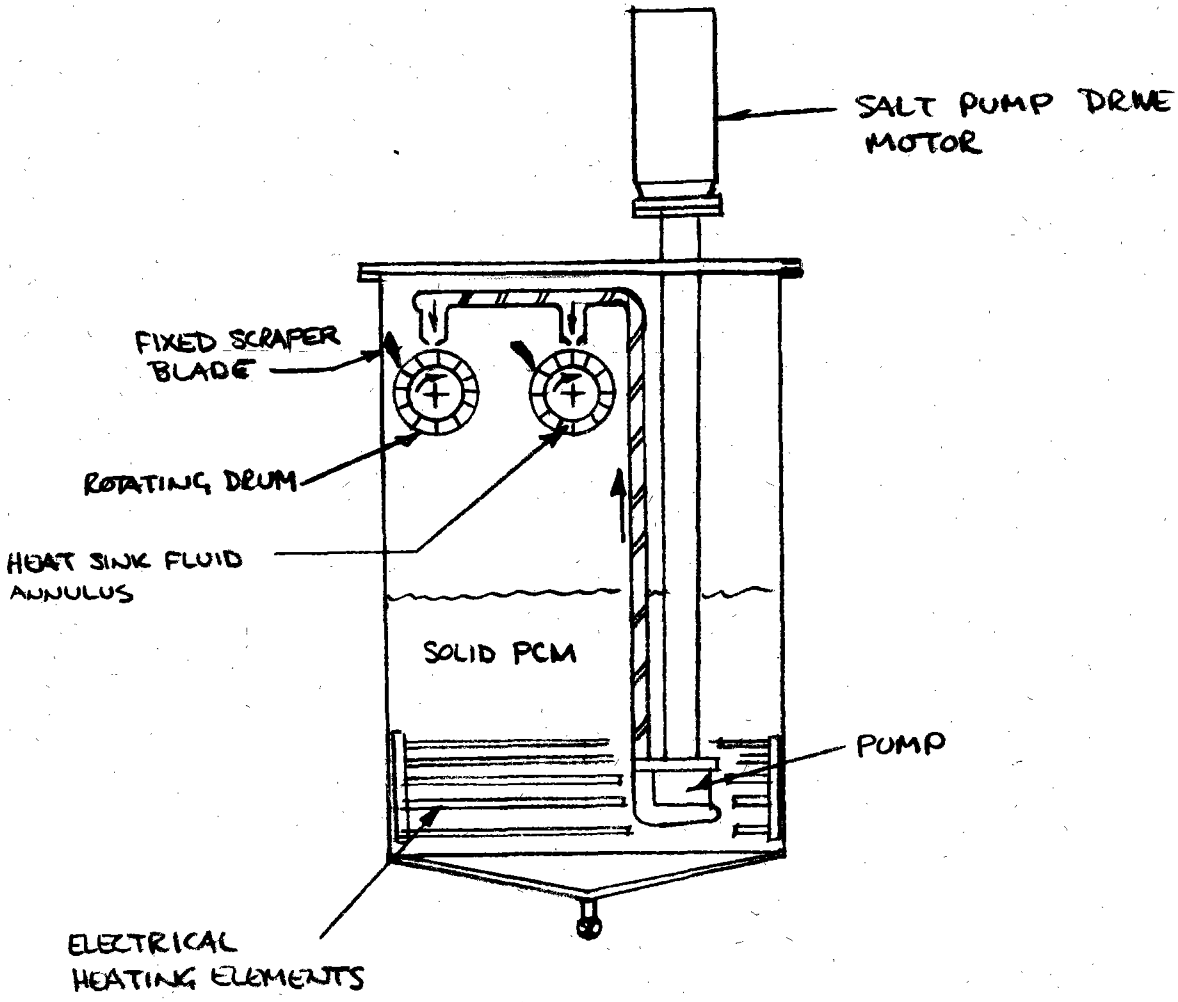


FIG 3 ROTATING DRUM HX CONCEPT

PROJECT SUMMARY

Project Title: Development of a Phase-Change Thermal Storage System Using Modified Anhydrous Sodium Hydroxide for Solar Electric Power Generation

Principal Investigator: B. M. Cohen

Technical Director: R. E. Rice

Organization: Comstock & Wescott, Inc.
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Project Goals: Study analytically and experimentally the performance of a phase-change TES unit operating in the mid-temperature range, develop a preliminary design, and estimate the manufacturing cost.

Project Status: The project comprised the following phases:

(1) Measurement of physical properties of the TES medium.

(2) Development of a reference design using a previously developed computer model.

(3) Design, construction, and testing of a 1/10 scale model TES system.

(4) Development of a preliminary design of a TES unit and manufacturing cost estimate.

Status is as follows:

The work of the project has been completed and the final report submitted in draft form.

Contract Number: NAS3-20615

Contract Period: March, 1977 to January, 1979

Funding Level: $124,395.00

Funding Source: NASA/LeRC

INTRODUCTION

In the generation of electric power from solar heat by means of a heat engine, storage of heat is necessary in order to make the power generation system independent of the solar insolation. The heat storage element of such a system is one of the more costly elements, and the cost goals for thermal storage have not yet been achieved.

One approach to thermal storage for solar-electric systems which offers a possibility for reducing the cost of storage is the use of thermal storage media which undergo phase changes between solid and liquid states or between two solid states within the operating temperature range, making the latent heats of the phase changes as well as sensible heat available for heat storage and retrieval.

This project has comprised an analytical and experimental study of the physical and operating characteristics of a phase change thermal storage system suitable for use in a solar total energy system whose solar collectors operate in the mid-temperature range, and estimation of its manufacturing cost.

HEAT STORING MEDIUM

The heat storing medium used in this work is tradenamed Thermkeep* and has the following composition:

Anhydrous NaOH (commercial grade)	91.8% by wt.
Sodium nitrate	8.0%
Manganese dioxide	0.2%

The commercial grade of NaOH commonly contains 1-2% of sodium chloride, 1/2-1% of sodium carbonate, and smaller amounts of other salts and hydroxides.

Salt baths of similar composition have been used industrially for many years at temperatures of 750 K and higher for metal cleaning and descaling. These baths are contained in large steel tanks. When the advantages of anhydrous NaOH as a phase change heat storage medium were recognized, this composition was used because of this existing industrial experience with the containment and stability of the material.

As a heat storing medium, Thermkeep has been under development for several years. Two commercial applications have been developed to the point of limited preliminary field testing. The first of these is an electrically heated off-peak storage device for domestic space heating designed especially for use with heat pumps. The second is a thermal storage water heater for commercial use which also uses off-peak power. Both these devices operate at a maximum temperature of approximately 725 K.

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* Registered trademark of Comstock & Wescott, Inc.

As a heat storing medium, Thermkeep has the advantages of

- ... high heat storing capacity with latent heats of fusion and a solid state phase change in the temperature range 566 K to 507 K,
- ... chemical stability and insignificant vapor pressure at temperatures up to 750 K,
- ... stability in contact with air allowing the venting of containment vessels to the atmosphere,
- ... compatibility with steel for containment and heat exchangers up to 750 K,
- ... low cost and ready availability, and
- ... large scale industrial experience as a metal cleaning salt.

THERMAL STORAGE UNIT

The thermal energy storage (TES) unit used in this project consists of a cylindrical steel vessel containing the Thermkeep, surrounded by thermal insulation.

Heat is charged into storage, and withdrawn from storage, by means of a single heat exchanger immersed in the Thermkeep. The heat transfer fluid is Therminol-66 (T-66), a petroleum based liquid which does not undergo a phase change. During charging, the T-66 enters the heat exchanger at the top and exits at the bottom. During discharging, the direction of flow is reversed.

The heat exchanger consists of a number of coiled steel tubes which are manifolded together at the top and bottom inside the vessel, forming parallel flow paths for the T-66. Figure 1 shows the heat exchanger, containing 25 coils, used in the experimental scale model TES unit described below.

The Thermkeep undergoes an increase in volume as it melts and to accommodate this, a clearance space must be allowed at the top of the vessel. This space is open to the atmosphere through a "breather" tube which allows air to enter and leave during cycling, and which insures that the vessel operates unpressurized.

SCOPE OF WORK

As a result of a prior contract from the Sandia Laboratories at Livermore, a computer model was available which describes the dynamic behaviour and calculates the manufacturing cost of a TES unit of the type described above. As the initial step, this computer model was modified and simplified to make it more suitable and economical to use in this project.

The work included the following tasks:

1. Experimental determination of the effect of accidental contact between Therminol-66 and Thermkeep at temperatures up to 613 K.

2. Determination of physical properties of Thermkeep: thermal conductivity, density and specific heat of the solid and liquid phases; heat of transition between phases; viscosity of the liquid phase.

3. The development of a reference design, using the computer model, of a TES unit having the following operating characteristics:

    .. Storage capacity of 3.1×10^6 kJ between 516 K and 584 K

    .. Maximum charge rate 1.8×10^6 kJ/hr with T-66 inlet temperature 584 ± 2 K

    .. Maximum extraction rate 1.0×10^6 kJ/hr with T-66 inlet temperature 516 ± 11 K and outlet temperature 582 ± 2 K.

4. The design and construction of a subscale TES system, of one-tenth the scale of the reference design. The subscale system includes a test bed to permit testing under operating conditions consistent with the operating characteristics.

5. The operation of the subscale TES system under a range of conditions and the collection of experimental data.

6. Correlation of the experimental data with results predicted by the computer model, and revision until satisfactory agreement was attained.

7. A preliminary design of a full-scale TES unit and estimation of its manufacturing cost.

PROJECT DESCRIPTION

The computer model referred to above is formulated around the TES design concept described above and predicts the response of the TES unit to any specified charging and discharging conditions including those of a specified solar daily cycle. In addition, it computes the manufacturing cost of the unit.

Figure 2 describes the specified solar daily cycle. Heat from the solar collectors is delivered to the TES unit by way of the heat transfer fluid T-66 at a temperature of 584 ± 2 K, and at a varying flow rate. Heat delivery starts at T4, increasing to a maximum of 500 kW at noon, and decreasing to zero at T1. The thermal demand of the power generator starts at T3 and remains constant at 250 kW until T2. No power is generated from T2 to T3. Heat is withdrawn from storage from T3 to T5, and from T6 to T2. Heat is charged into storage from T5 to T6 at a maximum rate of 250 kW.

Reference Design

The computer model was used to produce a Reference Design of the TES unit which would meet the operating specifications, and which was optimized on the basis of manufacturing cost and a Figure of Merit which is defined as

$$\frac{Q_O}{Q_O + Q_L + Q_A}$$

where Q_O is the daily heat output from storage, Q_L is the daily heat loss to the ambient, and Q_A is the daily auxiliary heat which is added to the output flow of T-66 during discharge to maintain its temperature within the required range of 582 ± 2 K. Q_A is arbitrarily limited to 10% of Q_O.

One-Tenth Scale Model

The Reference Design was used as the basis for the design of a 1/10 Scale Model TES unit which was built and tested. The scaling procedure adopted left the height of the unit unchanged, and decreased the cross section to one-tenth. This procedure leaves each heat exchanger coil and the associated Thermkeep unchanged, while reducing the number of coils by the scaling factor. The Scale Model thus has a substantially greater surface to volume ratio than the full size unit, and it was impractical to control insulation heat loss by means of insulation alone. The Scale Model was therefore equipped with an electrically heated shroud which permitted the thermal gradient within the insulation to be controlled, and thus reduce heat losses according to the scaling factor.

The Scale Model was instrumented with temperature sensors, and provided with accessory equipment to produce the required flows of T-66 at the required temperatures, and to follow automatically the requirements of the solar daily cycle.

Experimental Program

The test program consisted of four types of tests:

1. Charging and discharging at several different T-66 flow rates.
2. Stand-by tests to determine axial heat flows through the Thermkeep, heat exchanger, and vessel walls.
3. Cycle tests consisting of alternate charging and discharging at constant T-66 flow rates.
4. Cycle tests in which the charging and discharging corresponded to the solar daily cycle shown in Figure 2, with rates reduced by the model scaling factor.

In all cases, the experimentally determined data were correlated with results predicted by the computer model for the purpose of establishing the reliability of the computer model as a design tool. Altogether 65 experimental runs were thus correlated.

Figures 3 and 4 show the results of one typical correlation. The test consisted of three consecutive cycles. Each cycle consisted of a discharge phase followed by a charge phase. During the discharge phase T-66 at approximately 516 K and at a flow rate of 0.1 kg/sec (2 gallons/min) entered the bottom of the unit; these conditions were maintained for four hours. Then, for one hour (during which preparations were made for the next phase), there was no flow. During the charge phase T-66 at approximately 584 K, and at a flow rate of 0.1 kg/sec entered the top of the unit; these conditions were maintained for four hours, followed by one hour of no flow. Following this the next cycle was started.

Figure 3 shows the temperature of the T-66 at the outlet vs. time, during the discharge phase and the charge phase of the third of the three consecutive cycles, as measured, and as predicted by the computer model. Figure 4 shows the internal temperature distribution of the TES unit (Thermkeep temperature) from top to bottom at the end of the third cycle, as measured and as predicted.

The agreement between the measured and computed results are considered to be satisfactory, and the computer model is believed to be a reliable tool for the analysis, design, and fabrication cost prediction of phase change

TES units of the physical type described herein. The model can also be used to represent other non-phase change heat transfer media, and other phase change storage media for which the necessary thermal and physical properties are known.

The small deviations between measured and computed results are believed to result first, from a few secondary physical effects which are not fully taken into account in the computer model, and second, from some degree of inaccuracy in the temperature-enthalpy data for Thermkeep, which were used in the computer model.

Preliminary Design

The final step in the project was the use of the computer model to optimize a preliminary design of a full scale TES unit which meets the performance specifications when operating on the solar daily cycle, and which utilizes auxiliary heating of the T-66, in order to maintain its temperature within the specified range of 582 ± 2 K, during the discharge phases. The auxiliary heat is limited to 10% of the daily output from storage.

The principal variables affecting performance and cost of the TES unit are the quantity of Thermkeep and the surface area of the heat exchanger. The design was optimized to provide what was believed to be the best balance between the figure of merit and the manufacturing cost of the unit.

The estimate of manufacturing cost is based on a materials cost and a fabrication cost for each component. Materials costs are based on 1977 prices. Fabrication costs are based upon the actual fabrication costs of two Thermbank Electric Water Heaters which are similar in basic design, although smaller than the TES unit. Therefore, the computed fabrication cost is representative of production in very small numbers of units.

The principal features of the Preliminary Design are given below:

Vessel (steel) height and diameter	2.35 m
Heat exchanger (steel)	
Tube diameter	.635 cm
Tube length	27.7 m
Number of tubes	280
Insulation thickness	.609 m
Overall height and diameter	3.6 m
Weight of Thermkeep	18000 kg
Total weight	27300 kg
Daily output (solar cycle)	3.01×10^6 kJ
Insulation loss	3.25%
Auxiliary heating, Q_A	10.2%
Figure of merit	.882
Manufacturing cost	$33,700
Specific cost	$11.2/MJ

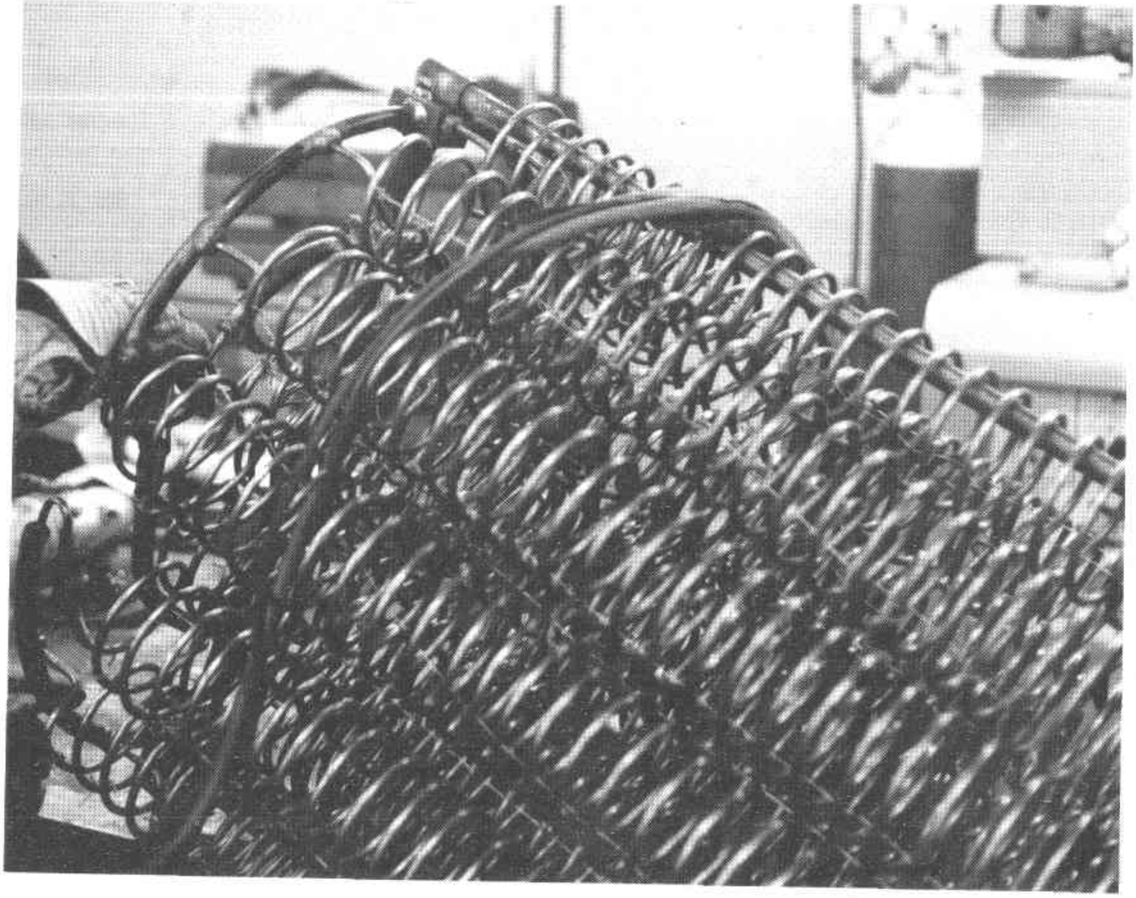

FIG. 1

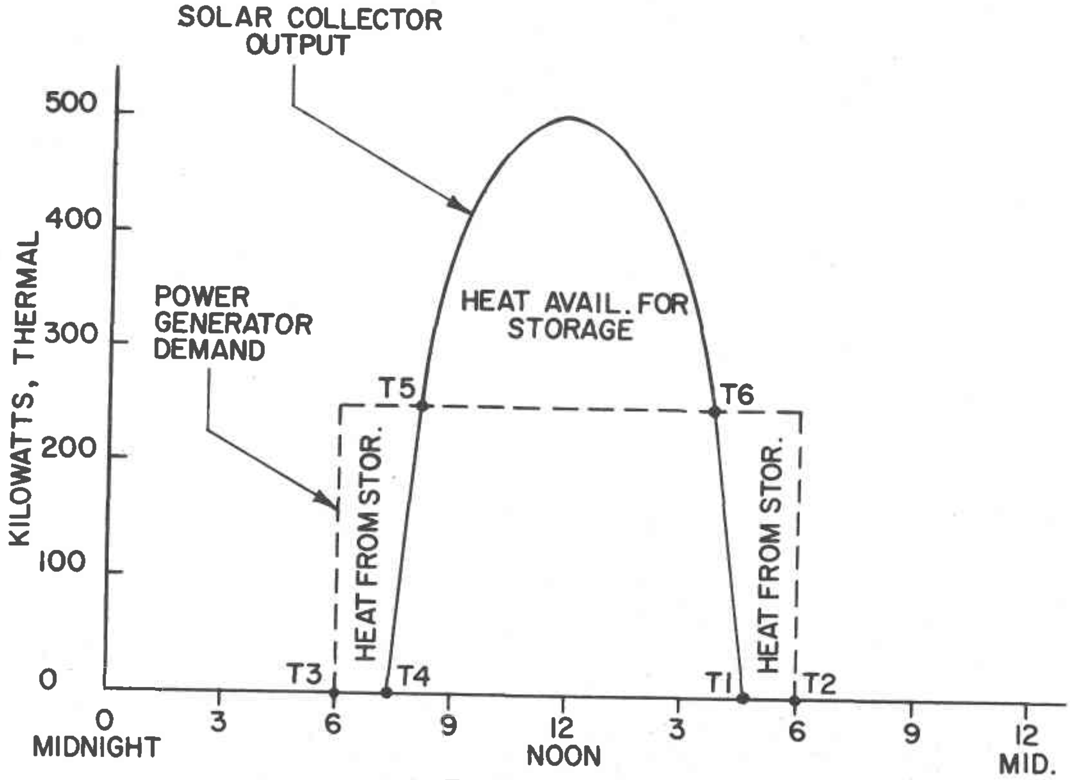
SOLAR COLLECTOR OUTPUT
POWER GENERATOR DEMAND
HEAT AVAIL. FOR STORAGE
HEAT FROM STOR.
HEAT FROM STOR.
T5
T6
T3
T4
T1
T2
KILOWATTS, THERMAL
500
400
300
200
100
0
0
MIDNIGHT
3
6
9
12
NOON
3
6
9
12
MID.
TIME, HOURS

FIG. 2

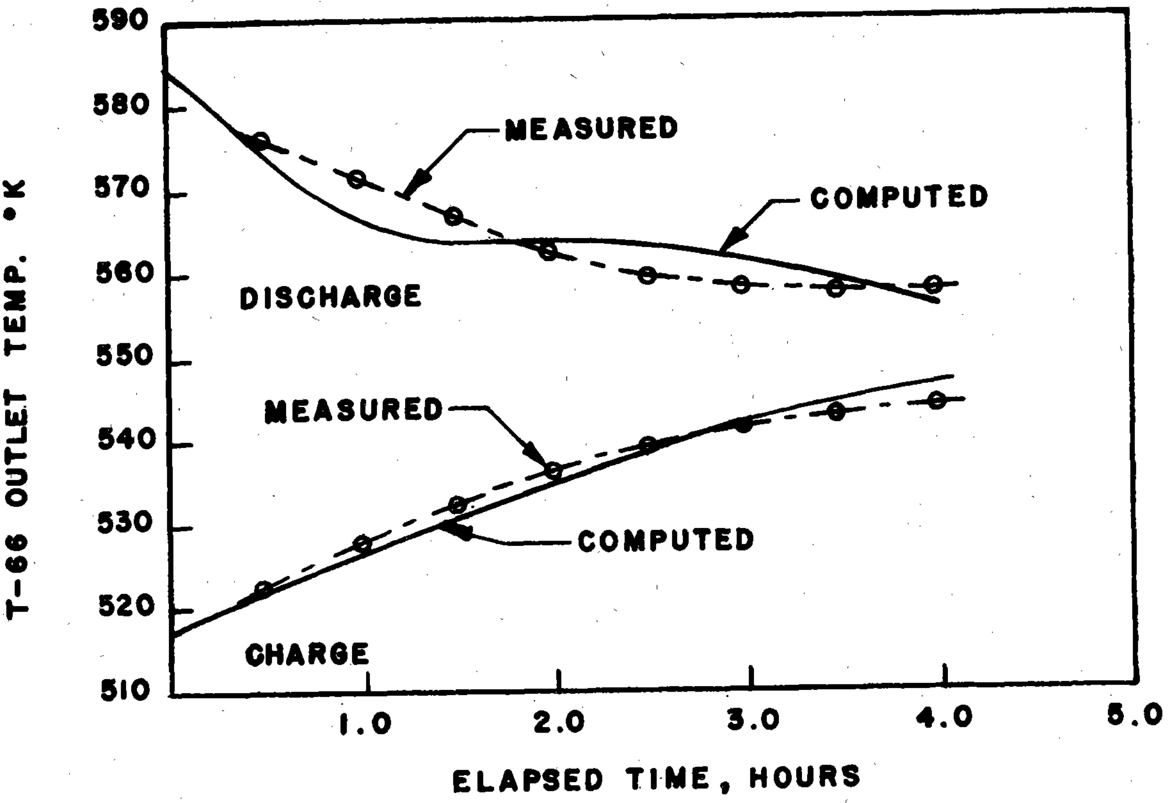
590
580
570
560
550
540
530
520
510
T-66 OUTLET TEMP. °K
MEASURED
COMPUTED
DISCHARGE
MEASURED
COMPUTED
CHARGE
1.0
2.0
3.0
4.0
5.0
ELAPSED TIME, HOURS

FIG. 3

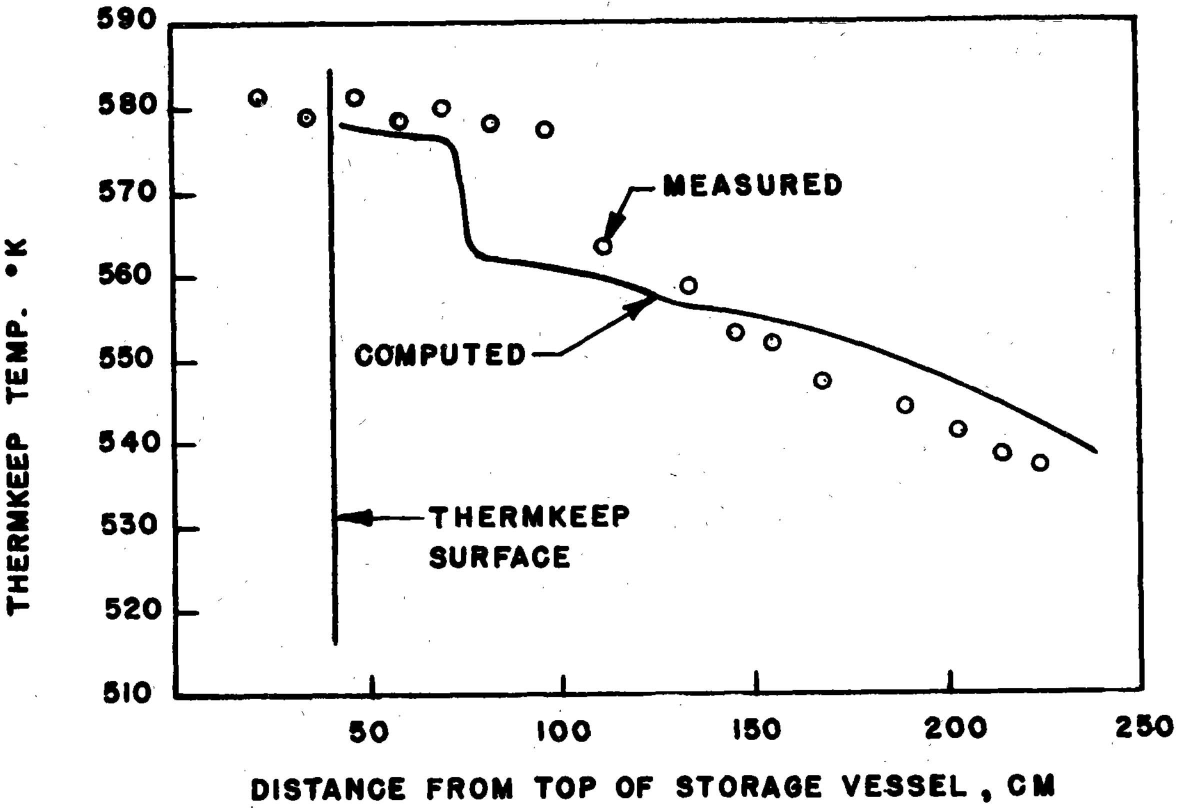
590
580
570
560
550
540
530
520
510
THERMKEEP TEMP. °K
MEASURED
COMPUTED
THERMKEEP
SURFACE
50
100
150
200
250
DISTANCE FROM TOP OF STORAGE VESSEL, CM

FIG. 4

PROJECT SUMMARY

Project Title: Mathematical Modeling of Thermal Energy Storage in Aquifers

Principal Investigator: Chin Fu Tsang

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Project Objectives: To use numerical models and other methods to: (1) study and understand the hydrodynamic and thermal behavior of an aquifer under a variety of possible situations when used for hot or chilled water storage; (2) estimate the efficiency of storage and retrieval; and (3) model field experiments.

Project Status:

1. A numerical model has been developed to examine a variety of situations associated with thermal energy storage. The following cases have been studied:
    - (a) annual cycle - seasonal storage
    - (b) semi-annual cycle
    - (c) a well partially penetrating the aquifer
    - (d) storage of water of different temperatures
    - (e) the effect of a clay lens in the aquifer
    - (f) inhomogeneity of the aquifer
    - (g) chilled water storage
    - (h) a two well system
    - (i) the possibility of consolidation or uplift
    - (j) natural regional flow
2. LBL organized and was the site of the Workshop on Thermal Energy Storage in Aquifers held May 10-12, 1978.
3. LBL assumed the responsibility of compiling and publishing a bimonthly Aquifer Thermal Energy Storage Newsletter.
4. Work was initiated to model a field experiment. Well test analysis was begun on data collected from Auburn University field experiments to verify aquifer parameters and geometry.

Contract Number: W7405-Eng 26

Contract Period: Continuing

Funding Level: $110,000.00

Funding Source: Department of Energy, Division of Energy Storage Systems.

MATHEMATICAL MODELING OF THERMAL ENERGY STORAGE IN AQUIFERS

Lawrence Berkeley Laboratory

Introduction:

The development of practical and low-cost methods for storing large volumes of thermal energy is of fundamental importance for the utilization of solar energy as well as the implementation of total energy systems. The concept of hot water storage wells was suggested by Rabbimov, Umarov and Zakhidov (1971), Meyer and Todd (1973), and others. The basic concept is to store the large volumes of hot water that have been produced in conjunction with electric power plants, solar energy collectors and other heat generating systems and use it in periods of heat demand. This would not only recover normally wasted energy, but would also greatly reduce thermal pollution around power systems. In addition, success of this type of energy storage would facilitate the implementation of large-scale total energy systems in which utilities would produce and market both electricity and useful heat.

The objective of the present study is to use numerical models and other methods to: (1) study and understand the hydrodynamic and thermal behavior of an aquifer under a variety of possible situations when used for hot or chilled water storage; (2) estimate the efficiency of storage and retrieval; and (3) model field experiments.

Description of Work and Technical Accomplishments:

The current project makes use of a numerical model developed at the Lawrence Berkeley Laboratory to investigate hot and chilled water storage. The model, called "CCC" for Conduction, Convection and Compaction, is based on the Integrated Finite Difference Method. It computes heat and mass flow in three-dimensional, water saturated, porous systems while concurrently simulating the vertical deformation of the system using the one-dimensional consolidation theory of Terzaghi. Thus, the following physical effects are included in the calculations: a) effects of temperature on fluid heat capacity, viscosity and density; b) heat convection and conduction in the aquifer; c) effects of regional groundwater flow; d) spatial variations in aquifer properties; and e) gravitational effects. The numerical model has been validated for examples for which analytical or semi-analytical solutions are available (e.g., Theis, 1935; Avdonin, 1964; Gringarten and Sauty, 1975).

The following cases have been studied:

1. Annual Cycle - Seasonal Storage

In this case, hot water is stored in the aquifer for ninety days in summer and is produced from the aquifer for ninety days in winter for heating. There is no injection or production during spring or fall. For successive cycles, the recovery temperature increases as the aquifer is heated up making it a more efficient hot water storage system. The percentage of energy recovered was greater than 80 percent after only a few injection-production cycles.

2. Different Cycle Periods

In addition to annual cycle storage, we also looked at the semi-annual cycle, that is: storage in fall, production in winter for space heating; and storage in spring, production in summer for air conditioning. Very similar results were obtained. The percentage of energy recovered for successive cycles is shown in Figure 1.

3. Well Partially Penetrating the Aquifer

Calculations were also performed assuming the well to be open only for the upper half of the aquifer. Although the buoyancy effect of low density hot water was clearly demonstrated, the percentage of energy recovered for successive cycles was only slightly affected.

4. Storage of Water of Different Temperatures

We have looked at storage of water at 120°C, 220°C and 320°C. We found that as far as the hydrodynamic and thermal behavior of the aquifer is concerned, the results appear to scale as (T_S-T_O), where T_S is the temperature of water stored and T_O is the original aquifer temperature.

5. Effect of a Clay Lens in the Aquifer

In this case the aquifer is divided into two parts by a clay lens with a radius of twenty meters. If the well is open only below the lens, the result of hot water injection and production is as shown in Figure 2 which displays the temperature contours after ninety days of injection and ninety days of subsequent production. The effect of the clay lens on these temperature contours is clearly demonstrated. However, it is found that the percentage of energy recovered is not much affected (Figure 1).

6. Inhomogeneity of the Aquifer

If the aquifer is composed of two layers, one more permeable than the other, then the flow and the temperature contours will be changed. An example in which one region is twice as permeable as the other is shown in Figure 3. The water tends to flow into the higher permeable region as would be expected. However, it is again found that the percentage of annual recovery is not much affected (Figure 1).

7. Chilled Water Storage

In addition to the study of hot water storage, we have studied the concept of storage of winter chilled water to be used in summer for air conditioning. If we assume storage of 4°C water for ninety days in winter, and production for ninety days in summer, then the production temperature after a few cycles is expected to be below 10°C for the entire production period.

8. Two Well System

In this case we study a system of two wells, where one well supplies the water that is heated and injected into the other well. In studies described above, the thermal front moves radially from the single well. However, in this case, because of the presence of the second well, the thermal front will be distorted. In Figure 4, the thermal fronts are shown as a function of the separation between the storage well and the supplying well. As indicated, if the two wells are at a reasonable distance apart, single well results are applicable. To study this case in more detail, we have performed a three-dimensional numerical modeling of the two well system. A fine mesh is used near the storage well to ensure an adequate description of the temperature changes in that region. Results of the calculations are shown in Figure 5. Here, the effect of the supplying well and the gravitational buoyancy effect are clearly indicated.

9. Possibility of Consolidation or Uplift

To demonstrate the capability of the model to calculate the consolidation or uplift effect, we have performed calculations based on two sets of arbitrarily chosen parameters. Results indicate that consolidation and uplift are strongly parameter dependent (i.e., site-specific).

10. Natural Regional Flow

The effect of natural regional flow has been studied using both a two-dimensional, steady-state, fluid flow model, and a three-dimensional model. Results indicate that a natural flow rate on the order of one meter per year will not adversely affect storage capabilities. Appreciable effects are found if the flow is unusually large (∿100 m/yr).

In addition to the above studies of various effects and possible situations that might occur in the field, we have also performed the following work during Fiscal Year 1979:

(a) Workshop on Thermal Energy Storage in Aquifers

LBL organized and was the site of the Workshop on Thermal Energy Storage in Aquifers held May 10-12, 1978. The purpose of the Workshop was to provide an exchange of ideas and technical information. More specifically, the Workshop reviewed the potential of thermal energy storage in aquifers; addressed possible technical, environmental and institutional problems; and examined storage projects currently underway. There were seventy-six participants including six foreign speakers who discussed aquifer storage projects in their countries. Proceedings from the Workshop are being printed.

(b) Aquifer Thermal Energy Storage Newsletter

At the request of DOE, Oak Ridge National Laboratory, and foreign participants at the Aquifer Workshop, LBL has accepted the responsibility of publishing a bi-monthly Aquifer Thermal Energy Storage Newsletter. The purpose of the newsletter is to keep workers in this field informed of major results and the current status of aquifer storage projects throughout the world. The first issue, compiled during August and September, consists of brief descriptions of storage projects discussed at the Aquifer Workshop.

(c) Simulation of Auburn University Field Experiments

Data is being collected from field experiments being conducted at Auburn University. Older data have been stored on the LBL computer and well test analysis of the field data has been initiated to verify aquifer parameters and geometry. By using a variable-flow well-test analysis method we hope to determine the properties of the aquifer and its nearby barriers. Once aquifer parameters have been determined, a computer simulation will be made of the aquifer when used for hot water storage.

Description of Planned Work:

1. A simulation study will be made of the Auburn University field experiments to understand the hydrodynamics and heat flow processes in these experiments and to calibrate and validate our numerical model. Results and the experiences of this study will be useful to other planned demonstration projects.

2. LBL will continue to be responsible for publication of the Aquifer Thermal Energy Storage Newsletter. Articles will be solicited from researchers throughout the world. The first issue was distributed to 116 persons including 33 foreign recipients in ten different countries.

3. Depending on the time available under the present level of funding, modeling of typical situations in thermal energy storage will be made. These modeling studies will include a calculation of daily cycle storage. A program will be written to include the effect of heat loss along the well bore as water is injected into or produced from the aquifer. If the percentage of heat recovery is high, this case will have particular application for solar power systems.

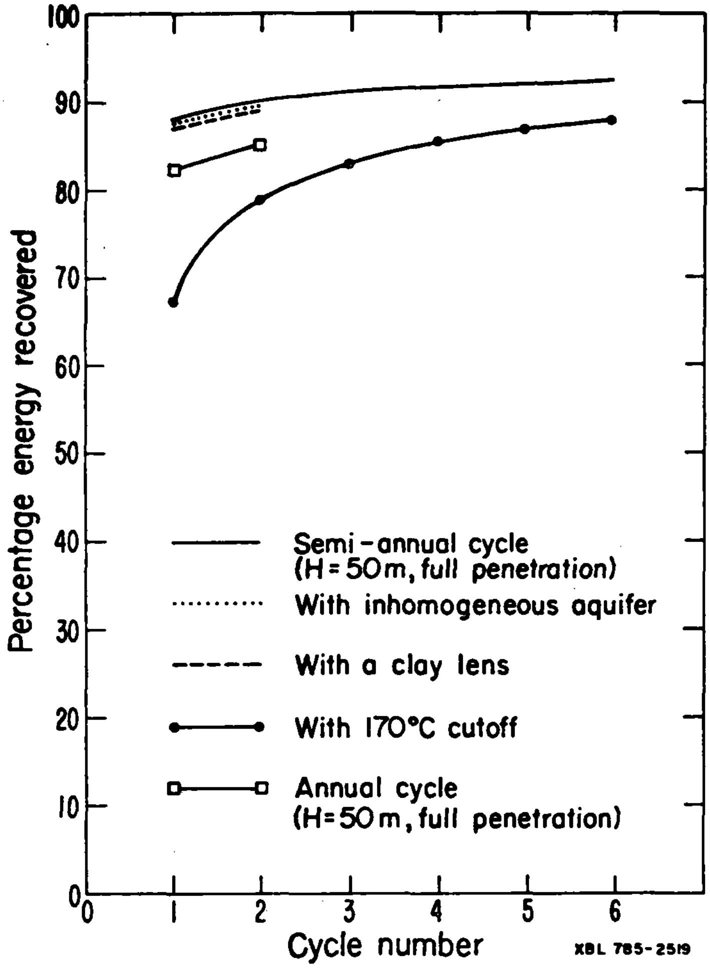

Figure 1

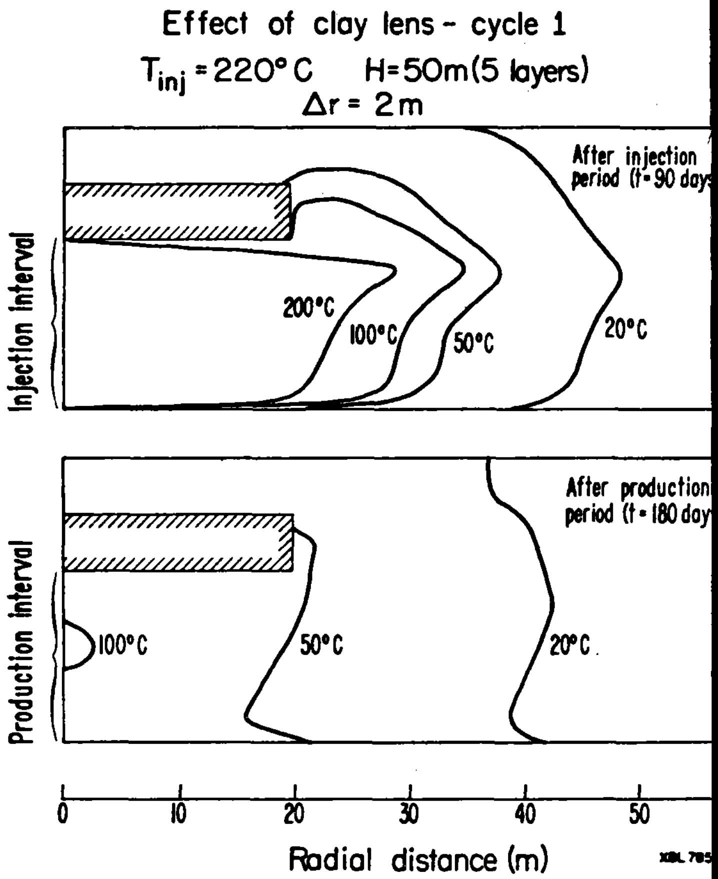

Figure 2

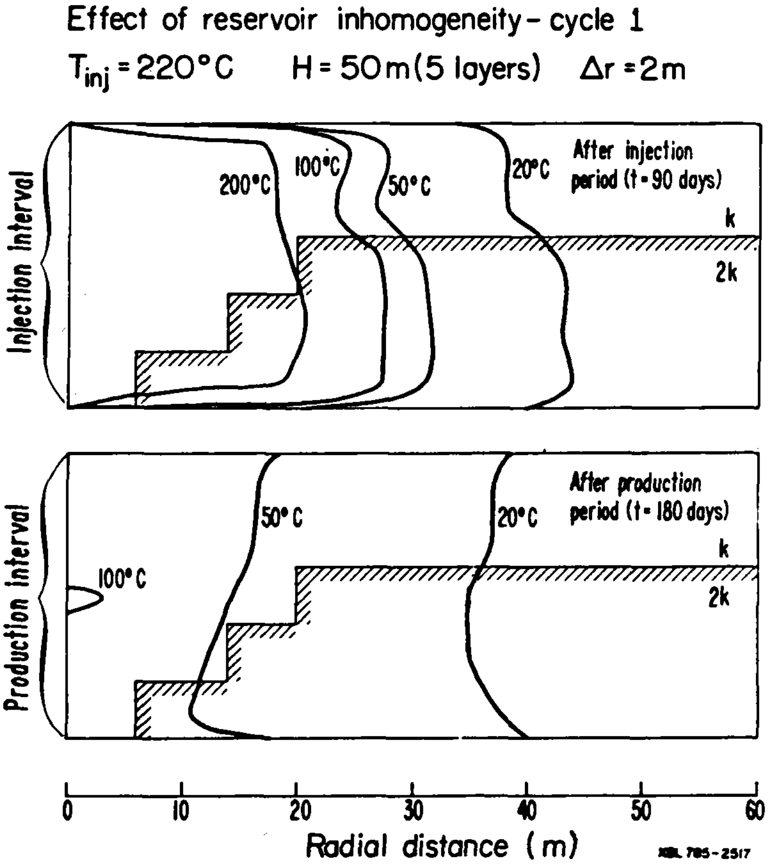

Figure 3

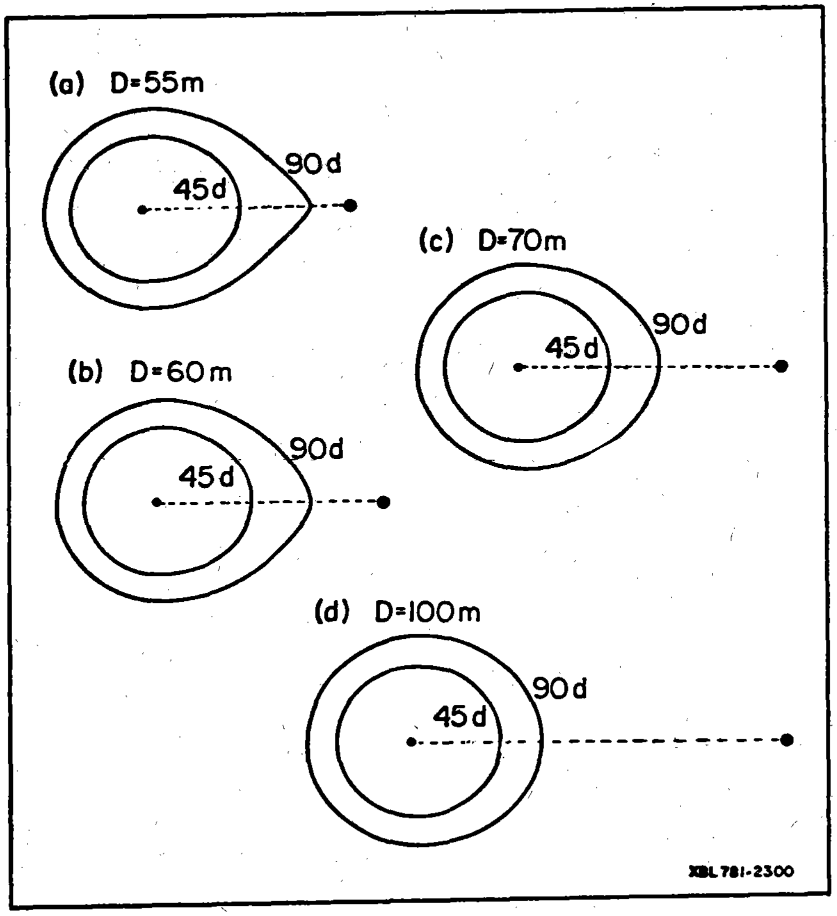

Figure 4

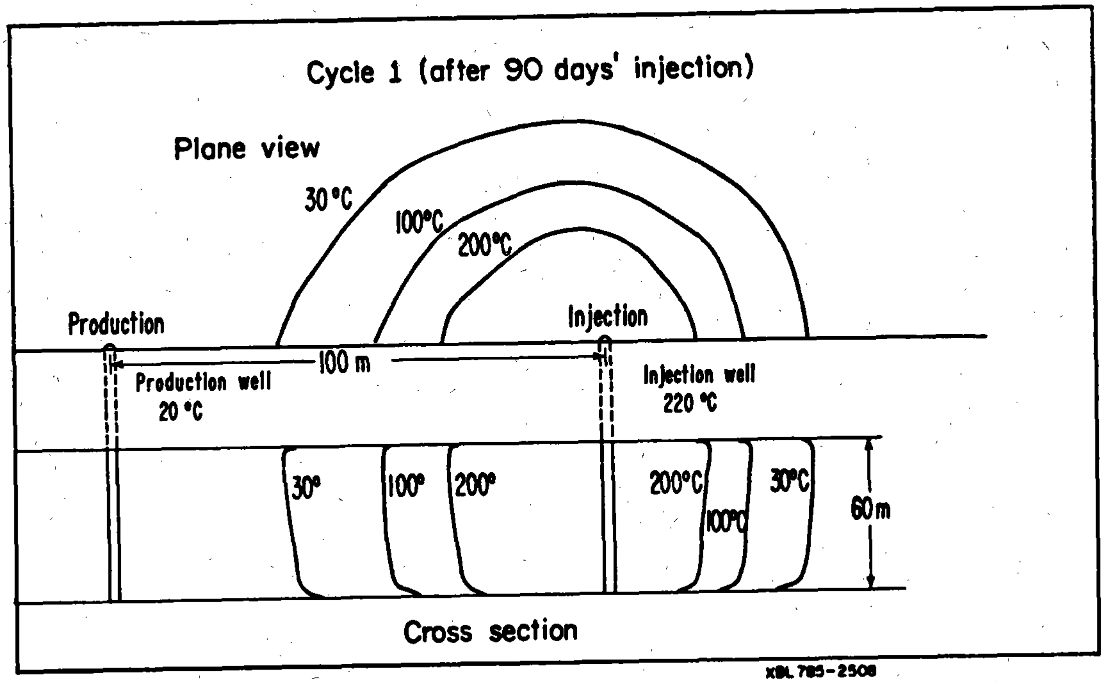

Figure 5

PROJECT SUMMARY

Project Title: Energy Storage-Boiler Tank

Principal Investigators: T. A. Chubb, J. J. Nemecek

Organization: Naval Research Laboratory
Code 7120
Washington, D. C. 20375
Telephone: (202) 767-3580

Project Goals: Development of a Heat-of-Fusion Energy Storage-Boiler Tank

Project Status: Laboratory studies with 55 lbs of salt are largely complete. Energy input step was verified with 12°C between temperature of liquid heat transfer fluid and 385°C melting point of salt (storage temperature). The salt eutectic ($MgCl_2$, NaCl, KCl) was found compatible with mild steel container material. M-terphenyl was found suitable as the heat transfer fluid for the proof of concept demonstration. A life test of 18 melt-freeze cycles was completed.

Site plans for 2 MWh storage facility are now complete. Bid package was prepared and construction proposals have been received.

Plans for the 2 MWh storage tank are well-advanced. Prototype salt cans have been received. Salt specifications have been defined. Heat transfer fluid (3500 lb) is on-hand.

Contract Number: EC-77-A-31-1024.A002

Contract Period: October, 1978 to September, 1979

Funding Level: $270,000.00

Funding Source: Department of Energy, Division of Energy Storage Systems

1. INTRODUCTION

Massive energy storage involves utilization of major tonnages of storage material. In (1) Nemecek et al. describe an energy-storage boiler tank in which heat is effectively transferred to and from large quantities of fusible salt by condensation and evaporation of heat transfer fluid. Temperature drops within the salt are minimized by making available large areas for heat conduction by encapsulating the salt in containers with a large aggregate surface area. In (2) Chubb et al. describe the coupling of the energy storage medium to a steam generator which functions as a condensation boiler. In this paper we describe laboratory studies carried out in support of plans to construct a 7.2 GJ (2 MWh) storage tank using these principles, and the design status of the 2 MWh tank.

2. LABORATORY STUDIES

Heat transfer studies have been carried out in a small insulated laboratory tank (.33 m ID, .41 m high) in which heat is applied to the tank by placing the tank on a 2 kW range element. The tank in its present configuration is shown in Figure 1. Insulation is provided by loose vermiculite which surrounds the sides and top of the tank to a thickness of 0.3 m during heat runs. The tank is used to study heat transfer from a pool of terphenyl fluid which covers the bottom of the tank to cans of salt which are stacked in the body of the tank. The assembly is instrumented with thermocouples that measure the temperature of the terphenyl liquid, the terphenyl vapor (near bottom, middle and top of tank), the salt in one can, and outside tank wall temperatures. Tank pressure and power input are also recorded.

The first series of runs were made using NaCl, KCl, $MgCl_2$ eutectic (MP 385°C) poured into 50 mm x 100 mm x 100 mm open steel cans. Before pouring, the salt was thoroughly dried by etch attack by the molten salt on aluminum metal shavings. Air was removed from the tank prior to initiation of heat runs. These runs taught the following:

1) Use of mixed terphenyls, e.g. Therminol 88, resulted in nonuniform temperatures in the tank due to fractionation. Under isobaric conditions o-terphenyl, which accumulates at the top of the tank, condenses at about 33°C lower temperature than m-terphenyl, which in turn condenses at about 17°C lower temperature than p-terphenyl.

2) On an initial heat run, new terphenyl heat transfer fluid should be carefully heated to drive off, by venting into a hood, any high vapor pressure contaminants that may be in the batch. Heated vent lines need to be used.

3) With relatively pure m-terphenyl (o-terphenyl 0.6%, p-terphenyl 8%) good temperature uniformity can be achieved if small quantities of higher vapor pressure materials are vented from the top of the tank.

4) Mounting a buffer tank above the main tank in such a manner that condensed liquid is returned to the main tank while high vapor pressure gases are accumulated in the buffer tank reduces the venting requirement for good temperature uniformity, so that only a few grams of heat-transfer fluid need be removed by venting during an energy input run.

5) Heat transfer from m-terphenyl liquid in the bottom of the tank into the melting salt interface can be achieved at acceptable heat transfer rates with a temperature drop never exceeding 12^{o}C.

6) Salt that melts and freezes in open contact with terphenyl vapor develops a porous crust that thickens with cycling and which could lead to salt overflowing the tops of the open cans if a large number of melt cycles were employed.

7) No serious corrosion problems occurred.

A second series of energy storage runs were made using purchased containerized salt. The salt was contained in 1 quart paint cans which have a 100 mm diameter. The salts were melt cycled 18 times. These heat runs taught the following lessons:

1) Some, but not most, of the paint cans leaked molten salt. (The salt cans depend on crimping of steel plus soft solder for sealing.)

2) All cans, except one, were not hermetically sealed by the lids. The one can that sealed itself off imploded or crumpled during one of the cool down periods. The can leaked and lost all its salt.

3) Despite the continual presence of an m-terphenyl vapor-salt contact, crusting did not build up to the point where the top surface of the salt reached the paint can lids.

4) Unlike salt solidified in the presence of dry nitrogen, the 18-times cycled salt did not freeze into a monolithic wall surrounding a single cavity; instead, the salt solidified into a rather porous, multiple cavity internal structure.

A study was made to determine the practicability of using 1 foot diameter salt containers with internal aluminum conductivity enhancement structures. A single heat run was made using a large salt container 0.3 m OD and 0.2 m high. The container was made of steel. It contained an internal aluminum tube-like structure equivalent to six 0.1 m OD tubes spring loaded so as to maintain aluminum-steel contact after melt. The aluminum conductivity-enhancement structure used metal 1.5 mm thick. The salt container was filled by pouring molten salt into the container. Unfortunately the salt fill was not properly premixed, and full melting was not subsequently achieved. During the heat run salt in the tank was not permitted to come into contact with terphenyl vapor. Lessons learned from this study were:

1) In the cold container salt shrinkage resulted in separation of the salt block with its embedded aluminum conduction enhancers from the steel container wall. Good thermal contact was not established until partial melting of the salt block occurred at 385°C.

2) Once partial melting occurred the temperature drop between steel wall and salt mid-interior was about 15°C, i.e. the aluminum conductivity enhancers worked as expected.

3) Because of the poor filling of the container the study needs to be repeated.

A measurement of the heat of fusion of the NaCl, KCl, $MgCl_2$ eutectic was carried out under the direction of S. C. Spiney of Dynatech Corporation using a drop calorimeter (3). His value was 240 kJ kg^{-1}. This value is less than that previously incorrectly measured by us. Parameters for a 3 m energy storage tank as listed in (1) require adjustment. New values are: Energy Stored, 7.2 GJ (2 MWh), Salt Mass, 30 tonnes, salt volume, 16.7 m^3 (based on liquid density of 1.8 gm cm^{-3}). These parameters apply to the 2 MWh demonstration tank described below.

3. PLANS FOR 2 MWh TANK

The 2 MWh tank is being constructed at NRL at the site of an old ammunition bunker which provides a concrete foundation -- 6.0 m square. The tank will be installed on a foam glass foundation 0.6 m thick. The tank itself is planned as a flat bottomed steel structure with a 50 mm thick steel plate bottom, and 10.0 mm thick cylinder walls. It is 3.0 m inside diameter and 3.6 m high. The top of the tank is flanged to receive a metal O-ring gasket 3.2 m in diameter and 6.0 mm diameter in cross section. A domed head with mating flange will act as the cover of the tank. The domed head is designed to contain the condensation boiler. The tank will be made of carbon steel, the head will use 316L stainless steel, the boiler, designed in accordance with reference (2), uses tubing made of 316L stainless. Vermiculite insulation will be used around the sides and top of the tank.

The tank will be heated by 150 kW electric immersion heaters. Present plans are to use tubular elements cast in aluminum heat conduction blocks for uniform distribution of the heating power. The heater will be placed inside the tank with power brought into the tank by MgO packed power feed-throughs or some other hermetic fitting. Terphenyl fluid circulation, as used during the energy removal portion of storage cycle, will be provided by a 4000 $l.hr^{-1}$ hot fluid circulation pump located in a small access chamber adjacent to the bottom of the tank. The heat transfer fluid will form a pool of liquid 0.3 m thick covering the bottom of the tank. The storage medium will be supported by a steel grid resting on the metal heater billets. These heater units sit on the flat bottom of the tank and are immersed in the heat transfer fluid.

The salt itself will be contained in vertical mild steel cans 1016 mm (40 inches) high and 105 mm (4 inches) in diameter. The cans will be made using seam spot welding, first to make a cylinder out of sheet stock and second to seal stamped closures into the top and bottom ends of the tubes. The top closure will contain a 32 mm (1.25") opening through which molten salt will be poured during filling. After filling, the opening will be closed by glue sealing a fusible lead sheet over the aperture thereby protecting the salt from moisture. It should then be possible to store the sealed cans under normal warehouse conditions prior to installation in the tank. Finally each can is fitted with an aluminum drip shield which loosely encloses the top end of the tube. The drip shield prevents m-terphenyl condensate from pouring into the tube opening.

The energy storage tank siting is being carried out in such a manner that the tank can be serviced using a light-weight traveling gantry crane, which can lift the lid of the tank and can aid in loading and unloading the salts. The site is planned so that the gantry will be able to service two tanks. It is hoped to construct a higher temperature super-heater storage tank in the same vicinity. The storage tank will be protected from the weather by a light weight roof, which is also removable. The insulating vermiculite is also removable, being transported to a Butler building by a vacuum piping arrangement.

The energy storage-boiler tank complex includes a pressurized water feed system. Water purity will be equivalent to distilled water. Steam will be generated at a temperature of about 370°C and pressure of 800 psia. After metering the steam will be delivered to a silencer.

A data acquisition system for the energy storage-boiler tank is being assembled by New Mexico State University. The system is based on the Hewlett Packard 3052A digital data acquisition system with remote readout. The main readout station will be in a lab module in one of the Naval Research

Laboratory buildings. The on-site portion of the digital data system, which includes the sensor selection circuitry, will be located in an instrumentation trailer just outside the storage tank enclosure.

Plans are to initiate tank operation without salts. The initial studies will outgas the heat transfer fluid, test the electrical heating and fluid circulation systems, evaluate vapor temperature distribution and test the operation of the condensation boiler and associated feed-water pumps. 30 t of salt eutectic will then be installed and the storage operation evaluated.

4. REFERENCES

(1) J. J. Nemecek, D. E. Simmons and T. A. Chubb, "Demand sensitive energy storage in molten salts," Solar Energy 20, 213 (1978).

2. T. A. Chubb, J. J. Nemecek and D. E. Simmons, "Energy storage-boiler tank: boiler design, materials compatibility tests," Proceedings of the 1977 Annual Meeting American Section of the International Solar Energy Society, 18-10 (1977).

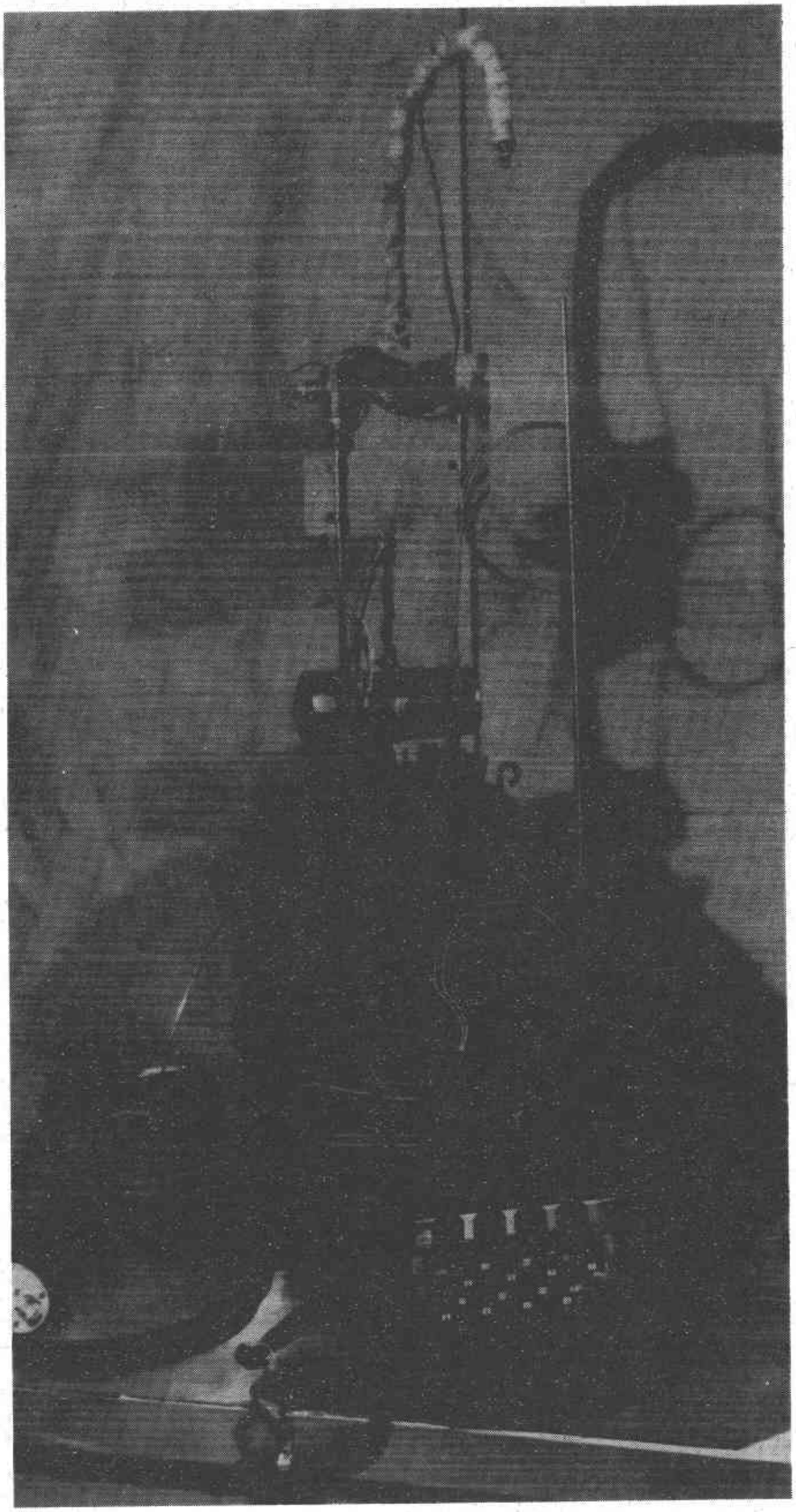

Figure 1. Laboratory Test Tank

Thermal Energy Storage Applications for Highway Vehicles with Stirling Engines

by

M. Magdy Farahat

Argonne National Laboratory
Chemical Engineering Division

Presented at

The Third Annual Thermal Energy Storage
Contractors Information Exchange Meeting

December 1978

PROJECT SUMMARY

Project Title: Thermal Energy Storage for Road Vehicle Propulsion Systems

Principal Investigator: M. M. Farahat

Organization: Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Telephone: (312) 972-4517

Project Goals: Develop a thermal storage system for application with a heat engine (e.g., Stirling, Rankine or Brayton cycle) to provide propulsion for highway vehicles.

Project Status: This project is divided into four phases as follows:

(1) System Studies: to assess technical and economic feasibility and produce conceptual designs. This phase has been completed by awarding two 9-month contracts to Sigma Research, Inc. and Thermo Electron Corporation. Final reports will be submitted by the end of 1978.

(2) Concept Development: by fabricating and testing first generation thermal energy storage components 18 months.

(3) Technology Validation: by refining first generation component designs to establish the proof-of-concept. 18 months.

(4) Demonstration: the TES Subsystem will be packaged, integrated with a suitable heat engine and installed in a compact urban vehicle chassis for test on a dynamometer and for road testing.

Contract Number: NASA/ANL Contract No. C-2325

Contract Period: March, 1977 to March, 1979

Funding Level: $250,000.00

Funding Source: NASA/LeRC

THE CONCEPT OF THERMAL ENERGY STORAGE FOR automobile applications could provide flexibility of heat supply for storage, and low pollution to the environment during use. The specific thermal energy storage of latent heat systems is high. When coupled to an advanced stirling engine via two-phase liquid metal heat transport, the mechanical energy density is high enough to make the system a viable competitor to both hydride and the battery storage systems. The use of fossil fuel recharging gives an overall energy efficiency appreciably higher than the forementioned systems.

In the early 1960's, NASA supported three programs to develop thermal energy storage systems for electric power generation in orbiting space satelites which would operate in a sun/shade cycle. Resultant testing was successful(1,2).

In 1964, the General Motors Research Laboratory installed a 22.5 kWs (kilowatt shaft power) TES/Stirling cycle engine into a Corvair vehicle ("Calvair")(3). Sensible heat was stored in alumina operating between 1144°K and 1810°K (1600°F and 2800°F), and contained in a Linde designed vacuum jacket tank. A demonstration road test was completed. The storage specific energy was estimated to be 300 Wh/kg with about 88 Wh/kg delivered to the driving wheels.

More recently, the Philips Research Laboratories successfully completed 1000 hours test of a 7.3 kWs TES/Stirling cycle engine in their laboratory(4). Both sensible and latent heat of the LiF storage media were utilized. A refluxing sodium "heat pipe" was used to transfer the thermal energy to the engine. The stored specific energy was calculated to be 470 Wh/kg of salt. Based on a Philips vehicle design study, about 150 Wh/kg could be delivered to the driving wheels.(5).

The Xerox Electro-Optical Systems is developing a heat pipe/thermal energy storage unit powering a Vuilleumier Cryocooler under Air Force contract F33615-75-C-2045(6). The storage specific energy for the TES media, $64MgF_2 + 30\ LiF + 6KF$, was calculated to be 220 Wh/kg.

A study of thermal energy storage/heat engine for highway vehicle propulsion was conducted by Mechanical Technology, Inc. (MTI) and NASA(7). Vehicle performance was evaluated with Lithium Fluoride as the thermal energy storage medium. The engines elected for evaluation were advanced Rankine Cycle, Close Brayton Cycle, and Stirling Cycle. A range of 160 kilometers was selected as the design goal for a vehicle subject repetitively to the SAE-J227 Metropolitan area driving cycle. A TES/Stirling was shown to be the most efficient among the three engines chosen, requiring 132 kWht.

A conceptual design study of thermal energy storage for road vehicle propulsion was initiated near the end of 1977 under the sponsorship of DOE/STOR and NASA/LRC and the technical management of Argonne National Laboratory. Two firms were awarded contracts for a 9-month period to perform the conceptual design studies; the final reports are due by the end of 1978(8, 9). Performance specifications for the TES System are given in Table 1a and 1b.

THE MTI STUDY

The thermal energy storage vehicle design was based on the prototype vehicle specification, compact passenger car, dated November 1973, prepared by the Alternative Automobile Power Systems Division of the Environmental Agency.

The engines selected as suitable candidate for adaptation to a thermal storage system were Stirling (ERDA-498DA), Rankine (SES Mark II), and Brayton (AiResearch Closed Cycle). Engine performance maps from published data provided the basis for engine analysis. The driving cycle used for calculating vehicle performance is the SAE Metropolitan Area Driving Cycle, SAE J-227. The total cycle time equals 300 seconds which results in a distance travelled of 3.19 kilometers. The 160 kilometer range is simulated by repeating the cycle fifty (50) times.

The calculations of performance consist of computing the power and speed at the wheels for each time increment of the driving cycle specified and then proceeding through every component of the power train. Fig. 1 shows the vehicle energy requirements from thermal storage as a function of engine heater head temperature. The Stirling engine was chosen because of its superior overall efficiency.

SIGMA RESEARCH, INC. STUDY

Sigma Research, Inc. was awarded a 9-month contract for the conceptual design study of a thermal storage system for automotive propul-

Table 1a - Required Heat Delivery Rates

Requirement	Minimum Heat Delivery Rate, kW	Duration of Heat Delivery	Other Conditions or Constants
1. Sustained power to achieve 161 km (100 mi) at 88.5 kph (55 mph)	55.5	1.82 hr	Drive immediately after full recharge.
2. Power for climbing hills	66.8	5 min	At any time during 161 km (100 mi).
3. Power burst for acceleration, passing and emergency maneuvers	197.4	15 sec	At any time during 161 km (100 mi).
4. Sustained power after 12 hours on standby in 293°K ambient air	55.5	1.36 hr	Drive, 12 hours after full thermal recharge.

Table 1b - Thermal Control Requirements Defined at the Output Heat Exchanger on the TES Side

Requirement	Heat Delivery Rate	Time Interval
1. Traffic Start (from idle)	5 to 15 kW @ 673°K (400°C) min.	0.2 sec.
2. Traffic Stop	15 kW to 5	0.2 sec.
3. Idle Power Control	Stable at 2 kW or less	indefinitely
4. High Power Burst	from 50 kW to 200 kW @ 673°K min.	1 sec.
5. Maximum Thermal Control Heat Leakage Rate Into Heat Transport Subsystem During Vehicle Standby (e.g., while parked in charged condition)	500 watts	indefinitely

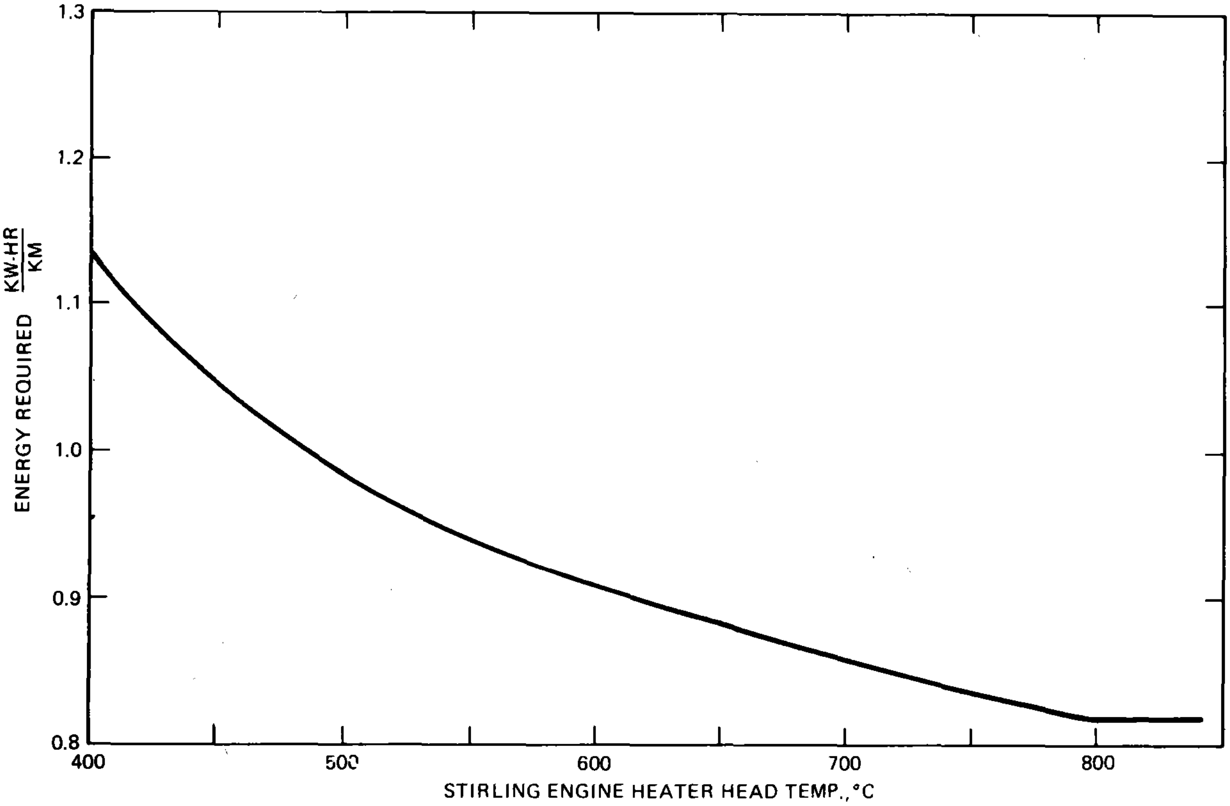

Fig. 1 - Stirling Engine Requirement for Metropolitan Driving Cycle

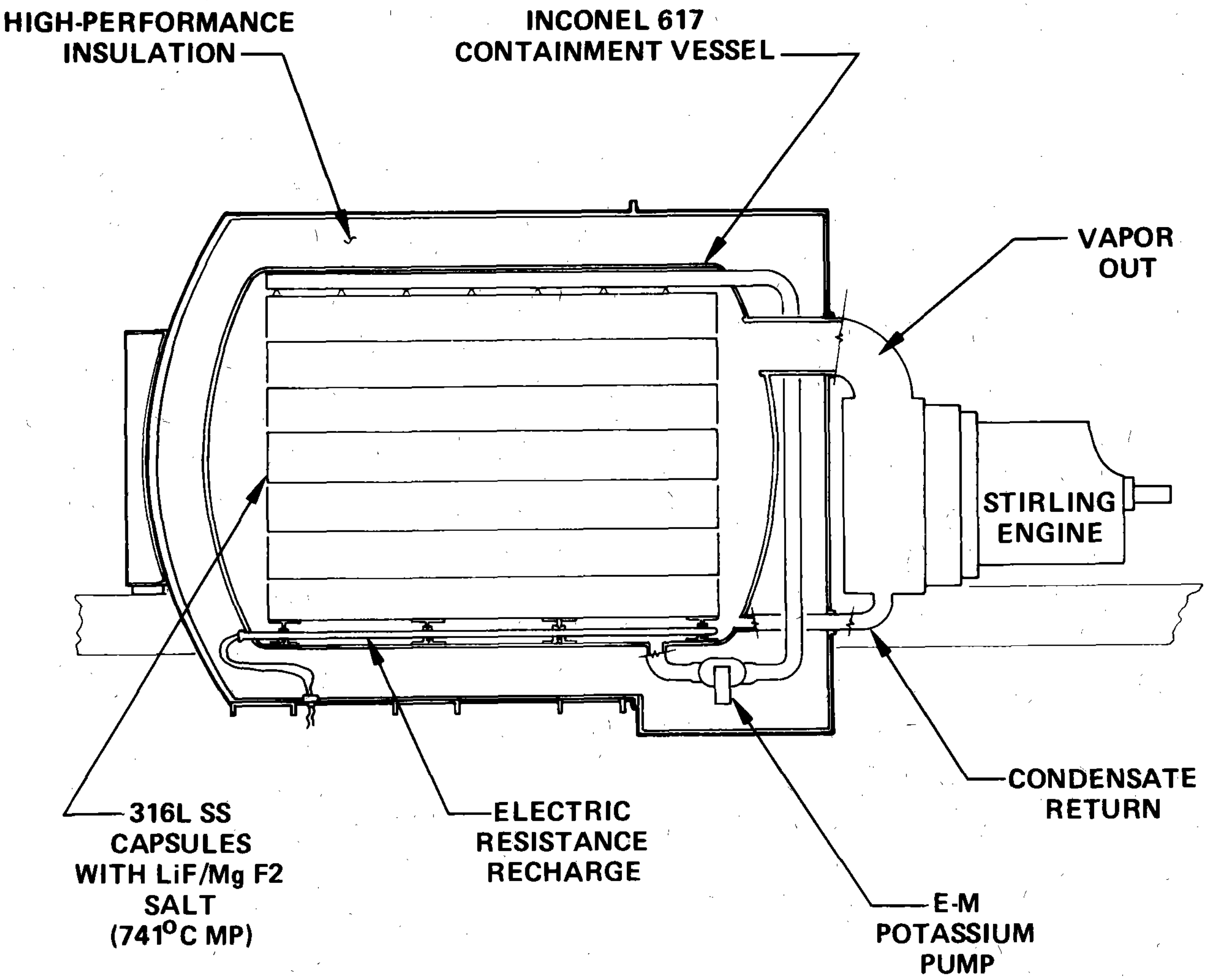

Fig. 2 - Baseline TES Configuration (Sigma)

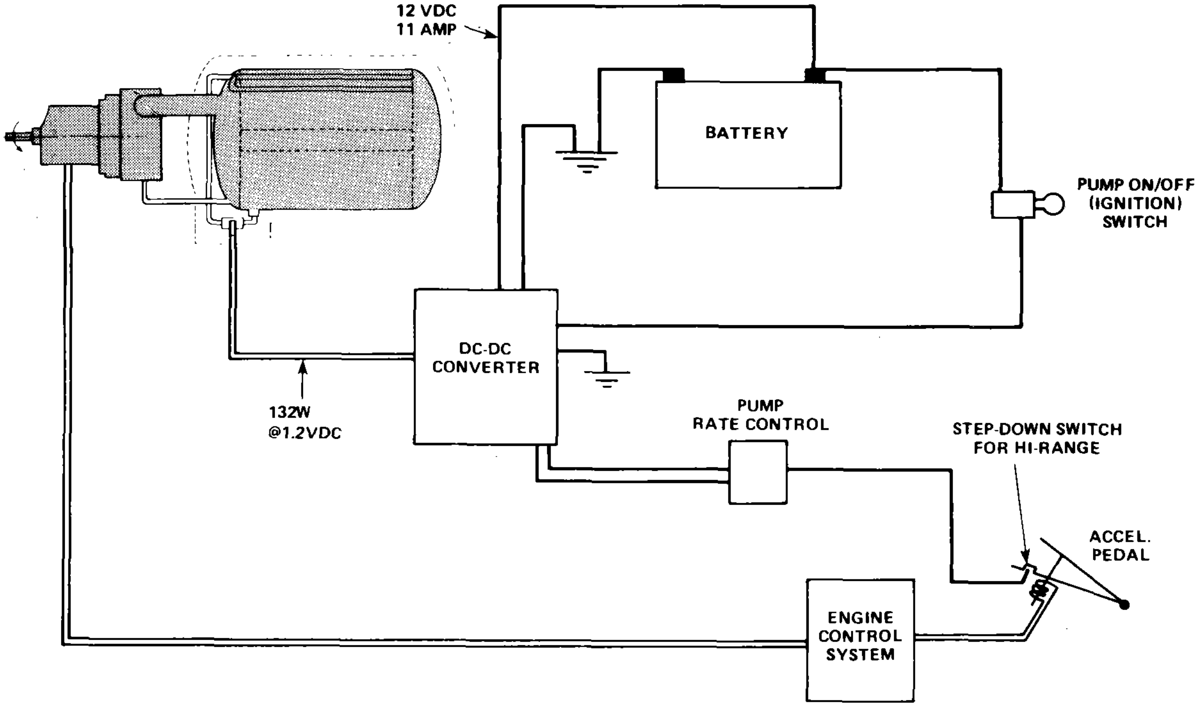

Fig. 3 - Heat Transport/Engine Control (Sigma)

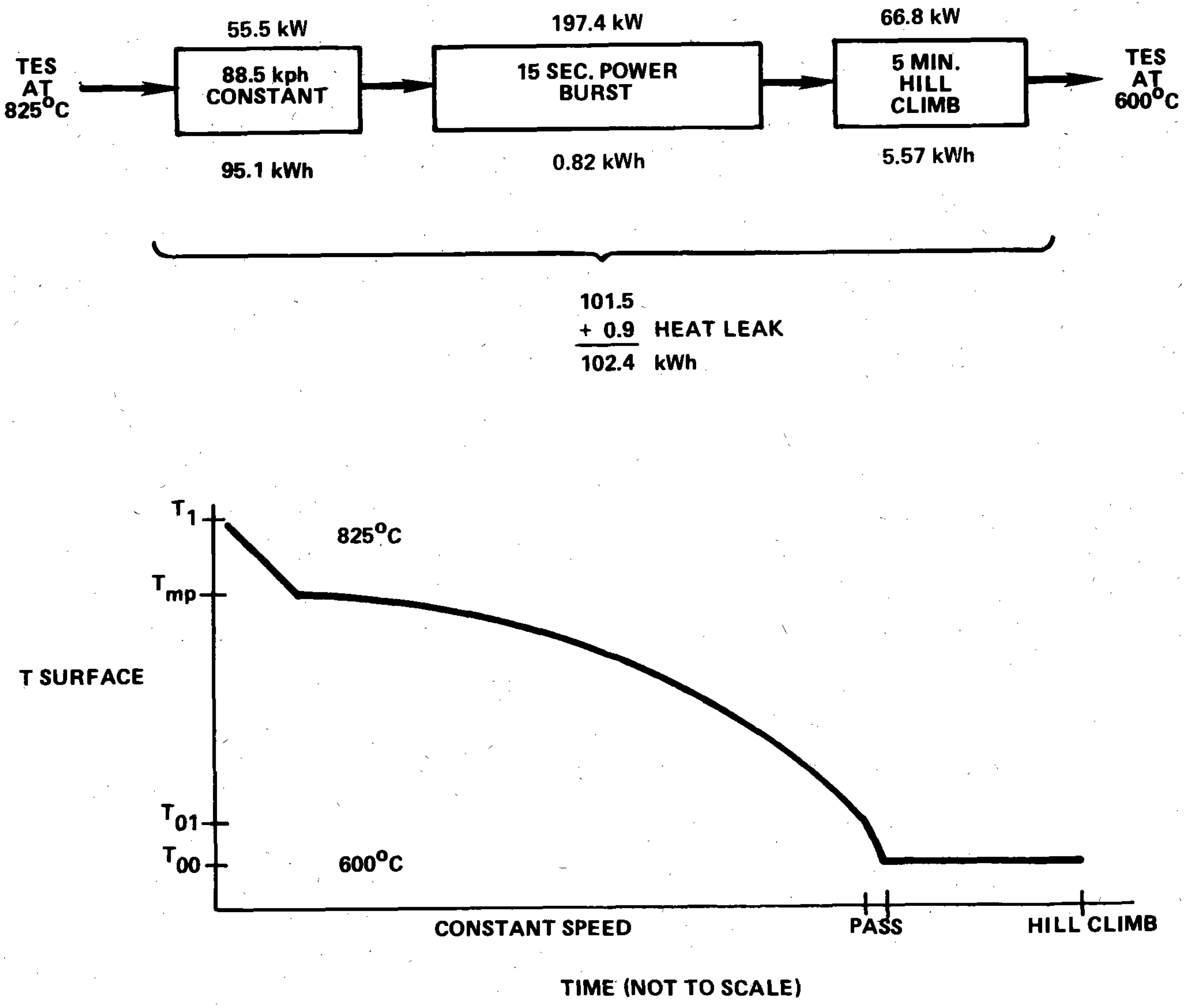

Fig. 4 - Operating Sequence and Temperature Profiles

TABLE 2 - BASELINE TES SYSTEM CHARACTERISTICS

VOLUME: 400 LITERS

COMPONENT	WEIGHT (kg)		THERMAL CAPACITY 600-825°C (kWh)
SALT (LiF/MgF_2)	285	SENSIBLE-SOLID	13.0*
		LATENT @ 741	72.7
		SENSIBLE-LIQUID	11.9
			97.6
CAPSULES, VESSEL, HEADERS, PUMP & HEATERS	125.2		4.5
POTASSIUM	5.5		0.3
INSULATION, COVER, VAC. PUMP	68.4		0
CONTROLS	15.9		0
	500		102.4

GRAVIMETRIC ENERGY DENSITY – 205 Wh/kg
(93 Wh/lb)
VOLUMETRIC ENERGY DENSITY – 256 Wh/ℓ
(7314 Wh/ft^3)
SPECIFIC POWER – >460 W/kg
(>209 W/lb)

*CREDIT GIVEN FOR ONLY 65% OF SOLID HEAT CAPACITY

TABLE 3 - BASELINE TES/VEHICLE PERFORMANCE

FULL CHARGE: 102.4 kWh (600-825°C)

RANGE

CONSTANT POWER 55.5 kw (55 mph)	161.7 km (100.5 mi)
CONSTANT SPEED + PASS + HILL CLIMB CYCLE (WITH 35 mph MINIMUM)	169.5 km (105.3 mi)
METROPOLITAN CYCLE (PER CONTRACT)	119.5 km (74.3 mi)

NOTE: IF MINIMUM SALT TEMPERATURE OF 400°C WERE UTILIZED, RANGE IS INCREASED ABOUT 16%.

OTHER

STANDBY HEAT LEAK:	INSULATION	.55 kw ←
	H. T. SYSTEM	→ .22
	TOTAL	.77 kw
RESPONSE TIME OF H.T. SYSTEM		<< 0.2 SECOND
ORIENTATION LIMITS:	DOWNGRADE LIMIT	~4% WITH FULL POWER

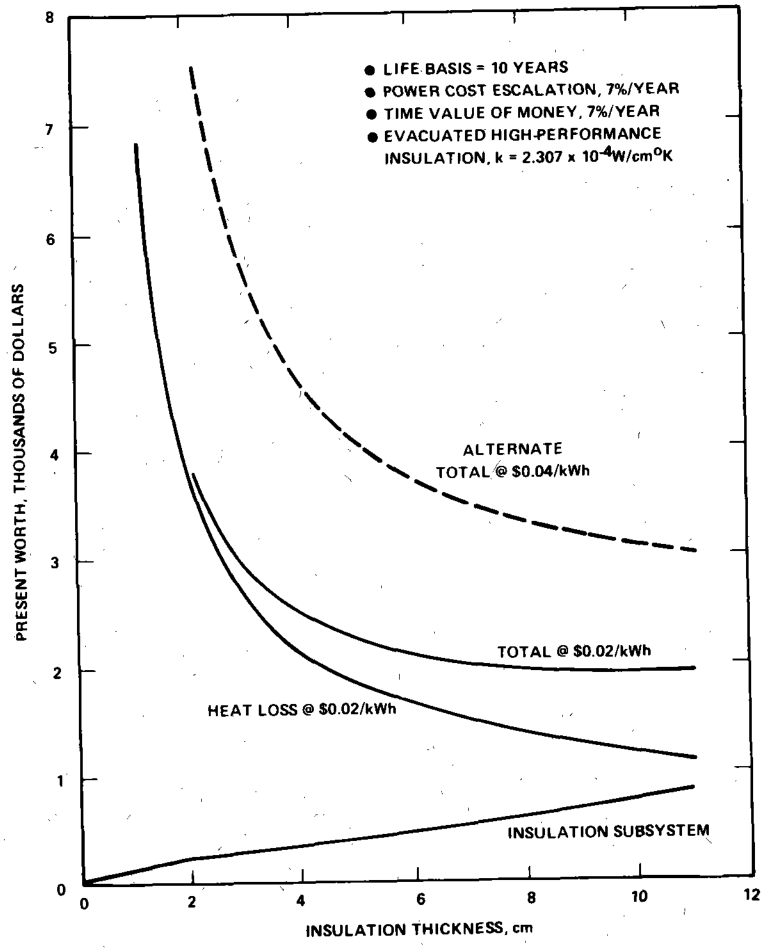

Fig. 5 - Cost of Insulation and Heat Leakage

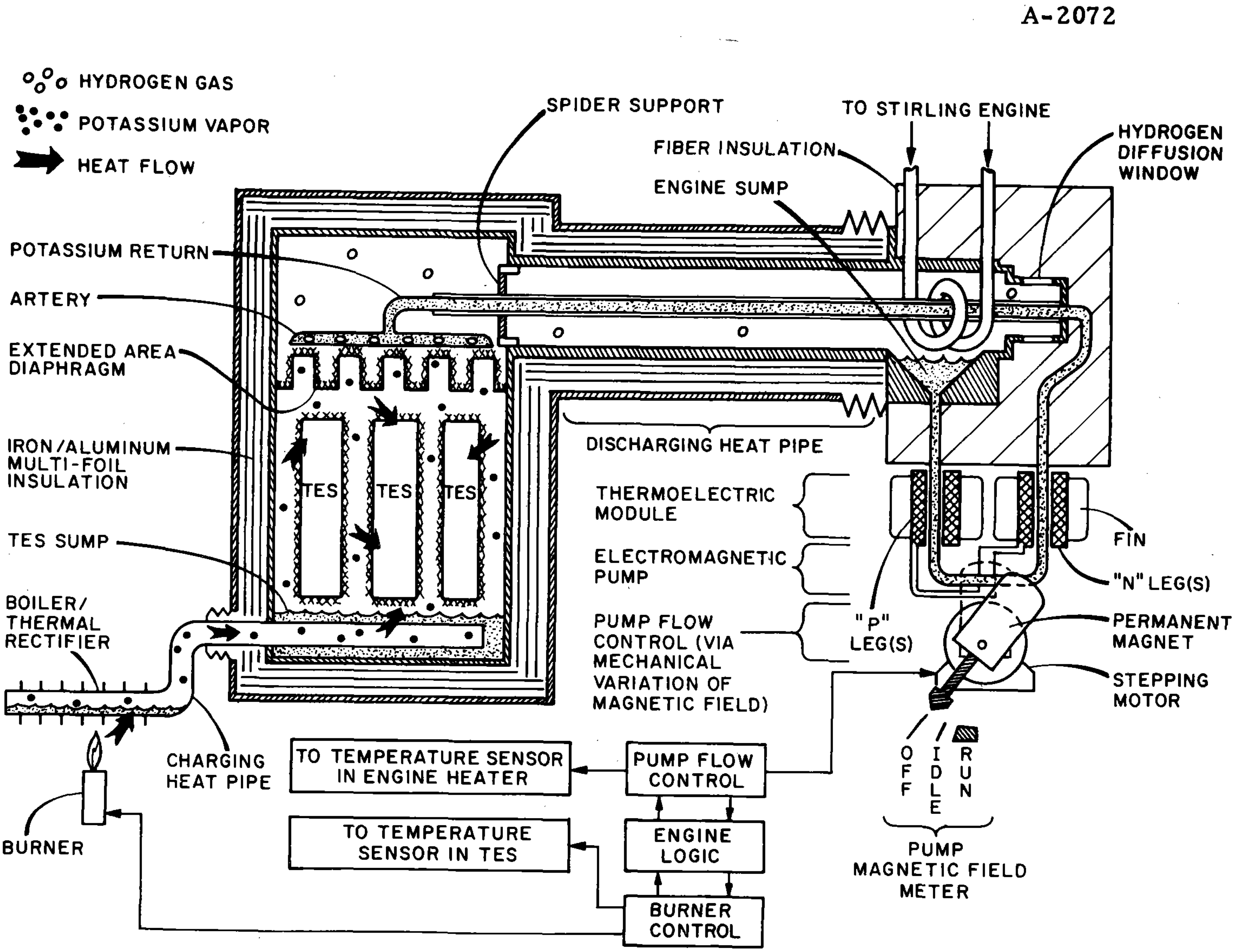

Fig. 6 - TES/Heat Transport/Engine Control (TECO)

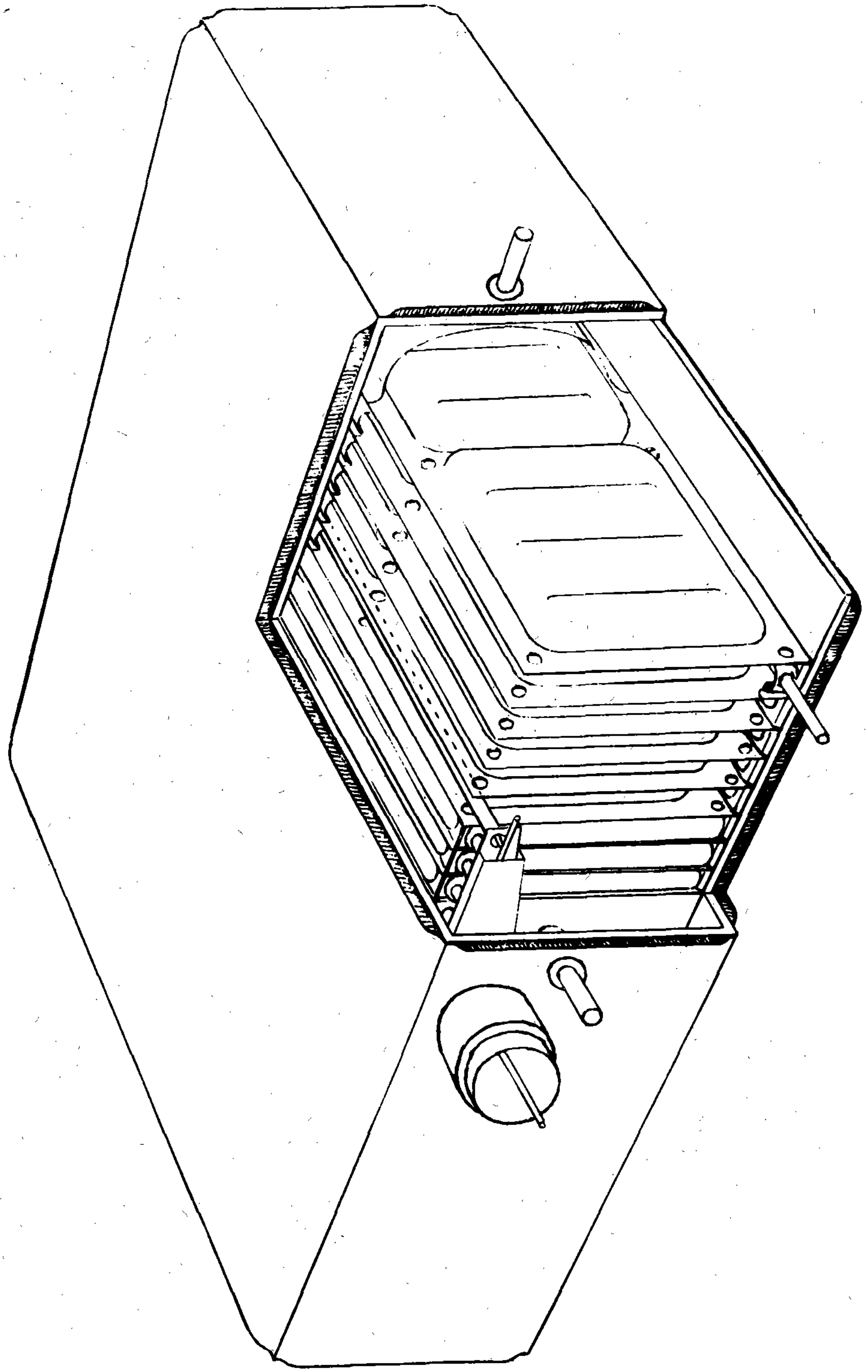

Fig. 7a - TES Revervoir - Rectangular Configuration (TECO)

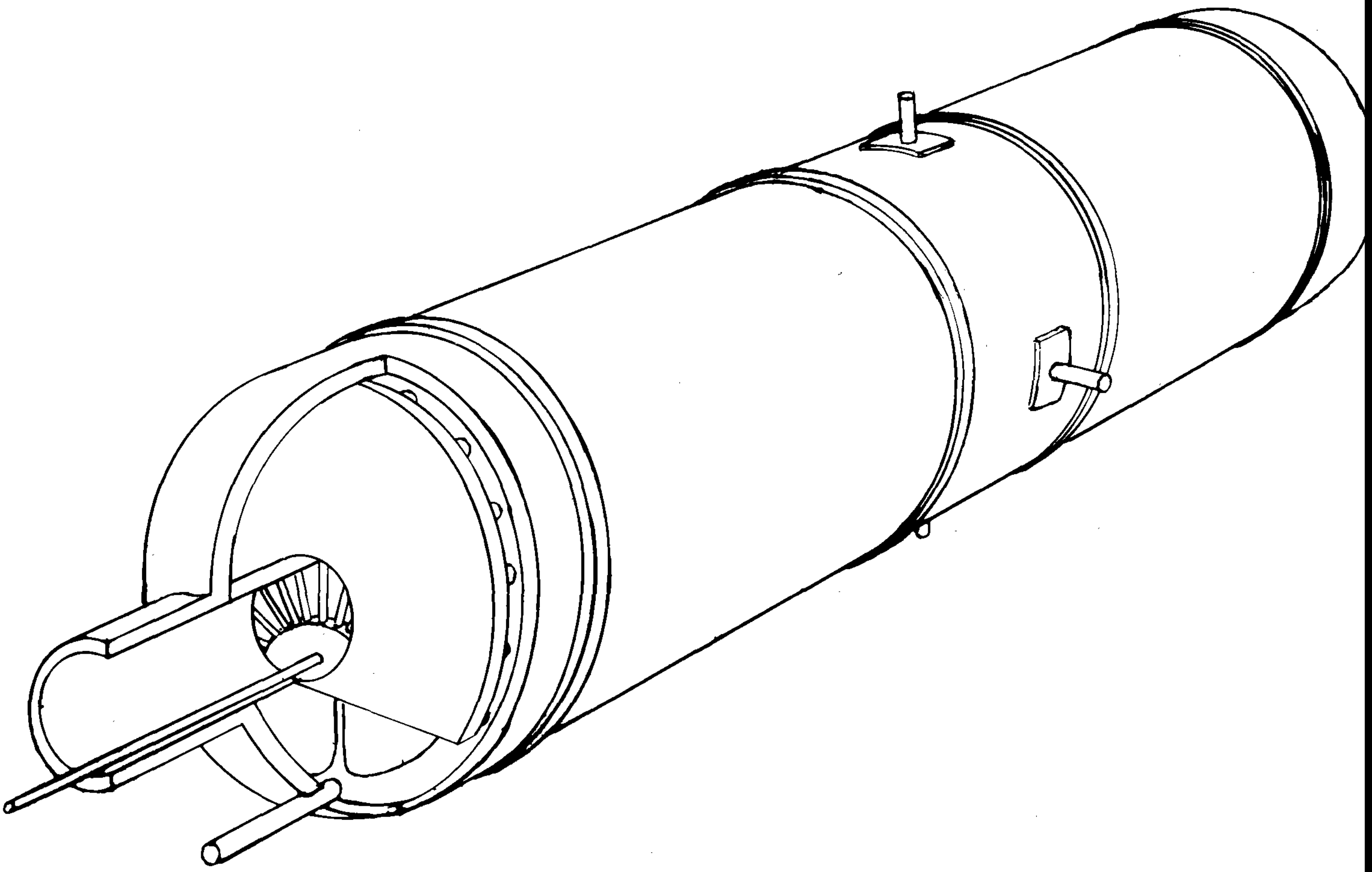

Fig. 7b - TES Reservoir - Cylindrical Configuration (TECO)

Table 4 - Comparison of Cylindrical and Rectangular Configurations after Normalization to 500 kg Total Reservoir Weight

	LiF		NaF/MgF_2
	Rectangular	Cylindrical	Rectangular
Salt	297 kg	269 kg	320 kg
Storage Capacity	152 kwhrth	128 kwhrth	99 kwhrth
Total Envelope Volume	0.38m^3	0.35m^3	0.34m^3
Gravimetric Storage Density	$0.304\frac{\text{kwhrth}}{\text{kg}}$	$0.276\frac{\text{kwhrth}}{\text{kg}}$	$0.198\frac{\text{kwhrth}}{\text{kg}}$
Volumetric Storage Density	$400\frac{\text{kwhrth}}{\text{m}^3}$	$398\frac{\text{kwhrth}}{\text{m}^3}$	$291\frac{\text{kwhrth}}{\text{m}^3}$
Equivalent U.S. Gallons Gasoline	3.7	3.4	2.4

sion. Sigma's base line configuration is shown on Fig. 2 and the proposed heat transport and engine control is shown on Fig. 3. Several candidate salts were reviewed having melting points between 713°C and 848°C. The high production selling price was then considered, and although NaF/MgF_2 appears to be the most economical to use when the ¢/Wh is considered, it was decided to use the LiF/MgF_2 eutectic. This is because of weight and volume restrictions on the system for a passenger vehicle application.

If the TES follows the driving cycle shown on Fig. 4, the required system capacity would be ∿105 kWh and the range is over 161 kilometers. The resultant salt capsule temperature is also shown on Fig. 3.

High performance thermal insulation was chosen to operate under relatively low vacuum (∿50 mm Hg). Examples of suitable insulator are Min K manufactured by Johns-Manville and Microtherm manufactued by Micropore Insulation Ltd., both of the porous silica type. The estimated cost and insulation thickness based on a 10-year life is shown on Fig. 5. Sigma's TES system characteristics and performance are given in Table 2 and 3, respectively.

Based on the above study, Sigma made the following recommendations: 1) It is desirable to reduce the operating temperature of the Stirling engine to 760°C maximum. This allows the use of lower cost alloy materials for the containment vessel and eliminates the use of cobalt in structural components. 2) The energy storage and power surge requirements may be lowered to be comparable to limited performance urban vehicles. This would reduce the system size and weight and provide a more energy efficient vehicle.

THERMO ELECTRON CORPORATION STUDY

Thermo Electron Corporation (TECO) investigated two candidate salts, LiF, the more efficient and expensive fluoride, and NaF/MgF_2 eutectic which is the least expensive non Lithium fluoride salt. The concept chosen by TECO shown on Fig. 6 incorporates a heat pipe for fossil fuel recharging. Two configurations for the containment vessel were studied; rectangular and cylindrical, Fig. 7a and 7b. A comparison between the two configurations is given in Table 4.

The thermal insulation of the containment vessel is of the vacuum multifoil type which is manufactured by TECO. This would reduce the heat loss through the containment wall to about 0.3 kW. The multifoil characteristics are given in Table 5.

The position of the TES container was suggested to be located between the vehicles wheels in a Ford Pinto size can as shown on Fig. 8. Home heating fossil fuel was postulated for the long term recharging and a schematic of the system is shown on Fig. 9.

Based on its study findings, TECO has recommended that the use of a dual fuel/TES offers many advantages over a TES only system. This includes a tenfold size reduction of the TES system, a substantial savings in the use of premium liquid fuels, in addition to retaining the convenience and flexibility of the current vehicles.

CONCLUSIONS

The performance and cost results indicate that a TES/Stirling Vehicle is competitive with hydride and battery operated automobiles. Previous experience with GM's Calvair automobile and Philips fused salt TES demonstrates the technical feasibility of the system.

RECOMMENDED THERMAL ENERGY STORAGE R&D

Short-Term (FY 79)
  Refinement of Cost Analysis
  Recharging Schemes and Fuels
  Public acceptability and risk assessment
Intermediate-Term (1980-1982)
  Choose concept
  Design and build hardware
  Assess performance and define manufacturing difficulties
Long-Term (after 1982)
  Integrate with advances stirling engine and assess performance
  Detailed economic analysis

Table 5 - Multi-Foil Insulation

No. of Foils	90
Material	Soft Iron
Weight	1.8 gm/cm^2 (3.7 lb/ft^2)
Heat Loss (1123°K → 300°K)	0.01 Watts/cm^2 (31.7 BTU/Hr-ft^2)
Insulation Thickness	1.27 cm (0.5 inch)
Total Heat Loss Through Multi-Foil Only	
LiF (A = 3.11 M^2)	0.31 KW (4.9%/Day)
NaF/MgF$_2$ (A = 2.82 M^2)	0.28 KW (7.2%/Day)
Compression Spacers Approximately Doulbe Heat Loss	

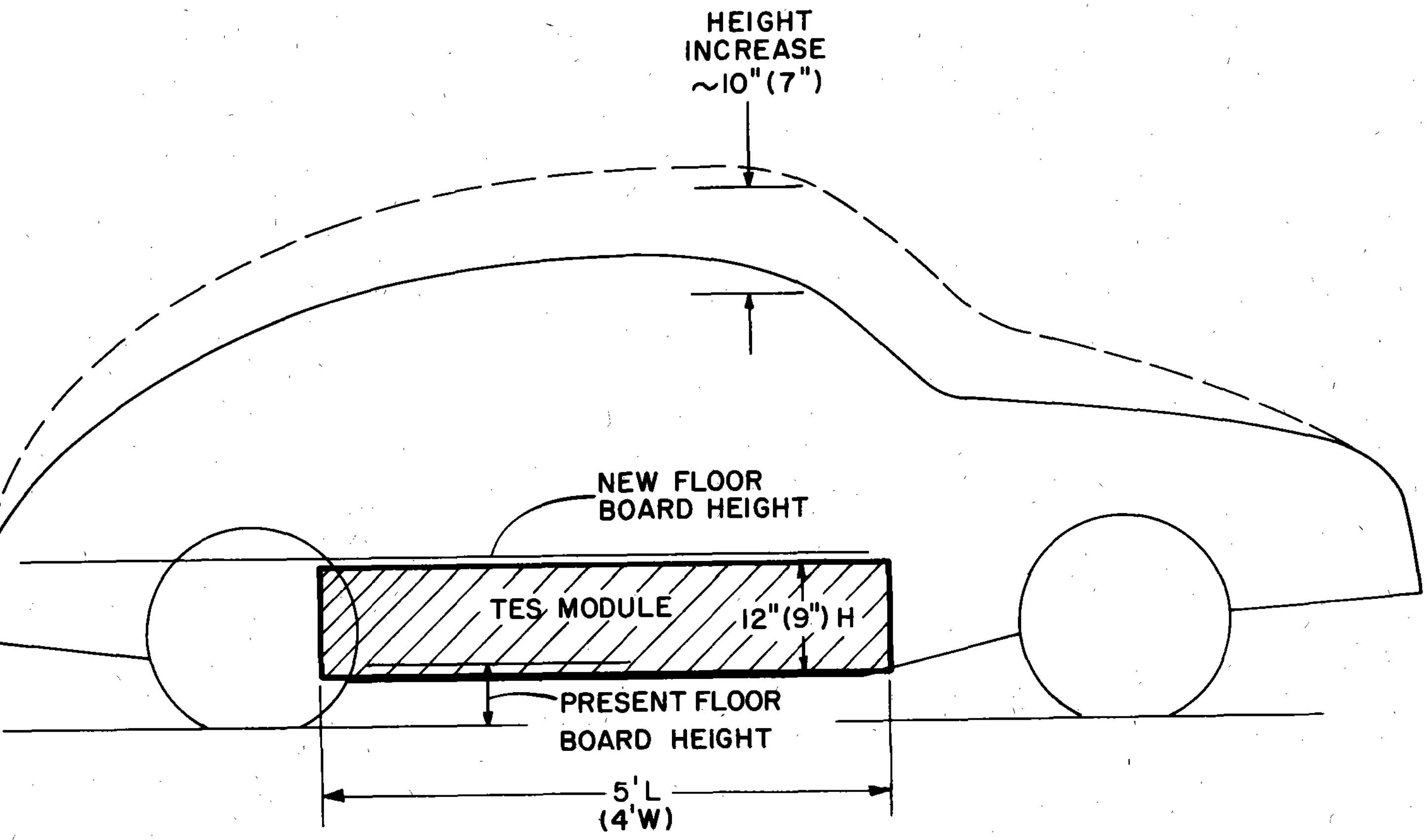

Fig. 8 - Location of TES Module in Ford Pinto-Size Car (TECO)

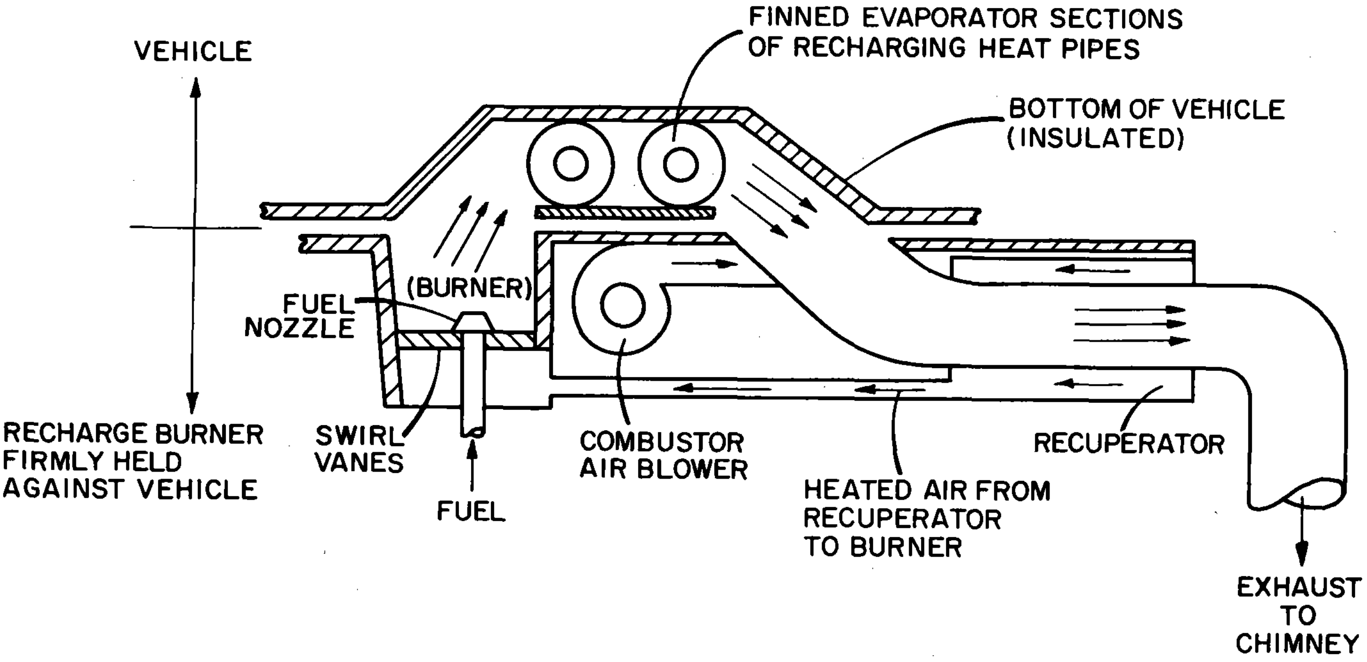

Fig. 9 - Schematic of Recharging System (TECO)

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PROJECT SUMMARY

Project Title: Research Studies for Adiabatic Compressed Air Storage

Principal Investigator: N. I. Hamilton

Organization: MIT/Lincoln Laboratory
Lexington, MA 02173
Telephone: (617) 862-5500 Ext. 7456

Project Goals: The objective is to investigate the applicability of compressed air energy storage in combination with thermal energy storage for use in electric utility power generation. The combination of solar thermal and off-peak energy shall be used in determining cost and performance models. Particular attention will be focused on the cost and performance of the packed beds for thermal storage.

Project Status: The scope of work consists of three tasks:

(I) Application of CAES to Solar Power.

(II) Preliminary Design Study of Adiabatic CAES.

(III) Thermal Storage in Packed Beds.

The technical effort has been completed with the following major conclusions:

(1) CAES for storage of solar thermal electric power is not practical because the combined capital cost is too high and the multiple conversions decrease efficiency.

(2) CAES compares favorably to pumped hydro for conventional utility storage.

(3) Use of available reservoirs can considerably reduce cost, time and risk.

(4) Thermal storage for adiabatic CAES is technically feasible and economically attractive (low incremental cost 1-7 to 4-6 mills/kwh).

Contract Number: EX-76-A-01-2295

Contract Period: August, 1977 to January, 1979

Funding Level: $75,000.00

Funding Source: Battelle Northwest

PACKED BEDS FOR THERMAL ENERGY STORAGE IN AN UNDERGROUND COMPRESSED AIR ENERGY STORAGE SYSTEM

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Lexington, Massachusetts 02173

ABSTRACT

A preliminary design study of a 200-MWe packed bed thermal energy storage unit for operating in the range 1000°F to 1500°F is described. This storage unit is considered for use in both conventional and solar-augmented systems. Also included is a 100-MWe system, part of which is compressed air and thermal energy storage, and part of which is a separate solar source, that feeds directly into the turbine.

1. INTRODUCTION

To date the use of packed beds has been confined to applications in chemical engineering and in the field of solar energy, where a few residential and commercial structures have incorporated thermal energy storage (TES). More recently [1,2] proposals have been put forward involving storage of the heat of compression in an underground adiabatic compressed air energy storage (CAES) system. Bascially a motor draws off-peak power from the electrical grid to drive an air compressor which drives the air through a packed bed, thereby withdrawing the heat of compression, and finally sending it cooled to a storage cavern. Upon release, the air returns through the bed, regains the heat of compression, and enters the turbine at a sufficiently high pressure and temperature to produce the necessary output power. A variation of this, described as a combined solar thermal-CAES system [3], involves the use of a solar central receiver which bypasses the packed bed and supplies hot air directly to the turbine on discharge, (see Figure 1). This paper will deal with the analysis, conceptual design and cost estimate of the packed bed for use in either the CAES or combined solar-thermal-CAES system.

2. MATERIALS FOR THERMAL PACKING

Half-inch granitic pebbles were chosen as the most suitable packing, as this affords a simple, inexpensive and reliable TES design. Salt storage is being considered as a possible future alternative but potential cost and reliability make it an unlikely near-term candidate. Refractory materials are more durable but are very expensive.

3. PARAMETRIC ANALYSIS

A single-phase conductivity model, which simulates the two-phase model of fluid flowing through a porous column [4], has been modified to incorporate forced convection by using an equivalent volumetric heat transfer coefficient h_{eq} that accounts for conduction and convection [5]. This model permits analytical solutions that can be simplified to obtain bed profiles and expressions for the thermocline slope and bed length required. Basic results of a parametric analysis are included in Table 1 below.

Parameter	Shorter Bed Length (m) Requires	To Increase Thermocline Slope (deg/m) Requires
T	larger	larger
ϵ	smaller	smaller
G	smaller	smaller
C_a	smaller	smaller
C_b	larger	larger
K_b	smaller	smaller
ρ_b	larger	larger
d	smaller	smaller
h_v	larger	larger
τ	smaller	smaller

TABLE 1. Influence of Parameters on Bed Length and Thermocline

Typically, the available off-peak energy supply and CAES system will specify the charging time, operating temperature and superficial air mass flow rate, G, which in turn specifies C_a, h_v. This leaves the choice of rock, and rock size, d, which in turn determines the rock density, ρ_b, heat capacity, C_b, void fraction, ϵ, and rock conductivity, K_b. Clearly, denser rock samples with a small pebble diameter and relatively high heat capacities are the best choice. Rock conductivity is not a significant factor for high air mass flow rates.

4. CYCLING ANALYSIS [6]

The mathematical and numerical models developed to simulate the transfer of heat from air to rock by conduction, convection, radiation and heat loss to the surroundings are included in a companion paper [7].

Presented at the annual meeting of the American Section of the International Solar Energy Society in Denver, Colorado, August 28-31, 1978.

The performance of a packed bed will vary according to the method of charging and discharging. Three basic cycles were considered.

4.1 Daily Cycle

The bed is charged and discharged daily with a total of 44 hours of charging and 40 hours of discharging per week. Maximum bed storage capacity is 12 hours. The combined solar thermal - CAES cycle is essentially the same as the daily cycle, and is treated as such.

4.2 Weekly Cycle

The bed is charged over the weekend for some 45 hours to maximum storage capacity, and then charged and discharged (discharge period = 2X charge period) on a daily basis.

4.3 Solar Cycle

This represents the non-adiabatic case in which the heat stored in the bed is supplied by a separate source, for example solar, on a daily basis. Discharge occurs only on Monday through Friday. The solar cycle being considered requires two packed beds, alternately charging for 9 hours each day and alternately discharging for 12 hours on weekdays only.

Figure 2 shows a typical set of successive charge and discharge profiles for one week. Notice that at the end of each successive discharge, the amount of residual heat, or heat left behind in the bed, has increased. This means that on charging, the air exiting the bed will be hotter with each successive charge. Ultimately a steady-state condition will be reached in which a linear temperature distribution exists along the bed at the start of a charge, and by the end of the charge period the exiting gas is almost as hot as the gas inlet temperature. At the end of the discharge, the bed is returned to the linear temperature distribution described above. The problem is how to cool the hot air after it leaves the packed bed and passes down to the cavern, while retaining the heat in the packed bed. If the exit pipe from the bed to the cavern passes down through the center of the compensating pond shaft, it acts as a counterflow heat exchanger, and the surrounding water removes the heat, allowing the air to reach the cavern cool (see Figure 1). This design overcomes the irreversibility problem and improves the thermal storage efficiency.

5. CYCLE PERFORMANCE

Figure 3 shows the history of the turbine inlet temperature for each successive discharge over a period of one week for the weekly cycle. The daily cycle, having the shortest discharge period, records the smallest drop in turbine inlet temperature, followed respectively by the weekly and solar cycles in order of magnitude. The comparison was made over a period of one week, the only varying parameter being the charge/discharge periods. However the weekly cycle showed the slowest accumulation of residual heat and the highest TES efficiency, defined as

$$\eta = \frac{\text{MW hrs out}}{\text{MW hrs in}}$$

The design air flow rate (Kg/Hr) may have to be changed if the available off-peak energy or the required on-peak energy is different than the example given. Thus a charge of (400 MWe) x (5 hrs) might be available instead of (200 MWe) x (10 hrs). In such a case, the flow must be altered to absorb or supply the available energy. As a test, the weekly cycle was selected and the flow rate increased fourfold on charging as compared to its discharge. This increase in flow rate caused a small decrease in TES efficiency and overall performance, but the changes are quite tolerable.

6. CONDENSATION AND RE-EVAPORATION

Air drawn into a compressor and compressed to pressures around 30 bars will enter the packed bed at an elevated temperature - say 538°C (1000°F). Upon reaching the pebbles at the cool end of the bed, water vapor will start to condense out at 234°C (454°F). At 100% relative humidity, the air drawn into the compressor contains about 2% of water vapor, which would produce hundreds of tons of water during the charge period. In a single-stage system, that is, a CAES system with a single compressor-turbine set and one packed bed, the water will simply run down into the water compensated cavern. However, in a multi-stage system the water would best be fed to the compensating pond shaft and pumped out to the surface. The maximum possible loss in turbine output resulting from this would be 2%.

7. RADIATION AND HEAT LOSS

Heat that is lost to the surrounding rock, typically, accounts for less than one percent of the charge input (MW hrs) whatever cycle is used, with an insulation U-factor of

$$0.159 \quad \frac{W}{m^2 \ {}^\circ K} \qquad \left(0.028 \ \frac{Btu}{Hr.\ ft.^2 \ {}^\circ F}\right)$$

Above 538°C (1000°F) radiation, although small in comparison to convection, is far greater than axial conduction and cannot be ignored in the heat transfer process. The temperature gradient changes as the hot side of the bed radiates axially down towards the cooler bed sections. The drop in temperature at the hot end can vary between 1 and 5 percent, depending on the length of the charge/discharge cycle. The effect of this re-distribution of heat [illegible] the bed is a more constant temperature output during discharge which is advantageous.

8. CONCEPTUAL DESIGN

In Figure 4 the bed length required for hours of storage is shown. Costs are almost directly proportional to bed length, therefore, by increasing

11. ACKNOWLEDGEMENTS

This paper is an account of work sponsored by the Division of Energy Storage Systems, Office of Energy Technology, Department of Energy, under Contract No. EX-76A-01-2295.

12. NOMENCLATURE

C_a, C_b	specific heat of air, rocks at constant pressure (KJ/Kg).
D	bed diameter (m).
d	pebble diameter (m).
G	superficial air mass flow rate ($Kg/m^2 hr.$).
hv	volumetric heat transfer coefficient ($W/m^3 {}^\circ K$).
K_b	rock conductivity ($W/m^\circ C$).
L	bed length (m).
η	TES efficiency.
ρ_b	rock density (Kg/m^3).
T	temperature (°C).
τ	charge time (hr.).
U	heat transmission factor ($W/m^2 {}^\circ K$).

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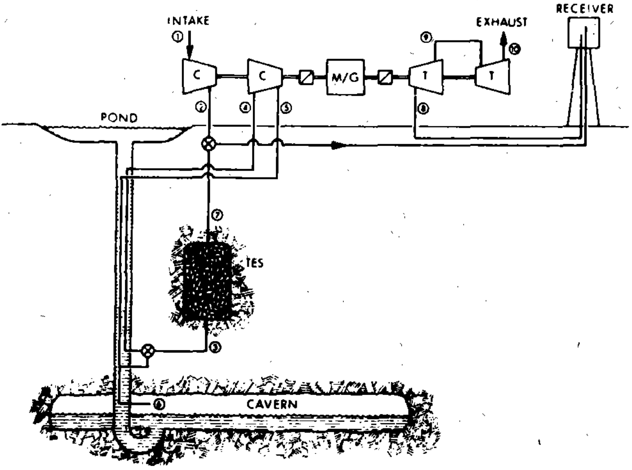

Fig. 1. Combined solar-thermal and compressed-air storage system.

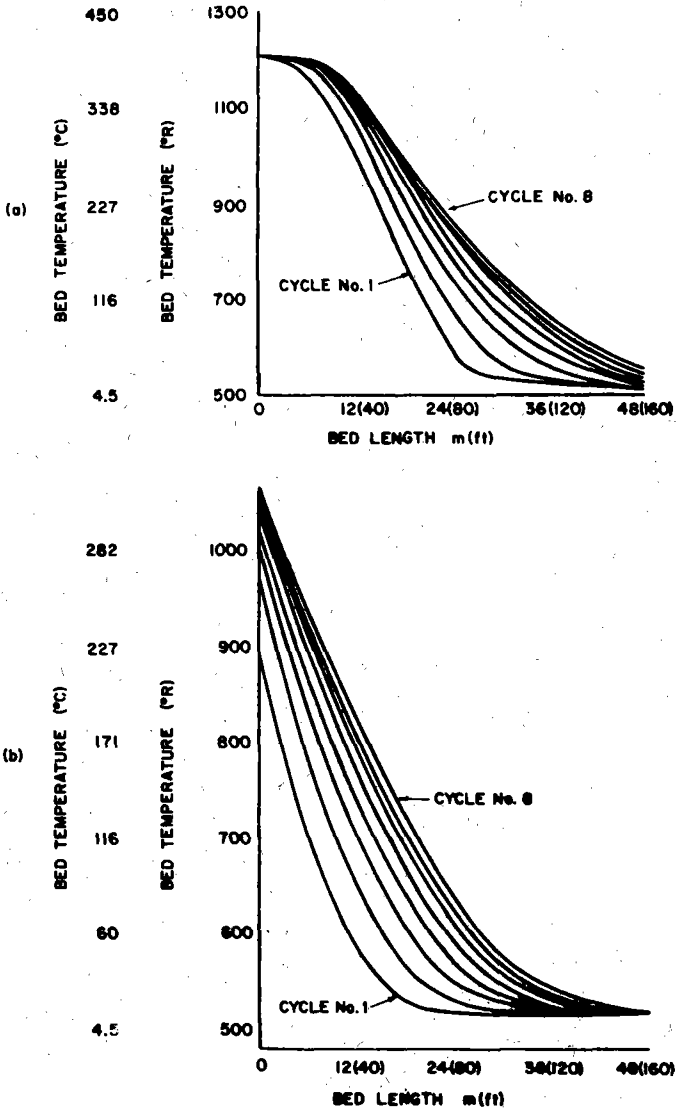

Fig. 2. Successive (a) charge and (b) discharge cycles for one week.

the number of hours of storage the cost effectiveness of the bed is improved. (More heat is stored per unit volume.) For the daily cycle, where the storage capacity is typically 10 hrs., the TES size is selected for the bed diameter (associated with one curve) that gives the minimum bed volume. In this case it is 36.5m (120 ft.). For the weekly cycle, where 45 hrs. of storage is required, a 55.5m (182 ft.) bed diameter gives the minimum bed volume.

To minimize dispersion of the thermocline, relatively low values of the superficial air mass flow rate should be maintained i.e.,

$$G = (732 - 2440) \frac{\text{Kg}}{\text{m}^2\text{hr.}} =$$

(150 - 500 $\text{lb/ft}^2\text{hr.}$). For a 200-MWe CAES system, the flow rate is very high, around 1.7×10^6 Kg/hr. (3.7×10^6 lb/hr.). This necessitates a bed length/bed diameter (L/D) ratio of 0.6 to 1.0. It was found that the larger the bed diameter for a given bed length, the higher the TES efficiency, although this effect was small.

Figure 5 shows the conceptual design. An insulation U-factor of

$$0.159 \frac{\text{W}}{\text{M}^2\,{}^\circ\text{K}}$$

is achieved by using 0.6m (2 ft.) layer of insulating firebrick surrounded by 0.3m (1 ft.) of diatomaceous earth on the sides and top. The bottom insulation layer is composed of 0.6m of insulating firebrick. The brick helps provide the pebbles with a firm support while the diatomaceous earth allows expansion due to heating.

The inlet piping is arranged in a hexagonal cluster of baffles spaced so as to ensure efficient heat transfer near the bed top. On the bed bottom the piping is curled over by using 45° elbow joints to prevent the pebbles from falling down the exit pipes into the cavern.

A 6.35-mm (1/4 inch) steel liner, backed by a high-strength, high-temperature cement prevents groundwater leakage into the cavity. The insulation provides for a liner temperature of less than 38°C (100°F) when the bed is operating at 816°C (1500°F). Thus the rock cavity is not subjected to any cycling stresses during charging or discharging. The rock bolts extend 9m (30 ft.) into the rock providing adequate cavity strength. The grout holes are sunken deep enough and sealed to prevent water seepage. Shorter rock bolts 0.9m (3 ft.) are used to hold the wire mesh and liner firmly. A pebble diameter of 12.7 mm (0.5 inch), along with the large bed diameter (182 ft.) gives a void fraction of 0.3 thereby ensuring that very little or no cold channeling takes place. Bed dimensions are as follows:

	200-MWe, 45-hr. storage	100-MWe, 12-hr. storage
Bed Length	30.5m (100 ft.)	20.0m (66 ft.)
Bed Diameter	55.5m (182 ft.)	34.0m (112 ft.)

9. COSTS

Table 2 shows the TES current cost breakdown for a 200-MWe system operating at 538°C (suitable for weekly cycle) and a combined solar-thermal/CAES 100-MWe system (daily cycle) operating at 432°C. This gives storage capital costs of $1.00/kWhr and $4.7/kWhr for the weekly and daily cycles, respectively.

	200-MWe, 45-hr. stor.	100-MWe, 12-hr. stor.
Excavating	3.828	1.013
Wire Mesh	0.255	0.104
Rock Bolts	0.864	0.35
Steel Liner	1.073	0.437
Welding	0.800	0.326
Crushed Rock	0.458	0.112
Shot Crete for Rock Support	0.28	0.114
High-Strength Concrete	0.76	0.31
Grouts	1.70	0.69
Bed Insulation	1.65	0.423
Piping & Insulation	0.79	0.307
TOTAL	12.458	4.186

TABLE 2. CAVITY COST BREAKDOWN ($\$ \times 10^6$)

10. CONCLUSIONS

Pebble beds appear to be suitable for thermal energy storage in an underground CAES system, whether the system is adiabatic or not. Residential heat accumulation ultimately demands an infinitely long bed, if the air is to be stored cool in the cavern. However the exit pipe to the cavern can act as a counterflow heat exchanger by passing down through the compensating pond shaft, where the air is cooled before reaching the cavern [3]. Thus the bed would oscillate about a steady-state condition going from an approximately half-charged to almost fully-charged condition during each cycle. The development of the temperature profile is such that the bed length or volume required does not increase linearly with charge, and the more heat that is stored, the cheaper the storage cost. The high air flow rate for the 200-MWe system demands a very large bed diameter to prevent dispersion of the thermocline. Although the energy delivered increases with a decreasing L/D ratio, the delivered energy cost is about the same over the range 0.5 to 1.0. A diameter much larger than 55.5m (182 ft.) is unacceptable because of the problems of inlet transfer and the possibility of a radial temperature distribution. The bulk of capital costs lie in the liner, piping and insulation, all of which are necessary whatever storage material is used. Choice of operating cycle depends upon the utility and what is available, and this will vary with location.

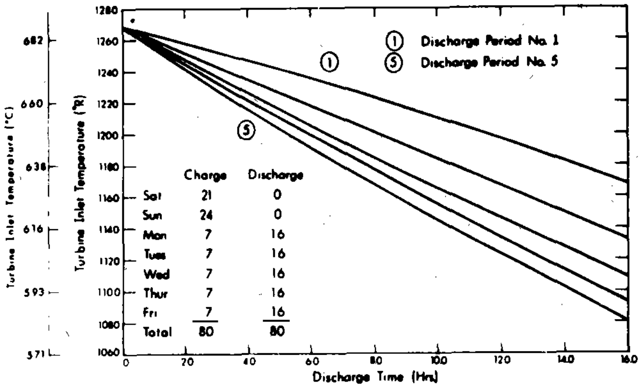

Fig. 3. Turbine inlet temperature (^{O}C) vs. time (hours) for successive discharge periods on a weekly cycle basis.

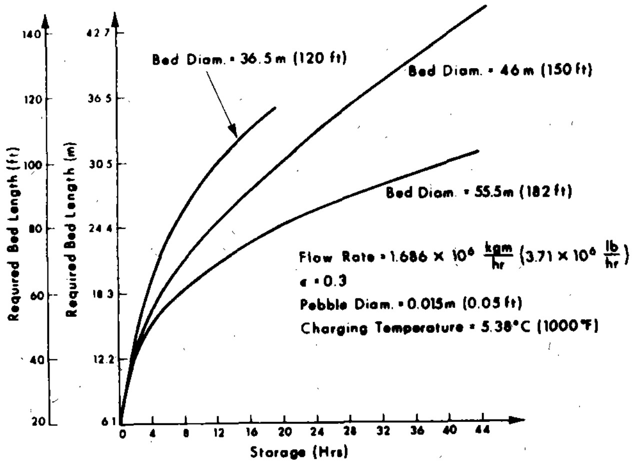

Fig. 4. Bed length required for storage hours during charging.

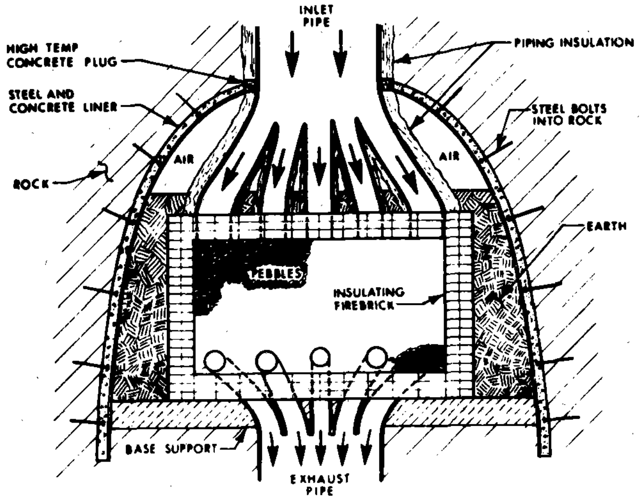

Fig. 5. Conceptual design of packed bed.

PROJECT SUMMARY

Project Title: Molten Salt Thermal Energy Storage Systems

Principal Investigator: T. D. Claar/L. G. Marianowski

Organization: Institute of Gas Technology
3424 South State Street
Chicago, IL 60616
Telephone: (312) 567-3672

Project Goals: (1) Define high-temperature TES concepts for water-Rankine electric generating plants and avanced solar-thermal power applications.

(2) Study cyclic and endurance behavior of candidate salts, primarily carbonates, in lab and engineering-scale modules.

(3) Investigate means of improving TES heat exchange performance.

Project Status: (1) Definition of a TES/water Rankine auxiliary peaking generation system has been completed.

(2) 8 kWhr TES unit containing $LiKCO_3$ has undergone 129 cycles over temperature range 505   50^{o}C (5650 hr) with very stable thermal performance.

(3) Design, fabrication and assembly of three lab-scale TES test stations are completed. Testing of candidate salt over 1000-1600^{o}F (538-871^{o}C) temperature range is in progress.

(4) Tests of porous aluminum heat conduction enhancement material for steam-superheating applications are nearing completion.

Contract Number: NAS3-20806

Contract Period: September, 1977 to December, 1978

Funding Level: $98,734.00

Funding Source: NASA/LeRC

INTRODUCTION

The major emphasis of this program is to investigate inorganic salts, primarily carbonates, as latent-heat storage materials for applications in the superheat region of conventional water-Rankine power plants and in advanced solar-thermal power concepts. (Viewgraph 1) Carbonate salt compositions are available over a wide range of melting points from 397°C (747°F) for the ternary (Li, Na, K)$_2$ CO$_3$ eutectic mixture to 858°C (1564°F) for Na$_2$CO$_3$. Evaluations of cyclic thermal performance and endurance of candidate salts are being conducted in lab- and engineering-scale TES modules with a passive heat-exchanger design. Post-test chemical and metallurgical analyses are being performed to assess salt stability and containment material limitations in these high-temperature TES applications.

PROJECT STATUS

A summary of the primary candidate carbonate salts is shown in Viewgraph 2. Salts are available over the temperature ranges applicable to both steam superheating and closed-cycle Brayton systems (air or helium) proposed for advanced solar-thermal plants. Melting points, heats of fusion, thermal conductivity, and costs (for technical grade carbonates) are included in this summary. Carbonate-based mixtures containing fluorides or chlorides are also being evaluated.

One of the TES concepts defined for the water-Rankine cycle (Viewgraph 3) consists of a multi-stage HX system employing salts with a broad range of melting points. The salt LiKCO$_3$ (505°C m.p.) is a candidate for a steam-superheating stage and has been studied in an 8 kW-hr$_{th}$ engineering-scale module built under a previous ERDA TES contract No. E(11-1)-2888 (DOE EY-76-C-02-2888). Engineering-scale Unit 2, containing ~150 lb. of LiKCO$_3$, was thermal cycled 129 times over a period of 5650 accumulated hours at operating temperature (505 ± 50°C) with essentially no change in thermal performance (Viewgraph 4). The appearance of the upper surface of solidified LiKCO$_3$ salt upon removal of the top cover at termination is shown in Viewgraph 5. The carbonate salt was very clean and free of any discoloration attributable to chemical interactions with the Type 316 stainless steel heat exchanger tube and containment vessel. Differential scanning calorimetry revealed only a very minor change in melting point — from 505° to 502.5°C — as a result of this long term exposure.

Experimental screening of candidate salts for storage-coupled solar-thermal applications is being performed lab-scale modules (5 in. high x 3 in. diameter with 1/2 in. O.D. central HX tube. The materials of construction are Types 304 and 316 stainless steel. These units are equipped with thermocouples to monitor salt temperatures at several radial distances from the HX during discharging with high-velocity air. Discharge heat fluxes are estimated from measured outlet air temperatures. A typical discharge curve for the salt K_2CO_3 - 49.4 wt % Na_2CO_3 is given in Viewgraph 6. Additional work is needed to further define and solve long-term endurance questions related to salt stability and compatibility with construction materials, as well as efficient and cost-effective HX design. Evaluation of low-cost, technical-grade salts is also required.

Incorporation of a continuous network of high thermal conductivity material in the salt phase has been explored as a means of enhancing heat transport through the solidifying salt zone. Heat-flux enhancement by aluminum in the form of a low-density porous reticulated matrix (Viewgraph 7) has been demonstrated in a lab-scale module containing the ternary eutectic 43.5 mole % Li_2CO_3, 31.5 mole % Na_2CO_3- 25.0 mole % K_2CO_3 (397°C m.p.). This aluminum material has shown excellent chemical compatibility in the salt at 450°C after 4,000 hours exposure. However, other metallic and ceramic enhancement materials have to be considered for the very high temperature solar-thermal systems, which operate above the melting point of aluminum (660°C). The dual requirements of high conductivity and long-term chemical stability in the candidate molten salts greatly limit materials selection. More detailed evaluations of enhancement materials selection, geometry, salt vs. enhancement thermal conductivity and HX design trade-offs are required to define cost/benefit factors for solar-thermal TES applications.

The next stage of TES systems development for solar-thermal applications will involve design and testing of engineering-scale modules employing (1) the most attractive (technical-grade) salts, (2) enhancement material/geometry concepts, and (3) construction materials showing best compatibility with candidate salts.

MOLTEN SALT THERMAL ENERGY STORAGE SYSTEMS

INSTITUTE OF GAS TECHNOLOGY
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PROJECT OBJECTIVES

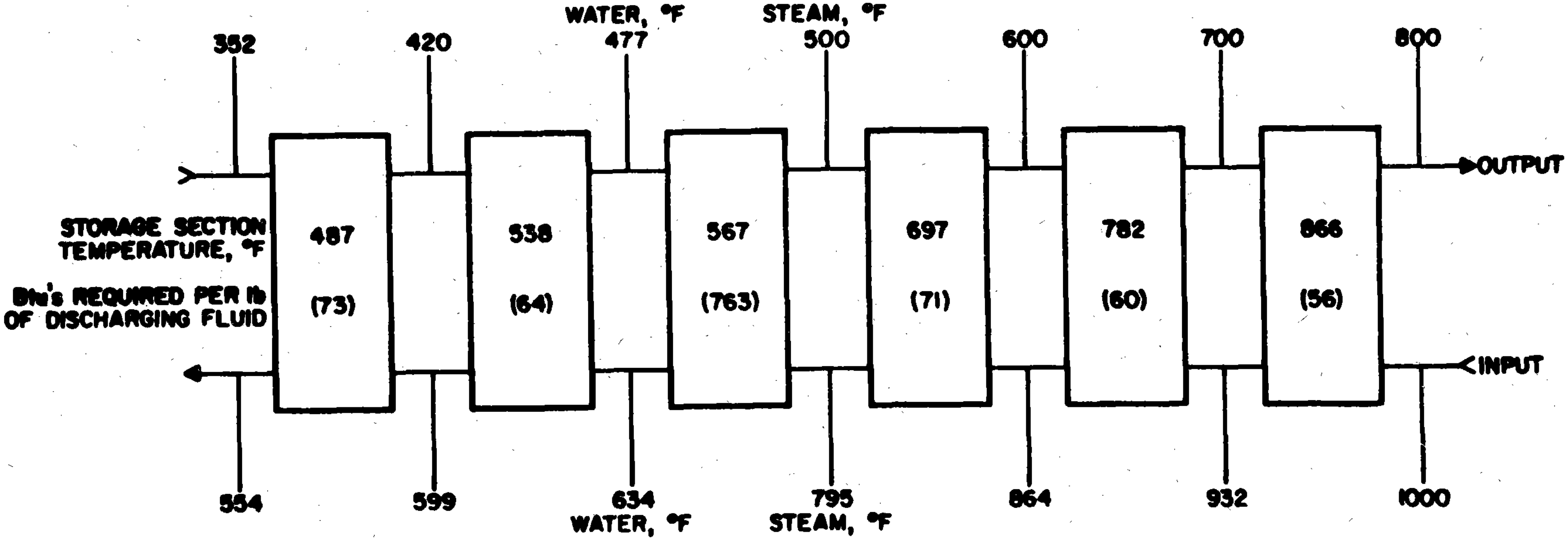
- DEFINE HIGH-TEMPERATURE TES CONCEPTS FOR WATER-RANKINE ELECTRIC GENERATING PLANTS AND ADVANCED SOLAR-THERMAL POWER APPLICATIONS.
- STUDY CYCLIC AND ENDURANCE BEHAVIOR OF CANDIDATE SALTS, PRIMARILY CARBONATES, IN LAB- AND ENGINEERING-SCALE MODULES.
- INVESTIGATE MEANS OF IMPROVING TES HEAT EXCHANGE PERFORMANCE.

VIEWGRAPH 2

CARBONATE-CONTAINING SALTS HAVING MELTING POINTS IN THE RANGE 750-1600°F

No.	Salt System	Composition (wt %)	Composition (mole %)	Melting Point (°C)	Melting Point (°F)	ΔH_f (Btu/lb)	Thermal Conductivity (Btu/hr-ft-°F) k(1)	Salt Cost ($/lb)
1	Li_2CO_3-K_2CO_3-Na_2CO_3	32-35-33	43-26-31	397	747	151	1.17	0.38
2	K_2CO_3-$MgCO_3$	68-32	56-44	460	860			0.16
3	Li_2CO_3-K_2CO_3	47-53	62-38	488	910	168	1.15	0.54
4	Li_2CO_3-Na_2CO_3	44-56	53-47	496	925	179	1.21	0.43
5	Li_2CO_3-K_2CO_3	35-65	50-50	505	941	148	1.09	0.45
6	Li_2CO_3-Na_2CO_3-K_2CO_3	20-60-20	28-58-15	550	1022	138	1.05	0.25
7	Li_2CO_3-Na_2CO_3-K_2CO_3	22-16-62	33-17-50	550	1022	129	1.13	0.33
8	$CaCO_3$-Li_2CO_3	44.3-55.7	37-63	662	1224			0.53
9	$BaCO_3$-Na_2CO_3	52.2-47.8	37-63	686	1267			0.08
10	K_2CO_3-Na_2CO_3	44.9-55.1	39-62	695	1283	102		0.10
11	K_2CO_3-Na_2CO_3	50.6-49.4	44-56	710	1310	100	1.00	0.11
12	Li_2CO_3	100	100	726	1333	261	1.13	0.93
13	Na_2CO_3	100	100	858	1564	113	1.06	0.03
14	K_2CO_3	100	100	891	1636	86		0.19

VIEWGRAPH 3



INPUT 1000 °F 2400-psia STEAM

OUTPUT 800 °F 550-psia STEAM

$\frac{\text{CHARGING MASS}}{\text{DISCHARGING MASS}} = 1.2$

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CONCEPTUAL TES UNIT: 800°F CASE

PERFORMANCE OF ENGINEERING UNIT NO. 2

SALT: 50 MOLE % Li_2CO_3 – 50 MOLE % K_2CO_3

MASS: 130 LB.

MELT PT. 505°C (941°F)

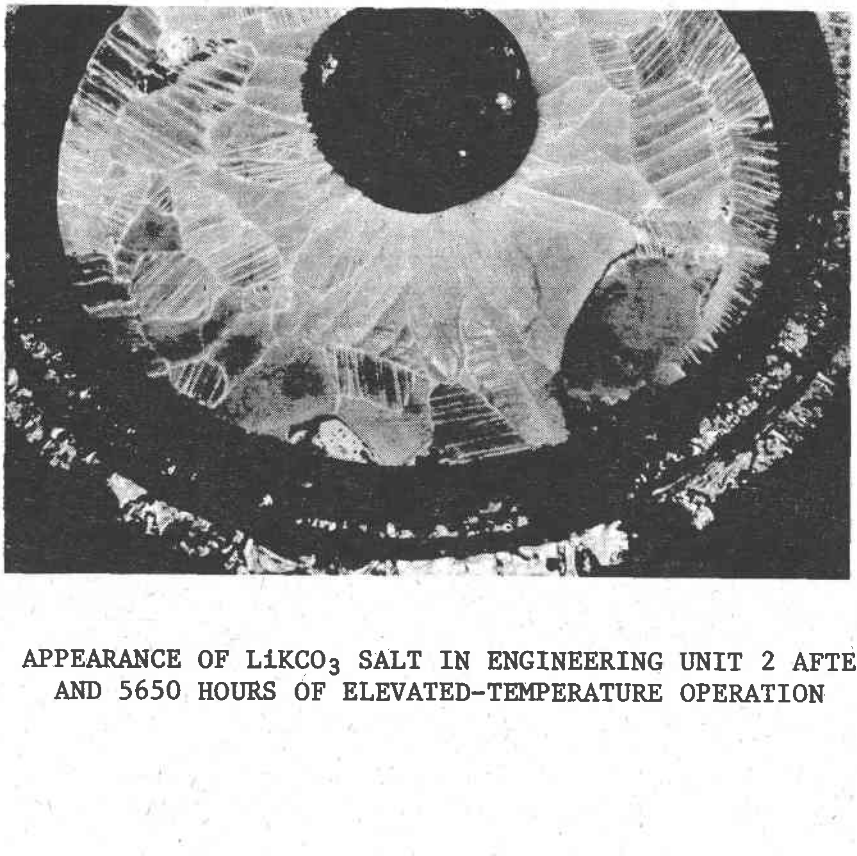
HEAT OF FUSION: 148 BTU/LB

DISCHARGE: 535°C TO 480°C

CYCLE NO.	OPERATING TIME, HR	DISCHARGE TIME, MIN	AVERAGE HEAT FLUX, $BTU/HR\text{-}FT^2$
2-15	500	315	4161
2-65	2900	330	3925
2-81	3550	330	3353
2-102	4400	330	3715
2-127	5360	345	3753

SYSTEM TERMINATED AFTER 5650 HOURS OF HIGH-TEMPERATURE EXPOSURE.

VIEWGRAPH 5



APPEARANCE OF $LiKCO_3$ SALT IN ENGINEERING UNIT 2 AFTER 129 CYCLES AND 5650 HOURS OF ELEVATED-TEMPERATURE OPERATION

VIEWGRAPH 6

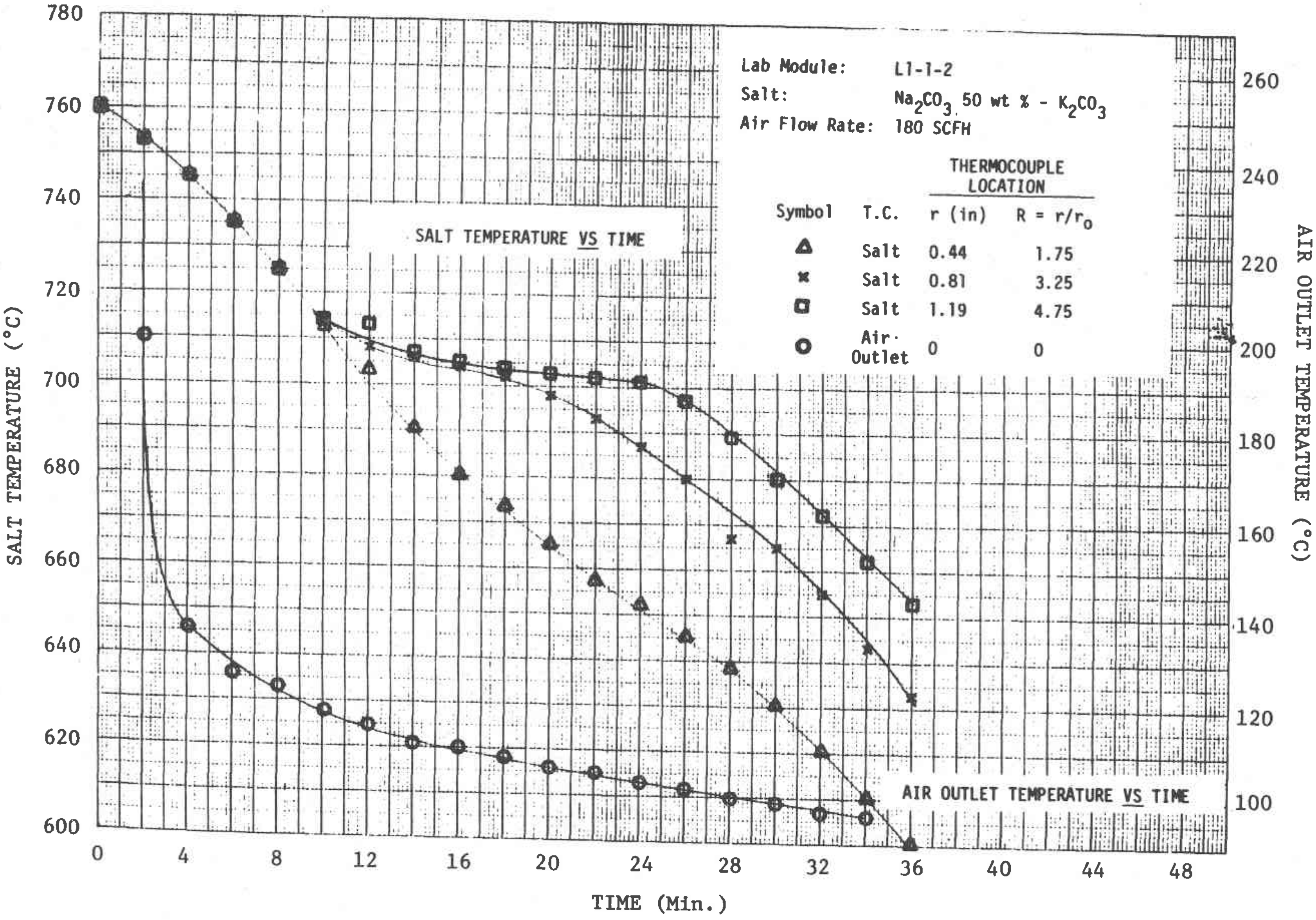
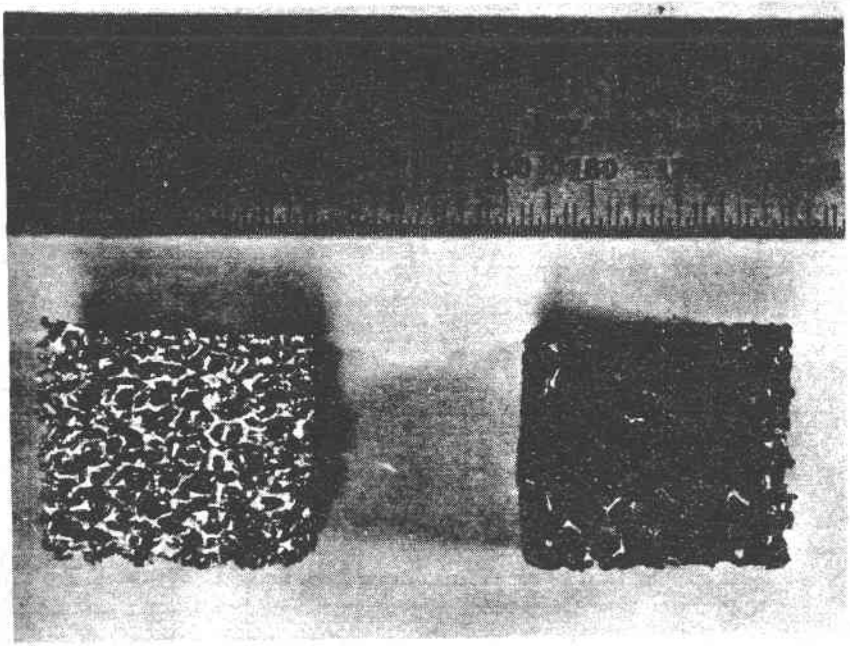


Figure 1. DISCHARGE PERFORMANCE OF 50.6 wt % K_2CO_3-49.4 wt % Na_2CO_3 at 180 ft^3/hr AIR FLOW RATE

VIEWGRAPH 7



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PHOTOGRAPH OF DUOCEL ALUMINUM MATERIAL AS-RECEIVED (Left) AND AFTER 528 HOURS EXPOSURE TO MOLTEN $Li_2CO_3/Na_2CO_3/K_2CO_3$ AT 450°C (Right)

PROJECT SUMMARY

Project Title: Heat Storage in Alloy Transformations

Principal Investigator: C. Ernest Birchenall

Organization: University of Delaware
Department of Chemical Engineering
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Telephone: (302) 738-2543

Project Goals: (1) Determine the density with which energy can be stored in solid-liquid phase changes in relatively inexpensive alloys, especially in eutectic transformations.

(2) Measure the heat capacities and coefficients of thermal expansion near the transformation temperature and the volume change during transformation.

(3) Find materials that can contain the best storage systems for long operating periods.

Project Status: (1) Several binary and ternary alloys of the less expensive elements with known eutectic transformations have been shown to have heats of transformation large enough to approach or exceed the best of those previously reported for other materials near their transformation temperatures.

(2) Calorimetric measurements continue on known eutectics and congruently-melting intermediate phases.

(3) Previously unknown eutectics that may have large heats of transformation are being sought. One new ternary eutectic has been identified.

(4) A new method for determining volume change during solid to liquid transformation has been instrumented and testing. The precision and limitations of the method have been explored using pure aluminum. Eutectic transformations in the Al-Cu and Al-Si systems have been measured successfully.

(5) Metallic container materials are being studied for chemical compatibility with the best eutectic alloys as alternatives to graphite or ceramics.

Contract Number: NSG 3184

Contract Period: July, 1978 to June, 1979

Funding Level: $91,027.00

Funding Source: NASA/LeRC

Heat Storage in Alloy Transformations

Heat storage in alloy transformations should be especially useful for those applications in which rapid heat transfer into or out of storage is necessary. Eutectics in the range of 450 to 580°C and also at about 950°C appear to be advantageous on the basis of energy storage density alone. Work in progress seems likely to supply eutectics that transform between 650 and 900°C. Extension to temperatures above 950°C is more likely to entail containment problems than difficulties in finding good eutectic alloys. Extension below 400°C with cheap metals may be difficult to achieve.

With the present limitations the most promising early candidate for the application of eutectic alloys is fast primary storage for a solar concentrator. In fact, an Omnium G solar power generator, capable of producing 7.5 kW_e plus 30,000 Btu of heat per hour of sunlight, uses aluminum in its storage-buffer. The stainless steel heat exchanger located at the focal volume of a parabolic reflector absorbs sunlight and generates steam to operate a reciprocating engine that drives the electrical generator. A modification of this type of system, supplied by David Namkoong, of NASA-Lewis, is shown in Fig. 1. For a larger system primary storage might be located behind the big reflector with a second small reflector relaying light to storage from the focal volume. However, mirror parameters may limit system size independent of the placement of the storage system.

Storage for large solar power sources to match intermittent energy supply to round-the-clock demand or buffer-storage at fossil-fueled power plants to match constant heat generation to varying power demand appear to be possible large-scale applications. Intermediate scale storage in industrial installations that have large consumption of heat would permit energy to be taken during off-peak hours for use during peak-load periods where differential rates encourage that mode of operation. In some instances, where the transformation temperature of the alloy matches the process temperature, the storage system also could serve as a thermostatic control. Proper distribution of such installations throughout a power system might reduce greatly the peak to off-peak changes.

In the work reported at last year's meeting only alloys containing Mg, Si, Al, Cu and Zn had been studied. Adhering to the criterion of low cost and ready availability, we plan to add Ca and P to this list, although only one Ca alloy has been made so far. Last year's report also identified the following contributions to energy storage density for a eutectic transformation, in approximate order of decreasing importance:

1. heat of fusion of the elements,
2. heat of formation of any participating intermetallic phases,
3. difference in entropies of mixing of liquid and the solid phases,
4. difference in heats of solution in liquid and in the solids.

Anticipated heats of transformation have been calculated as a rough guide to which eutectics should be measured carefully.

Alan Riechman had measured heats of transformation of five binary and two ternary alloys for which eutectic temperatures and compositions were published and for which our theory predicted good storage densities. These results are shown in the figure. The most disappointing is Mg-0.29Zn, but zinc vaporization may have lowered that result, just as magnesium vaporization may have depressed the Si-0.471Mg result at the highest temperature. Diana Farkas has remeasured the heat of transformation of the Mg-Zn eutectic and revised the calculations based on new data for the intermediate alloy phase. The large difference in DSC results between the heating and cooling cycles may indicate that the first solid phase to form is a metastable intermediate. These values and those for two new ternary eutectics are included in Table 1. A previously unreported ternary eutectic, 56 w% Cu-27Si-balance Mg, has been found that transforms at about 750°C, appropriate for use in the solar-focussing power system. Numerous other ternary liquid compositions were shown to freeze by non-eutectic paths. All of the alloys investigated, except those high in calcium, have shown no tendency to attack graphite. Calcium may be a problem only at higher temperatures.

Fig. 2 compares some pure metals and non-metallic eutectics with metal eutectics. Keep in mind that the non-metallic salt mixtures have heat conductivities from one to two orders of magnitude poorer than alloys as a general rule. Also the lithium compounds are relatively expensive. Their advantage in storage capacity is not so great on a volume basis as it appears to be on the mass basis used here.

James McGraw[*] used the Advanced TES System Sizing Computer Program developed by Boeing Engineering and Construction[†] to compare thermal storage using Al-Cu-Mg and Al-Si alloy eutectics with the best salt eutectics with nearly the same transformation temperatures and with alternate modes of matching generation to consumption in an industrial system of 50 MW capacity, where 10 MW is to be stored from each daily 8 hr of off-shift to use during the 16 hrs of maximum work. The Al-Cu-Mg system appeared to have an advantage over $NaCl-MgCl_2$ at 800 K (1000 F) while Al-Si may have been slightly less favorable than 7 CaF_2/54KF/39NaF at 1090 K (1500 F). The Al-Cu-Mg system had a higher projected capital cost than the gas turbine peaking unit to meet the same demand, but the pay-back time because of lower operating cost for the TES system was only one-half year.

Volume change must play an important role in heat exchanger design for a phase-change storage system. Our new technique to measure this property, first demonstrated by Dr. Andrew Harrison, has been refined by Silvia Balart. Excellent reproducibility for melting aluminum has been demonstrated, and Al-Cu and Al-Si eutectics have been measured. These results are given in the appended tables. There remains a difficulty with

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[*] Senior paper in Mechanical and Aerospace Engineering under Prof. J. Moszynski, May, 1978.

[†] ERDA Contract EY-76-C-03-1300, July - Dec., 1976.

the apparent coefficient of thermal expansion near room temperature which is not completely resolved. However, that affects only the ease of measurement and not the critical results in the range from just below to just above the transformation temperature. The table shows that the volume changes are moderate, on the order of 5%, whereas some salt eutectics have volume changes exceeding 20%. Our X-ray absorption method should be applicable to any sort of material that can be prepared in non-porous condition and has sufficient ductility to flow when heated inside the absorption cell.

Future Plans

Our search continues for more complex alloys with different transformation temperatures and hopefully improved energy storage density. We shall try to learn why the thermal expansion coefficients at low temperature are erratic, but also continue to measure precisely the volume changes during transformation. In addition Nikil Nagaswami is beginning a program to seek solid alloys that can be fabricated by conventional methods and still serve as inert containers for the eutectic systems that offer the best heat storage in each temperature range. It is expected that satisfactory service will depend upon the ability of the eutectic and the container to form a very slowly-growing reaction layer on the container surface. Metallographic and SEM studies on small samples will be used for the initial screening. Once the containment problem is clarified we shall devote more effort to identifying appropriate applications and to small-scale demonstrations of the alloy storage media.

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	180 + 30	1.04s 1.151
*Mg-0.14Zn-0.14Ca	673	405		--
*Al-0.35Mg-0.06Zn	720	406	310	1.73s
Al-0.375Mg	724	376	310	1.621
*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-0.30Cu-0.07Si	844	561	423	--
Al-0.12Si	852	571	515	1.49s 1.271
*$MgZn_2$	961	259	220	--
†Zn-0.42Cu-0.15Mg	978	313		
†Cu-0.157P	987			
†Cu-0.42Mg	995	235		
*Si-0.35Cu-0.28Mg	1023	892		
†Cu-0.49Si	1076	308		
Si-0.471Mg	1219	1212	805	

*New results

†To be measured soon

Table 2. Density Changes for Al and Two Al Eutectic Alloys

T°C	Density in kg/m^3		$\Delta V/V_S$	
	Measured	Tabulated	Measured	Tabulated
	Pure Al			
20(s)	2680	2699	0.0745	0.0769 0.0759
660(s)	2560	2549		
660(l)	2370	2368-2410		
760(l)	2355	2338		
	Al - 17.5 a/o Cu			
20(s)	3506	3570	0.051	0.050
548(s)	3424	3400		
548(l)	3258	3290		
748(l)	3186	3200		
	Al - 12 a/o Si			
20(s)	2626	2639	0.048	
579(s)	2553			
579(l)	2445			
779(l)	2382			

Fig. 1. Power conversion system with solar input and alloy heat storage.

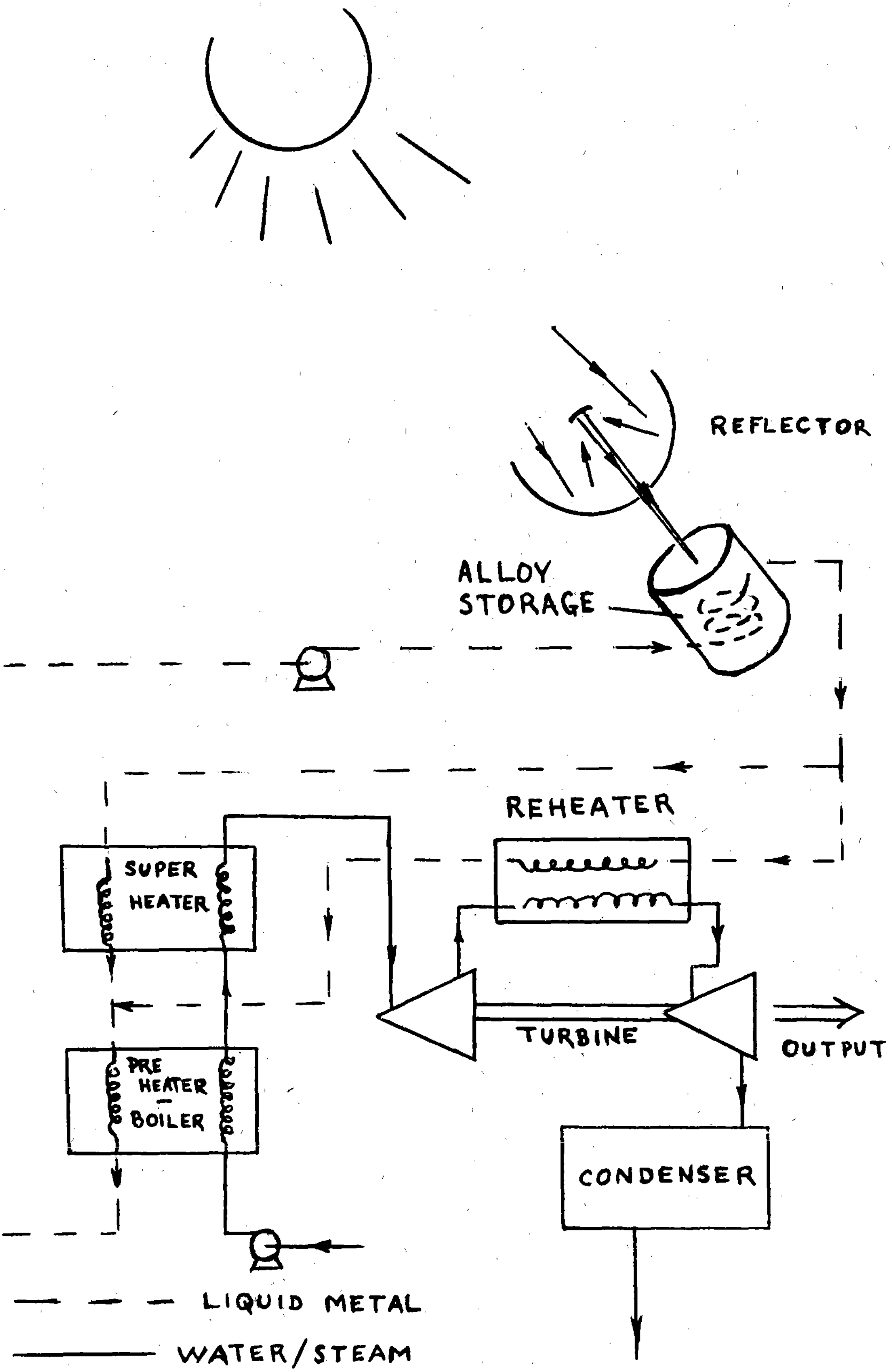
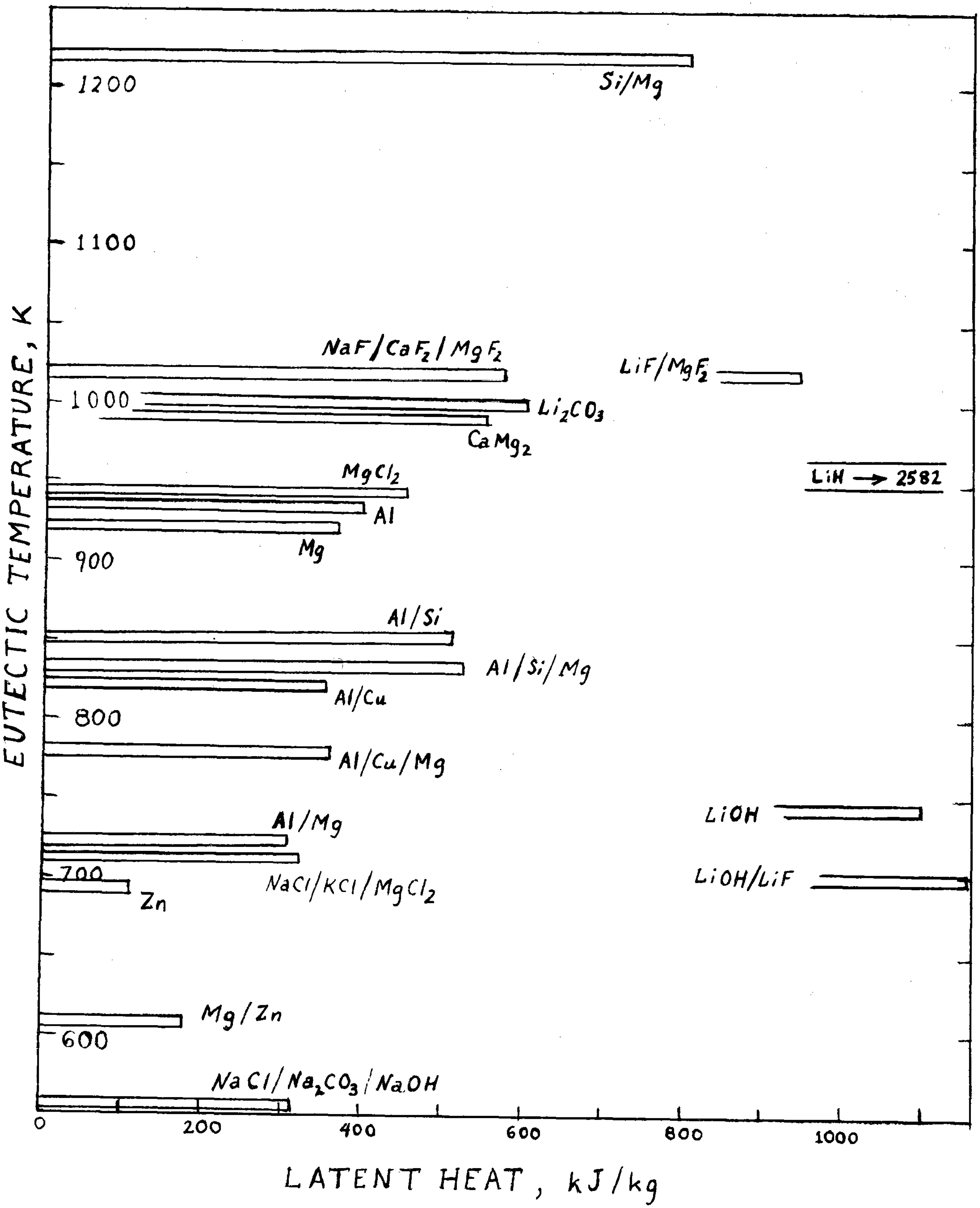


Fig. 2. Comparison of maximum heat storage density per unit mass for some eutectics and congruently melting phases.



PROJECT SUMMARY

Project Title: Heat Transfer in Thermal Energy Storage Systems Based on Phase Change

Principal Investigator: N. Shamsundar

Organization: University of Houston
Department of Mechanical Engineering
4800 Calhoun
Houston, TX 77004
Telephone: (713) 749-2683

Project Goals: Develop design methods, design graphs and obtain thermal performance data on latent heat storage devices.

Project Status: This project is divided into five phases as follows:

(1) Obtain design data for shell and tube heat heat exchangers.

(2) Develop simplified design formulae.

(3) Compare predicted thermal performance with experimental data.

(4) Develop methods for treating time-dependent loads.

(5) Study new prediction models.

The project status on these is as follows:

(1) Complete data obtained.

(2) Formulae developed for several cases.

(3) Experimental data scanty. Experiments being conducted.

(4) Successful method developed.

(5) Model to account for liquid superheat developed and verified.

Contact Number: EG-77-C-04-3974 (Task V)

Contract Period: May, 1977 to August, 1979

Funding Level: $110,000.00

Funding Source: Department of Energy, Division of Central Solar Technology

I. Purpose

The purpose of this project is to study the heat transfer in thermal energy systems involving the use of a phase change material for energy storage. Accurate design data, methods for predicting the thermal performance of heat exchangers incorporating a PCM, etc. are lacking, and will be made available as a result of the work of this project.

There are some physical aspects of the heat transfer in these storage devices which have not been modelled so far and their influences need to be considered. These aspects are being studied under this project. Analytical calculation schemes are developed and experiments undertaken where necessary to support the predictions of theory.

Even where computational techniques are available to assess thermal performance, using these techniques is often very costly. Therefore, simple design formulae that are easy to use and reasonably accurate were developed.

II. Background Information

Thermal storage in the form of latent heat has several attractive features. Large amounts of energy can be stored in small volumes, and careful design will enable the fluctuations in temperature between storage and recovery periods to be kept small. It is necessary to not only model the various physical aspects of the phase change accurately, but to have at hand design formulae and thermal performance charts. Information of this type has been rather scanty. A systematic study of important aspects such as time dependent heat loads, geometrical arrangement, optimum tube sizing, etc. has been lacking.

III. Project Description

IV. Results

1. Application of Available Computational Techniques to Practical Heat Exchanger Designs

Shell and tube heat exchangers of many types have been studied extensively, and complete results on the thermal performance are available. Graphs of heat flux against time, frozen fraction against time, etc. are available for various tube arrangements and spacings. Effectiveness-NTU (Number of Transfer Units) charts have been developed to aid designing heat storage units of this type, taking into account three-dimensional effects and time dependent loads.

A general purpose, multidimensional computer program was developed in colloboration with the Mathematics and Statistics Department of the Oak Ridge National Laboratory. The program is capable of calculating the heat transfer by conduction in an arbitrarily shaped lump of material that may comprise several different substances, with several heating/cooling possibilities that can be time dependent. The program is functional and has been used to study some novel heat exchanger geometries.

2. Development of Methods for Treating Time Dependent Loads

In a heat storage unit with a heat transfer fluid exchanging heat with a PCM, the flow rate and the inlet temperature are functions of time that are regulated to satisfy a specified load demand.

Figures 2 and 3 display the thermal performance results for the shell and tube heat exchanger shown in Figure 1. The flow rate of the heat transfer fluid is different in the two cases shown in Figs. 2 and 3, such that the convective heat transfer coefficients differ by a factor of fifty. That the variation of heat flux with time ($\hat{Q}$ versus τ) is markedly different for the two cases is evident upon inspection of the two figures. In practice, the flow rate (which corresponds to the Biot number Bi in the figures) is not a constant as assumed in obtaining the figures, but is regulated as said above. Calculation of the thermal response of the heat storage unit to the many conceivable load curves that may be imposed on it involves a very arduous computational task.

To make the solution of this problem tractable, use is made of a similarity rule discovered by us recently. This rule enables a single graph to be used for representing the thermal response for a very wide range of flow rates (Biot numbers). Figure 4 shows the effectiveness of the similarity rule in bringing together the data for Biot numbers from 0.1 to 100 -- a very wide range indeed.

Based on the similarity rule, effectiveness - NTU charts have been developed. In these, the frozen fraction of the PCM is used as a parameter in order to make the charts applicable even when the load is time dependent. For any specified load variation, one only needs to evaluate an integral related to this variation before using the effectiveness-NTU charts.

3. Simplified Design Formulae

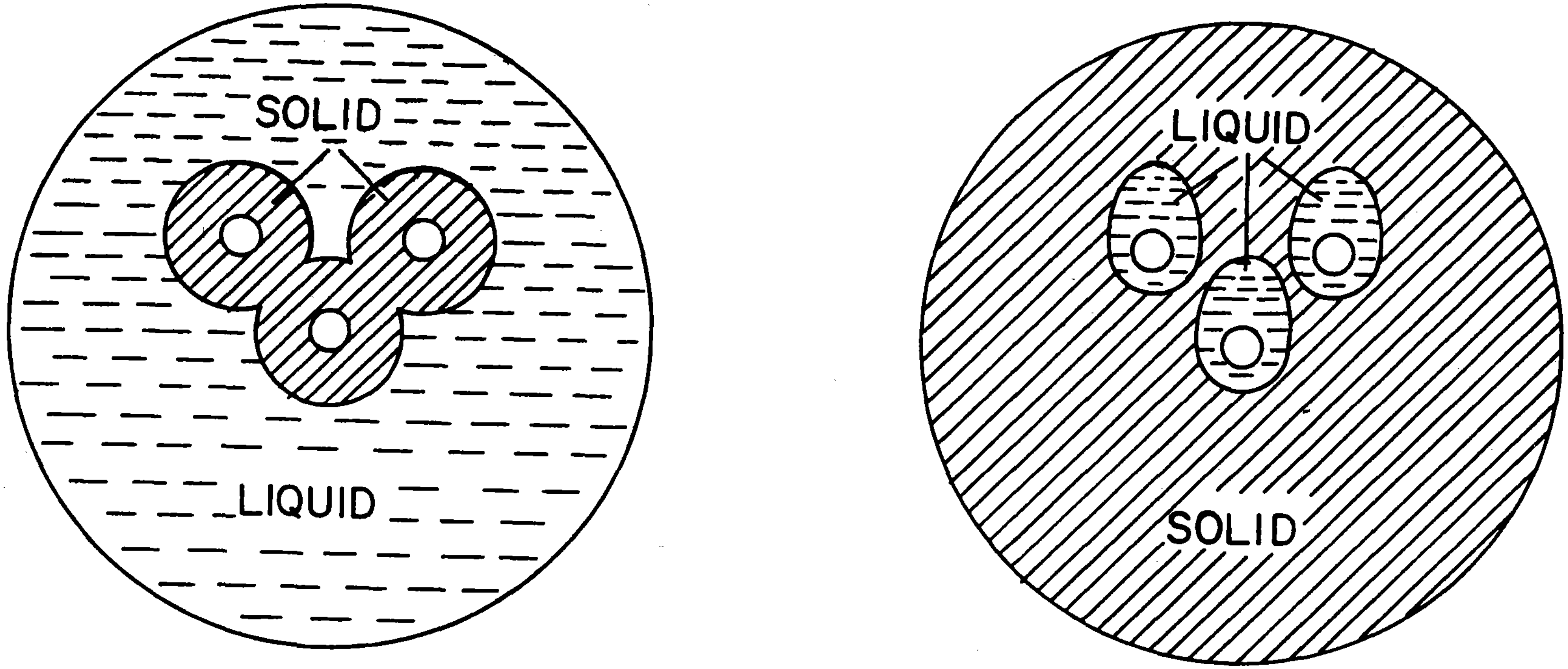
Such equations have developed for several one-dimensional geometries and a few two-dimensional situations. The formulae are suitable for design calculations with only a hand calculator.

4. Comparison With Experimental Results

Two experiments are under way. In one, the unsteady boiling of water outside PCM containing metal tubes is studied to measure heat transfer rates for comparison with analytical predictions. In the second experiment, the effect of circumferentially nonuniform cooling on the surface of a PCM container upon the location of the shrinkage cavity is investigated. For this purpose, PCM is frozen in a special mold with a rectangular cross-section. The sides of the mold are provided with coolant passages through which metered amounts of hot water under pressure can be passed. The flow in each of the four passages is separately controlled. The mold can be taken apart and the cast PCM is then sectioned for measuring the size and location of the cavity.

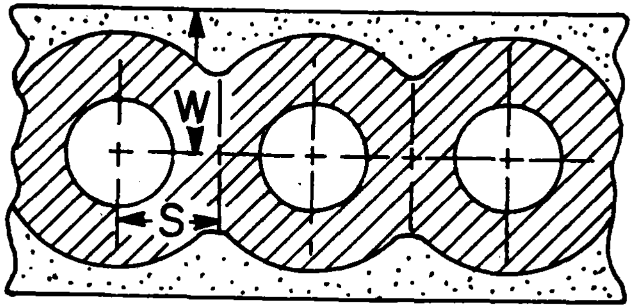
5. Model to Account for Liquid Superheat

When superheated liquid PCM is cooled, part of the superheat is dissipated before the latent heat that is stored in it becomes available. The initial cooling is complicated by natural convection in the liquid, but is rather short in duration. We have developed a simple way of accounting for the initial superheat that is superior to the now used Nessellmann approximation. In the latter, the actual latent heat of the PCM is replaced by a fictitious value that is equal to the sum of the latent heat and the superheat. Our method uses the actual latent heat, but time is counted from the instant that solidification first occurs. In both these models, the objective is to perform a phase change calculation without considering superheat. The dashed lines in Figure 3 validate our model.



(a) RECOVERY

(b) STORAGE



(c) THERMOCRETE

Figure 1. Schematic Diagrams of Shell and Tube Heat Exchanger for Latent Heat Storage and Thermocrete Brick Wall

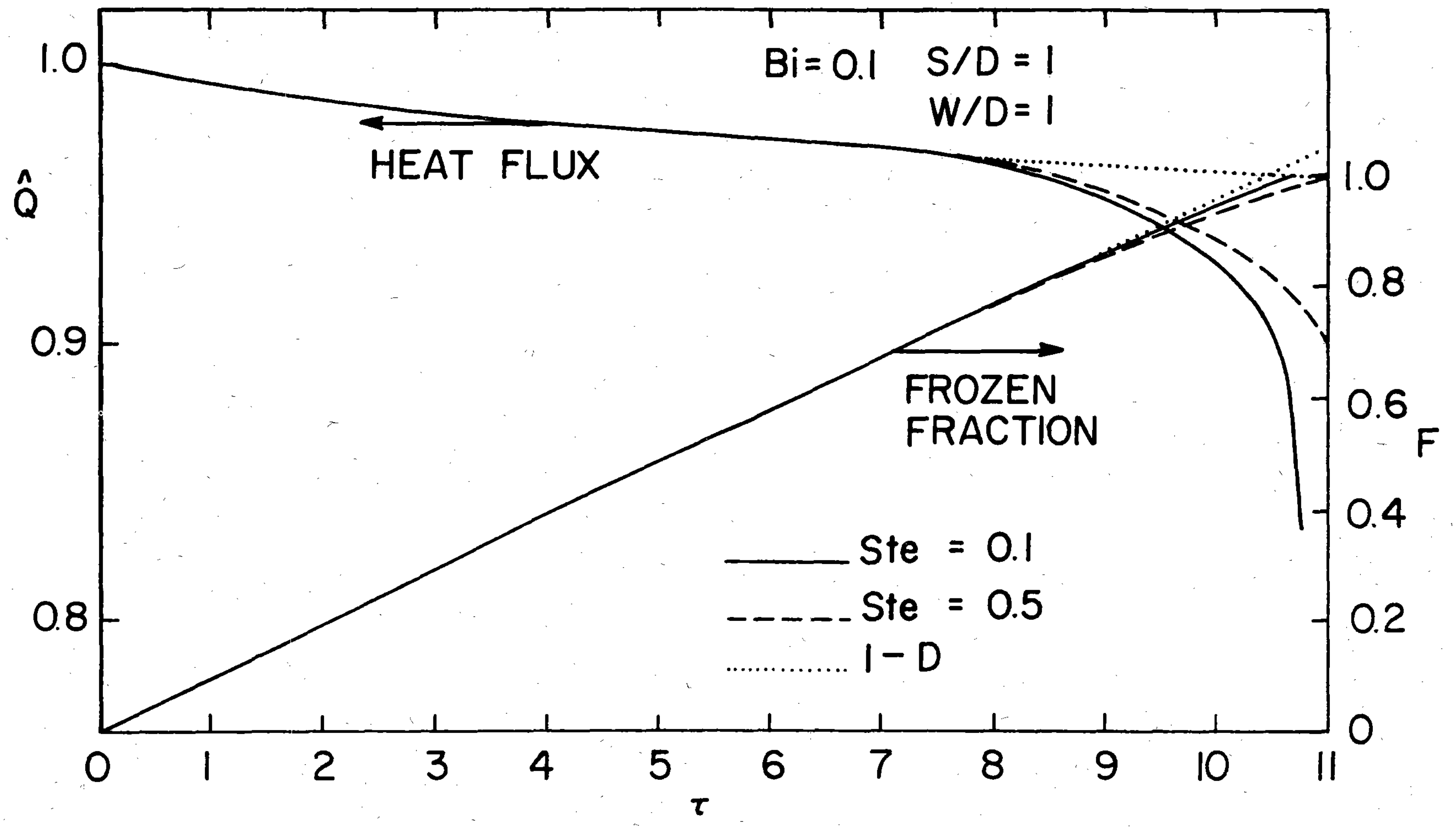


Figure 2. Timewise Variation of Heat Flux and Frozen Fraction, and Influence of Stefan Number for In-line Arrangement, Bi = 0.1

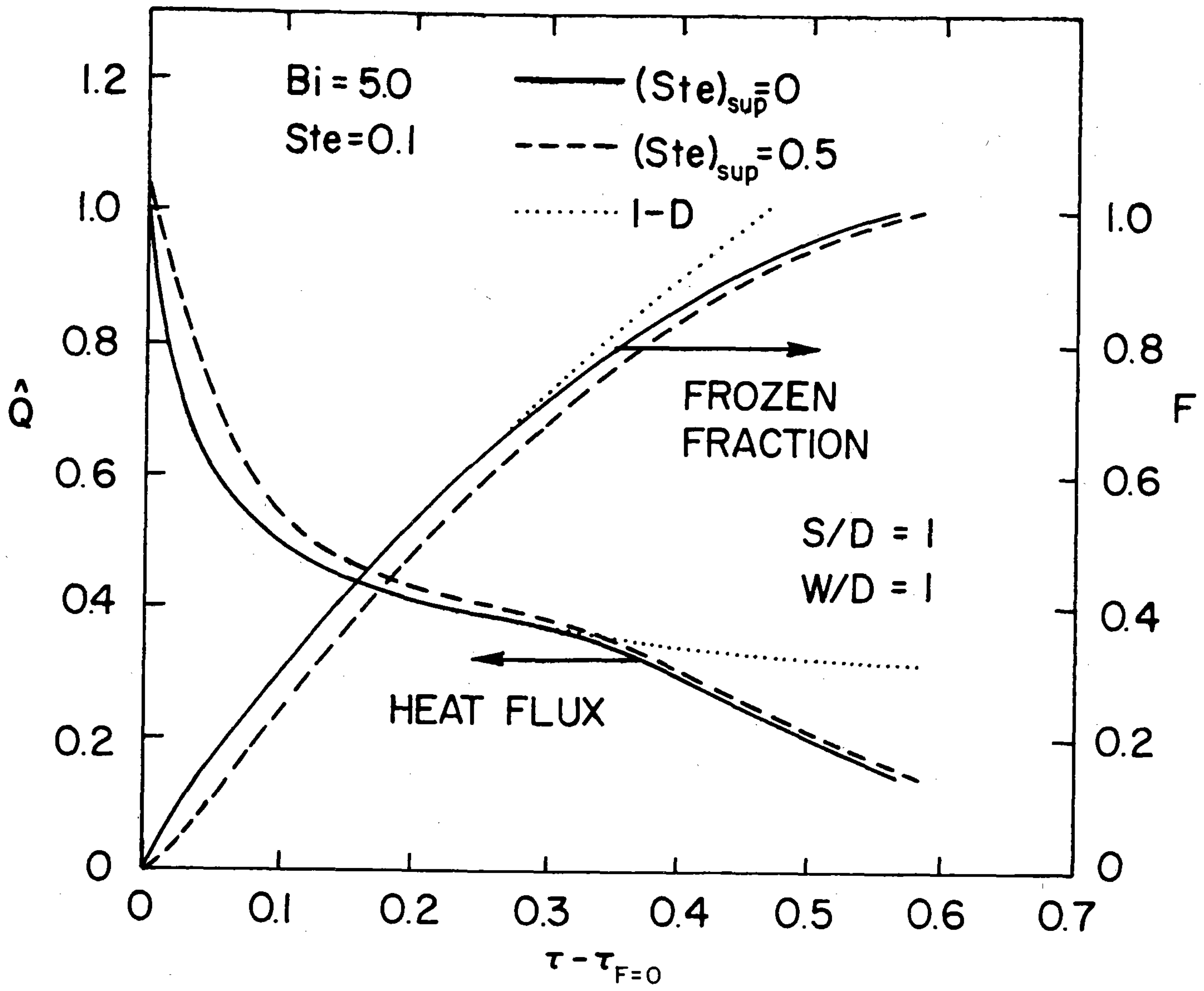


Figure 3. Timewise Variation of Heat Flux and Frozen Fraction, and Influence of Superheat for In-line Arrangement, Bi = 5.

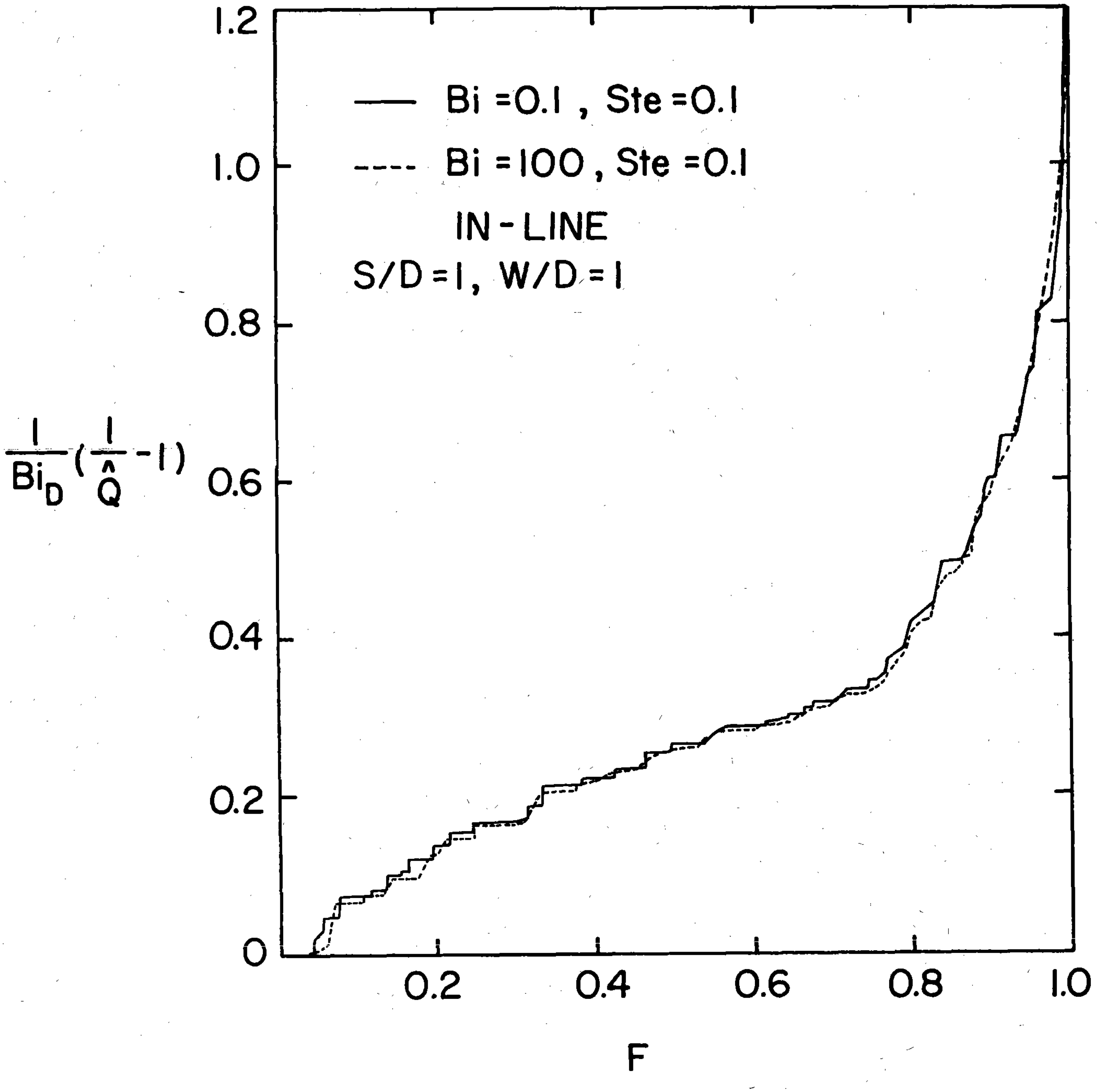


Figure 4. Demonstration of validity of similarity rule

U. S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Title: Combined Thermal Storage and Transport for Utility Applications

Principal Investigator: Walter Hausz

Organization: General Electric Company—TEMPO
P.O. Drawer QQ
Santa Barbara, California 93102
Telephone: (805) 965-0551

Project Objectives: This project parallels a study of thermal energy storage for utility applications supported both by DOE/NASA-LeRC and by EPRI, which selected several concepts for detailed conceptual design for utility peaking power applications. This project examines technical and economic factors of thermal energy transport to off-site customers, in combination with the extraction and storage concepts of the paralleled study.

Project Status: The four tasks of the project are: (1) Identification of Applications, (2) Technical and Economic Study of Concepts, (3) Determination of Benefits, and (4) Development Program Recommendations:

1. A literature survey of current and forecast energy consumption as process steam or direct heat in the industrial, commercial, and residential sectors has collected relevant reports. Total market in the temperature ranges applicable to the storage and transport media being considered are being estimated.
2. Technical and Economic Study of Concepts. Considers extraction of thermal energy from conventional coal and nuclear plants. The transport media examined include high temperature water (HTW) at temperatures up to 200°C, hot oil to 260°C, and molten salt (eg HITEC) to 460°C. Steam is also considered to test the advantage of latent heat availability versus low specific volume. Cost data on the cost elements of thermal transport have been collected, and design and cost equations formulated.
3. Determination of Benefits. As of this writing (November 13, 1978) only literature collection on this task has been done.
4. Recommendations: Not yet begun.

Contract Number: EPRI RP-1199-3

Contract Period: September 1 - December 31, 1978

Funding Level: $27,600.00

Funding Source: EPRI: Fossil Fuel and Advanced Systems, Energy Storage;
William Stevens

U.S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY (November 28, 1978)

Project Title: Evaluation of Prestressed Cast Iron Pressure Vessels (PCIV) for Coal Gasification

Principal Investigator: Robert E. Thompson

Organization: Westinghouse Advanced Energy Systems Division
P. O. Box 10864
Pittsburgh, Pennsylvania 15236
Telephone: 412/892-5600

Project Objectives:

(1) To establish the technical, economic, and safety characteristics of coal gasification reactors based on the application of prestressed cast iron vessel technology.

(2) To evaluate these characteristics in comparison with those of coal gasification reactors based on welded steel and prestressed concrete pressure vessel technology.

Project Status:

The approach being followed in this study is to define representative top level requirements, derive and analyze a gasifier PCIV conceptual design, evaluate the applicability of existing technology, identify the ASME code modification that would be required to cover this type of vessel, and compare the PCIV characteristics to those of welded steel and prestressed concrete vessels for coal gasifiers. In addition, the results will be interpreted in the context of their applicability to high temperature thermal energy storage applications.

The project status is as follows:

(1) Top level requirements for the PCIV have been identified for the reference application of a "Bi-Gas" process gasifier of 55,000 tons per day coal capacity.

(2) A preliminary conceptual design for the PCIV has been defined and is being analyzed in order to arrive at a final conceptual design. Appropriate materials and their characteristics have been defined to support concept definition and evaluation.

(3) Recommended ASME code modifications are in the process of being defined.

(4) Evaluation of the PCIV characteristics have been initiated.

Contract Number: ET-78-C-01-3013

Contract Period: July 10, 1978 - February 9, 1979

Funding Level: $238,193

Funding Source: Department of Energy, Division of Fossil Energy Programs and Division of Energy Storage Systems

INTRODUCTION AND BACKGROUND

The development of processes to convert coal to gaseous fuels that can substitute for the deplenishing supply of natural gas is a high priority element in the Nation's guest for long term energy self-sufficiency. The use of such processes requires that attention be paid, at an early date, to the fabricability and practicality of the pressure vessels needed to contain the coal gasification reaction key to the process being considered. It also is apparent that there is a high level of commonality between the design considerations for coal gasifier vessels and for high temperature thermal energy storage vessels.

The commercial development of coal gasification systems results in stringent requirements for the large pressure vessels to be used as gasifiers. In a commercial coal gasification system, the reactors, if fabricated from welded steel, might be 175 feet high and 30 feet in diameter, with 8 inch thick walls. These sizes may very well affect the feasibility and cost of the commercial systems.

The maturity of pressure vessel technology follows the natural evolution of industrial development. Steel vessels are most mature, followed by prestressed concrete, and then prestressed cast iron (PCIV). This evolving process results from industrial needs for vessels of increasing size, increasing severity of requirements, fabrication technology, economics and construction schedules.

Shop fabricated steel vessels are size limited primarily by transportation constraints; therefore, in large sizes significant field assembly and welding must be utilized. Steel vessels must also be designed to simultaneously satisfy all the functional requirements of leak tightness, pressure loads, compatibility with the thermal and fluid environment, and safety.

Prestressed concrete pressure vessels have evolved as one solution to the size constraints of steel vessels. Inherent in the design is the separation of functional requirements where a metal liner with appropriate insulation, is used to provide leak tightness and to interface with the thermal and fluid environment. The concrete provides structural capability in a reduced thermal environment, while the prestressing tendons provide the tensioning force in an ambient environment to keep the concrete in compression. The redundancy of the prestressing tendons provides assurance of pressure capability and easy inspection. The significant disadvantages of prestressed concrete vessels are: project schedular effects due to site construction needs, poor thermal-physical properties, complexity of the liner/cooling system needed to assure leak tightness and low concrete temperatures, the large vessel outside dimensions, and the installed cost. The technology status for prestressed concrete pressure vessels is such that it has been reduced to practice in Europe and the U.S.A.

A natural evolution to retain the best features of the prestressed concrete vessels while overcoming their disadvantages is to replace the concrete with prefabricated cast iron. In this type of vessel, cast iron "building blocks" are poured and machined, under factory quality assurance procedures at foundry, assembled at the construction site by appropriate stacking, and prestressed with a tensioning system similar to that used for prestressed concrete vessels. This prestressed cast iron casting technology has the inherent features of reducing the impacts and constraints attributed to the use of both prestressed concrete and welded steel pressure vessels.

From the studies and assessments made to date, it appears that the prestressed cast iron pressure vessel offers significant potential in terms of technical, economic, and safety criteria for large pressure vessels. The technology has broad application to any industry requiring large pressure vessels, such as the chemical, petroleum, and similar industries, and may be particularly attractive in coal gasification and thermal energy storage applications where the pressure vessel can be a dominant cost and feasibility factor.

Improved economics is one of the major postulated advantages for the PCIV. In addition, the PCIV is not size limited. It can be designed, manufactured, shipped, and erected for any site to meet the requirements of the largest coal gasifier deemed economically desirable.

Another desirable feature of the PCIV is that it simultaneously lends itself to both standardization and flexibility. With a limited number of "building blocks", (i.e., circumferential sectors with and without piping penetrations, top and bottom head blocks, blocks for major process or maintenance penetrations), a multitude of vessel sizes and configurations can be constructed. The pouring and machining of the castings thereby becomes a standardized factory operation, analogous to an "assembly line", while the arrangement of the standard blocks for a particular process and plant size affords the flexibility to meet the requirements of individual installations.

Since the PCIV is not a monolithic structure, it can also be field modified if it is necessary to change the location of a nozzle, repair damage, or, in the extreme, to disassemble the vessel for relocation or disposal.

With these and other potential advantages in mind, it is the objective of this study to make a technical, economic, and safety evaluation of a high temperature prestressed cast iron gasification vessel. These evaluations will provide the necessary quantitative information to confirm or refute the identified potential advantages of the PCIV.

PROGRAM

The current program consists of the following seven tasks to be accomplished over a six month period followed by reporting:

1. Definition of reference application requirements
2. Conceptual design
3. Assessment of materials properties and casting capabilities
4. Technology evaluation
5. Comparative assessment
6. Identification of ASME code modification
7. Program management

The study is being conducted by the Westinghouse Advanced Energy Systems Division with the assistance of other Westinghouse Divisions and with important subcontract contributions from the Dravo Corporation. The DOE Project Manager is Mr. Thomas J. Nakley, Office of Fossil Energy Programs.

CURRENT STATUS

In order to provide a sound basis for evaluations and comparisons, the same reference application case was selected for this study as was selected for the Reference 1 study. The reference case is that of a "Bi-Gas" process gasifier for 55,000 tons of coal per day feed rate. The intent of the resulting PCIV top level requirements, a partial list of which is given in Table 1, is to maintain the same internal dimensions and conditions as would be associated with other types of vessels so that the process is undisturbed. Thus, the advantages and disadvantages of a PCIV for this application can be realistically assessed. The top level requirements are being used in the concept definition and evaluations now in progress.

Candidate materials for use in this PCIV application have been considered and a preliminary identification of materials made. However, it should be recognized that the PCIV concept allows relatively great latitude to select materials so as to enhance desirable characteristics, such as to minimize installed costs. Therefore, materials investigations are continuing and it is expected that some of the materials identified will be replaced by other materials as the study progresses.

The approach being followed in deriving the design concept is to proceed through three iterations of the concept, each of which is analyzed sufficiently to identify desirable modifications. In addition to the usual design considerations, manufacturing and field erection considerations are being included throughout the design process to help insure that an economic practical concept is derived.

Figure 1 shows an overall view of the second iteration of the concept. This design is currently being analyzed and evaluated and will probably be modified to some degree as the final concept. The preliminary concept of Figure 1 is made up of laminated top and bottom heads and 14 cylindrical rings. Each ring

TABLE 1

DESIGN REQUIREMENTS FOR PCIV COAL GASIFIER VESSEL
(Partial Listing)

Inside Diameter (PV Liner)	24' 11"
Inside Height (tangent to tangent)	125 ft.
Operating Pressure (max.)	1200 psig
Operating Gas Temperature (max.)	3000°F
Design Temperature (PV liner)	500°F
Operating Temperature (PV liner)	≤450°F
Service Life	25 years
Startup/Shutdown Cycles	2 per year
Gasification Process	"Bi-Gas"
Coal Feed Rate (per vessel)	55,000 tons/day
Applicable Design Standard	ASME Code (Modified)
Component Transportation	Standard Railway

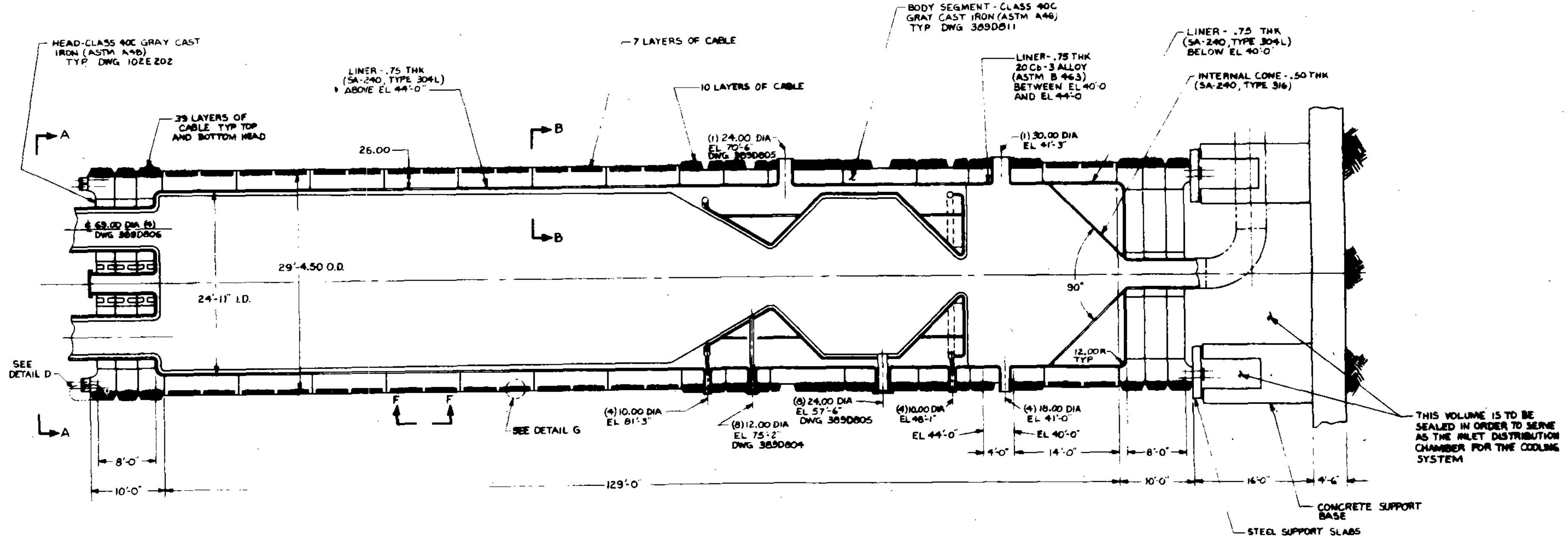

HEAD-CLASS 40C GRAY CAST IRON (ASTM A48) TYP DWG 102E202
39 LAYERS OF CABLE TYP TOP AND BOTTOM HEAD
LINER - .75 THK (SA-240, TYPE 304L) ABOVE EL 44'-0"
7 LAYERS OF CABLE
10 LAYERS OF CABLE
BODY SEGMENT - CLASS 40C GRAY CAST IRON (ASTM A48) TYP DWG 389D811
LINER - .75 THK 20 Cb-3 ALLOY (ASTM B 463) BETWEEN EL 40'-0 AND EL 44'-0
LINER - .75 THK (SA-240, TYPE 304L) BELOW EL 40'-0"
INTERNAL CONE - .50 THK (SA-240, TYPE 316)
A
A
B
B
26.00
(1) 24.00 DIA EL 70'-6" DWG 389D805
(1) 30.00 DIA EL 41'-3"
℄ 69.00 DIA (6) DWG 389D806
29'-4.50 O.D.
24'-11" I.D.
90°
12.00R TYP
SEE DETAIL D
F
F
SEE DETAIL G
(4) 10.00 DIA EL 81'-3"
(8) 12.00 DIA EL 75'-2" DWG 389D804
(8) 24.00 DIA EL 57'-6" DWG 389D805
(4) 10.00 DIA EL 48'-1"
(4) 18.00 DIA EL 41'-0"
EL 44'-0"
EL 40'-0"
8'-0"
10'-0"
129'-0"
4'-0"
14'-0"
8'-0"
10'-0"
16'-0"
4'-6"
THIS VOLUME IS TO BE SEALED IN ORDER TO SERVE AS THE INLET DISTRIBUTION CHAMBER FOR THE COOLING SYSTEM
CONCRETE SUPPORT BASE
STEEL SUPPORT SLABS

Figure 1

is made up of eight hollow cast iron blocks and each head layer is also made up of multiple blocks. The blocks surround a steel liner and are prestressed both vertically and circumferentially. Current plans are for each ring to be assembled and circumferentially prestressed on the ground and then lifted into place as a ring. Vertical prestressing will then be applied after stacking is complete. Concept analysis and assessment is currently in progress.

Reference:

1. "Cost Study, Shop Assembly vs Field Assembly of Heavy Wall Coal Gasifier Reactor Vessels"; Chicago Bridge and Iron Company; FE-2009-13; December, 1976.

U. S. DEPARTMENT OF ENERGY

THIRD ANNUAL
THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Applications of Thermal Energy Storage to Process Heat Storage and Recovery in the Paper and Pulp Industry.

Principal Investigator: J. H. Carr

Organization: Boeing Engineering and Construction Company
P. O. Box 3707
Seattle, Washington 98124

Project Objectives: Determine the impact of thermal energy storage (TES) on energy usage and economics in the paper and pulp industry.

Project Status: The study has been completed and the final report distributed (report is numbered CONS/5082-1 and NASA CR 159398).

Contract Number: EC-77-C-01-5082

Contract Period: September 1, 1977 - September 30, 1978

Funding Level: $140,945

Funding Source: Department of Energy
Division of Energy Storage Systems

1.0 INTRODUCTION AND APPROACH

The paper and pulp industry in the United States consists of approximately 350 companies, operating 750 plants. This industry ranks fifth in the manufacturing group as well as being one of the largest users of fossil fuels.

In certain 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. The storage applications studied represent one technique that would act to smooth the "swings" in demand that must be followed by the boilers and permit fossil fuel firing at a reduced rate.

The Weyerhaeuser Company's Longview, Washington paper and pulp mill served as the study site. Potential industry wide impact was estimated by using a telephone survey to determine the number of plants in which hog fuel substitution for fossil fuels could result from the application of TES.

2.0 LONGVIEW PLANT CHARACTERISTICS

The Weyerhaeuser Longview plant is typical of pulp mills where economic use of Thermal Energy Storage is possible. The total steam demand is such that it is less than the capacity of the baseloaded boilers for a significant portion of the year's operation. This excess baseload capacity and adequate hog fuel supply are the primary requirements for hog substitution for fossil, using TES. The amount of substitution is a function of the annual steam demand as well as the size and number of the steam demand transients. The steam demand transients and the plant layout dictate the types of storage devices that can be considered.

A number of possible process system alternatives where TES could be employed at the Longview plant were identified. The two process alternatives determined to have the greatest potential for TES use are shown in Figure 1. Storage concepts for each process alternative were considered. Figure 2 shows a summary of the results. It was found that the current technology status and high discharge rate capability of steam accumulators resulted in a significant advantage over the other TES concepts. A relative costing of steam accumulators against the packed rock bed/intermediate working fluid TES approach is shown in Figure 3. The accumulator approach is superior for storage times less than 1 hour, and discharge rates less than 150,000 lbm/hr. Although designed for a given nominal steaming rate, e.g., 100,000 lbm/hr, for a given storage time, accumulators can tolerate much higher rates for short periods. Based on these considerations, steam accumulators were selected for conceptual design.

Steam accumulators store steam by transferring the latent heat of vaporization to water. In the variable pressure accumulator, charging steam from a high pressure header bubbles through saturated water contained under pressure in a steel vessel. The steam condenses and transfers energy to the water, raising the water's temperature and pressure. On discharging, to a low pressure header, the steam pressure above the water surface is reduced causing the water to evaporate, supplying steam but lowering the water's temperature and pressure.

Constant pressure accumulators absorb steam during low demand periods and preheat boiler feedwater, which is stored at desired temperature and pressure. During periods of peak steam demand, feedwater heating is slowed or stopped, and the boiler feed is maintained from the preheated water stored in the accumulator.

The paper and pulp operation at Longview consists of process systems and a power plant which supplies steam to the processes, and the power generation turbines. The power plant consists of a series of boilers, turbines, pressure reducing valves, desuperheaters, deaerators, and condensers. Figure 4 is a simplified plant schematic showing the interconnection of the components. The plant has eight boilers currently in use, including one hog fuel boiler, three recovery boilers and four fossil fuel (oil/gas) boilers. A summary of the boiler characteristics is given in Table 1. There are five turbine generators in the plant, one driven by 1250 psig steam from the hog fuel boiler and the remaining driven by 600 psig steam. All five turbines provide steam at either 40 or 140 psig. The 40 psig deaerator heats feedwater for the 600 psig boilers. The 140 psig deaerator heats feedwater for the hog fuel boiler.

Steam swing data were obtained from metered boiler steam flow charts for several individual days, typical of the year's average operation. These charts showed the step changes in steaming rates of base loaded boilers, and the minute-by-minute changes in output from the load following fossil fuel boiler(s). The steam demand profiles for each day were simplified by assuming that all process steam demand transients occur in the 140 psig and 600 psig headers. Demand fluctuations at the 40 and 140 psig deaerators were calculated for the "no storage" case and subtracted from the raw flow data, resulting in a calculated 140 psig process steam demand. These demand data were inputs to the analysis of operation with storage. Table 2 presents steam swing characteristics of the four selected representative days.

3.0 TES PERFORMANCE ANALYSIS

A math model of the Longview steam supply system was developed to examine the effects of integrating TES into the system. The model allows the investigation of both the economic and operational impacts of installing a TES system. The key area of economic concern is that of fuel substitution. The increased percentage of total steam demand that can be supplied by burning hog fuel, and the resultant decrease in the use of fossil fuel, is the major cost factor to be compared with system fabrication and installation costs. The amount of electricity generated in the plant will also be affected by the introduction of TES. Steam generated by fossil fuel and hog fuel, as well as electrical generation, were outputs of the model.

Allowable frequency of hog firing rate changes was established by Weyerhaeuser's operating personnel. Hog fuel substitution potential is strongly affected by this judgement, and for the Longview boiler the minimum average interval between changes was set at 15 minutes. This restriction applies to both the base case and the storage cases, and is an index of the limited load following capability of this boiler. The maximum rate of chage of the steaming rate of the Longview hog fuel boiler was assumed to be 3×10^6 (lb/hr)hr.

Table 1 BOILER CHARACTERISTICS

NUMBER	TYPE	STEAM FLOW, 10^3 LB/HR			PRESSURE, PSIG	TEMP., ^{o}F	ENTHALPY, Btu/LB
		MAX	BASE	MIN			
1	Red Liquor	130	110	80	600	700	1351
2	Recovery						
6	Hydrogen	40	40	40	"	"	"
	Oil/Gas	100	0	0*	"	"	"
7	Oil/Gas	200	0	50	"	"	"
8	Oil/Gas	250	0	120	"	"	"
9	Oil/Gas		0	50	"	"	"
10	Black Liquor Recovery	500	400	300	"	"	"
11	Hog Fuel	550	550	200	1250	935	1458

*Assumes H_2 firing at minimum boiler steaming rate.

Table 2 STEAM DEMAND CHARACTERISTICS

DATE	NUMBER OF SWINGS	MAX. DEMAND EXCURSION, 1,000 lb/hr	MAX. DEMAND SWING, 1,000 lb/hr		MAX. SWING RATE, 1,000 lb/hr/min	
			Up	Down	Up	Down
6-24-77	245	235	130	170	60	56
6-25-77	281	199	165	120	104	220
6-29-77	258	555	395	460	55	64
7-21-77	220	350	200	170	115	38

The operation of the math model is represented in Figure 5. Program inputs are read and process steam demands are obtained from tabulated data. Initial values of deaerator and desuperheater flows are added to the process demands. The exact values of these flows cannot be calculated in advance, thereby making the model iterative in nature.

The model determines the required valve settings throughout the plant to meet the total steam demand. Boiler firing rates are calculated to match the required steam flows. The model performs a thermodynamic balance of mass and energy flows, resulting in new desuperheater and deaerator requirements, which result in new total steam demands. The model iterates until the change in desuperheater and deaerator flows is below a specified value.

In non-storage cases, the hog fuel steaming rate target is set so as to keep the fossil fuel boiler output at a target value above its minimum. In cases where storage is present, the hog fuel rate setting algorithm also considers storage inventory and whether it is filling or emptying. The hog fuel steaming rate is adjusted to its new target only if 15 minutes has elapsed since the last change, or if steam is being vented to the sky. After the model has run a full day's demand data, it integrates desired data over the day and prints the results.

The model operating without storage was verified by reviewing the predicted values of steaming rates of the boilers, flows through pressure reducing valves, amount of steam venting ("skying"), and amount of electricity generated with the Longview plant personnel. The model thus verified was updated to conform to 1980 operating strategy assumed the ability of the hog fuel boiler to operate at its design steaming capacity of 550,000 lbm/hr, and to change its rate as often as every 15 minutes without violating environmental standards.

4.0 RESULTS

Fossil energy savings depend on (1) the performance of the TES system, (2) the frequency with which the hog boiler firing rate may be adjusted and (3), the availability of reserve hog fuel boiler steaming capacity to accept thermal load transfer from the fossil fuel boiler.

Figure 6 shows the variation of the four-day-averaged fossil fuel boiler steaming rate as a function of the hog fuel boiler change interval, for operation with and without TES. Smaller change intervals indicate more steam demand following capability on hog firing. Operating without storage, less fossil fuel supplied steam is required at smaller change intervals. Thus, fossil fuel savings available from the use of TES, compared to non-storage operation, are shown to become smaller as the change interval becomes smaller, i.e., as the hog fuel boiler becomes more responsive. Figure 7 shows that for a 15 minute change interval, fossil fuel boiler steaming rate reductions of 64,000 to 71,000 lbm/hr are available with constant or variable pressure steam accumulators. This corresponds to fossil fuel conservation per TES installation on the order of 100,000 bbl of oil per year.

Conceptual design configurations of accumulators sized for Longview are shown in Figure 8. The variable pressure design is considereably larger than the constant pressure design, but does not require the separate deaerating heater. A control system is required for both accumulator systems. The conceptual design for the control system consists of a minicomputer, CRT terminal, printers, and data storage. The minicomputer receives process measurements from the existing analog control system in the plant, analyzes the measurements and their trends over the immediate past, and makes decisions as to the desired set points for hog fuel boiler steaming rate and accumulator flows. The terminal allows monitoring of system status and controlling of system operating parameters. The printer provides records of pertinent system data. The data storage contains the programming algorithm for the minicomputer. System installation costs with either accumulator type and controls are estimated as $560,000 as shown in Figure 9.

Installations of this type appear very attractive as investment opportunities. As shown in Figure 10, an after-tax R.O.I. threshold of 15% is exceeded with marginal hog fuel prices as high as \$30 per bone dry ton (BDT) or $\$1.67/10^6$ BTU in fuel, and annual-average thermal load transfers as low as 35,000 lb. steam/hr.

5.0 INDUSTRY SURVEY

A survey was performed to estimate the extent to which power plant TES could affect fossil fuel consumption within the whole pulp and paper industry. The source of initial survey data was the American Paper Institute, a pulp and paper trade association with broad membership. API supplied the names and locations of 117 reporting mills burning bark and hogged fuels. Telephone contact was made with the steam plant superintendents of 55 mills. Each superintendent was asked whether fossil fuel was fired in his plant to follow swinging steam demand, while hog fuel boilers were operated below capacity, and whether excess hog fuel was available. Mills whose superintendents answered yes were included as candidates for TES systems. Months per year of required slowdown, and size of downswing to be absorbed were also determined. Several mills reported that new boilers were being installed, or plant changes were being planned which were expected to result in excess hog boiler capacity, with fossil fuel boilers to be used for following steam transients. These latter mills were also included as TES candidate mills.

Of the 55 mills contacted, six were in the excess hog fuel boiler capacity situation all year, four were in the situation half the year, and six expected to be in it by 1980. Average swinging demand to be absorbed in these plants was ± 60,000 lbm/hr. Extrapolation of this sampling to the full list indicates the near term potential fossil fuel savings from this TES application to be 3.2 million barrels of oil per year.

6.0 CONCLUSIONS

As a result of this study, and providing hog fuel boiler capacity is sufficient to accept load transfer from the fossil fuel steam supply system while maintaining environmental compliance, it is concluded that steam accumulator swing smoothing installations represent one effective energy conservation measure in the paper and pulp industry.

- o Typical installations will permit fossil fuel savings in the order of 100,000 bbl/year.
- o Typical installations will provide an after-tax R.O.I. in the order of 30%.

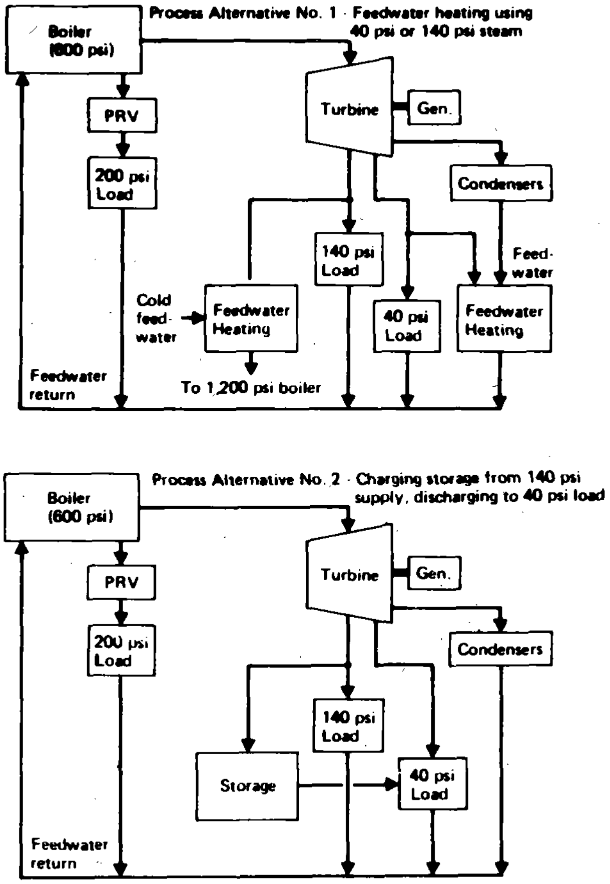


Figure 1. Potential Applications of TES to Longview Mill

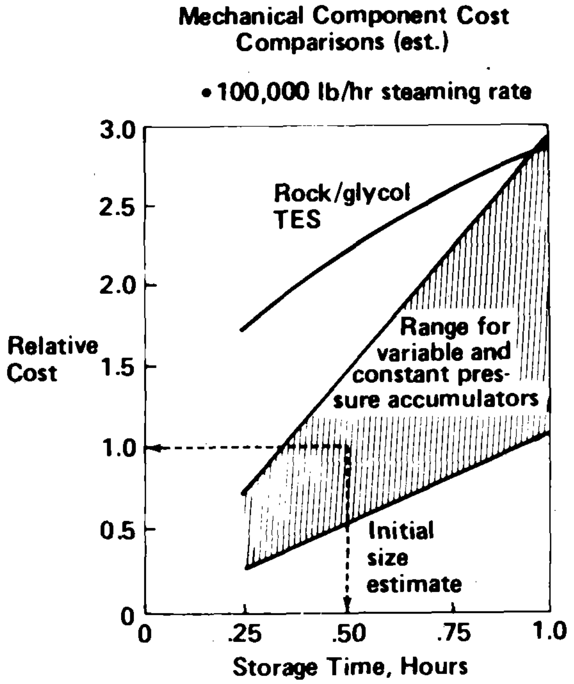


Figure 3. Relative Cost Comparison

TES System Candidate	Development Status	Thermo-dynamic Interface	Operational Flexibility
Sensible heat - rock/oil	Development testing	Poor - viscosity problem	Adequate - max. rate fixed by H/X sizing
Sensible heat - rock/glycol	Variation of rock/oil concept	Adequate in concept	
Sensible heat - water	Fully developed - steam accumulators	Excellent	Excellent - can trade rate for time over large range
Latent heat - hydroxides	Component testing	Adequate in concept	Adequate - max. rate fixed by H/X sizing
Latent heat - other salts & metals	Developmental testing	Melt temp. too high	

Figure 2. Storage System Candidates Comparison

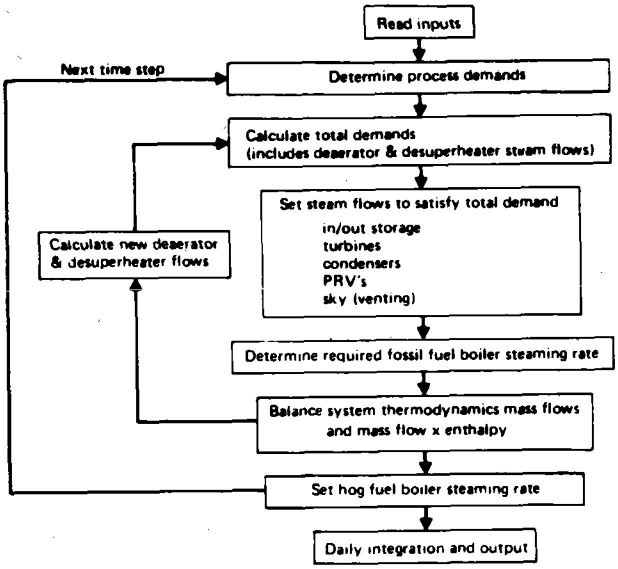


Figure 5. Industrial Process Heat Math Model Schematic

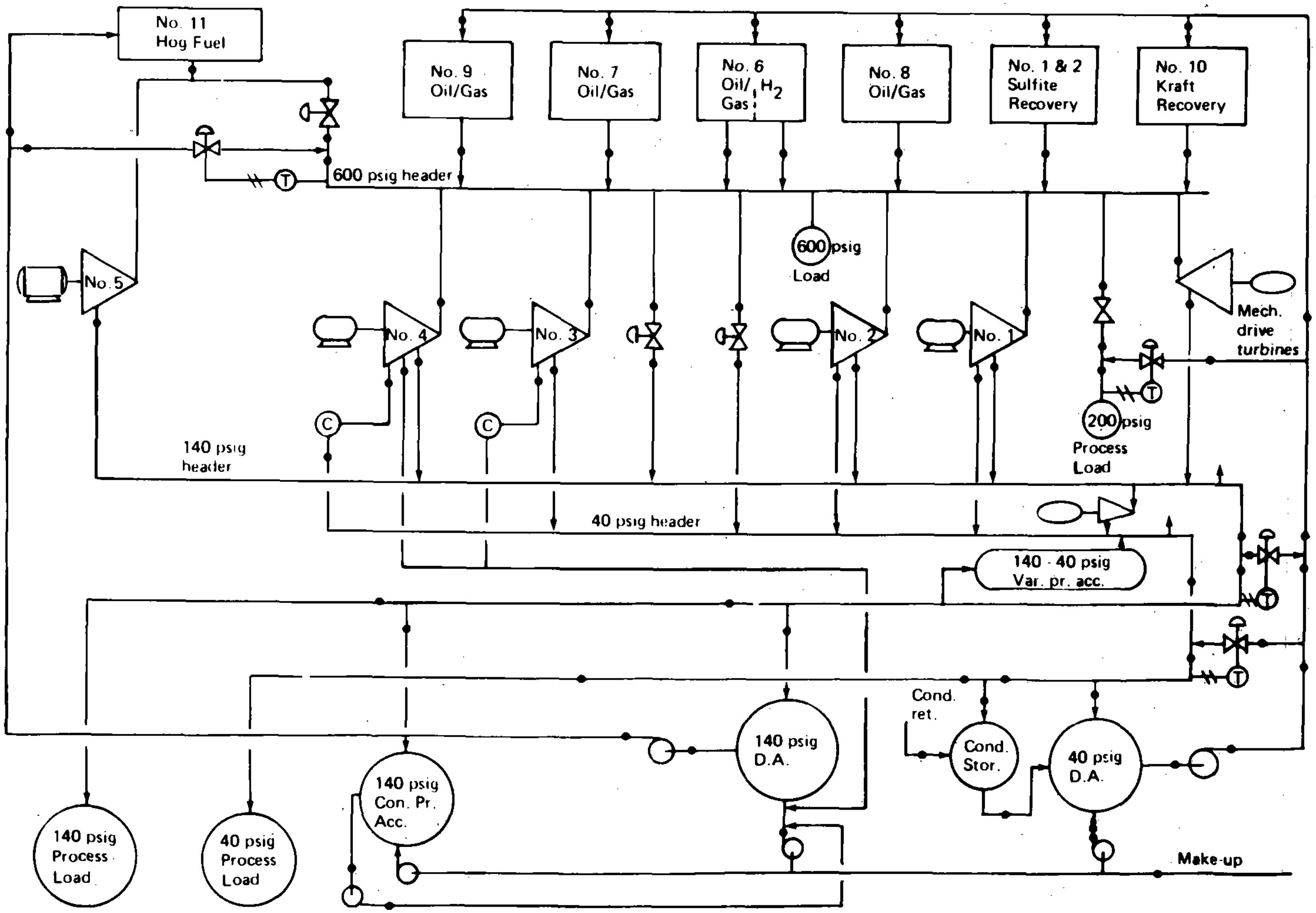


Figure 4. Longview Plant Schematic for Thermodynamic Model (with Storage)

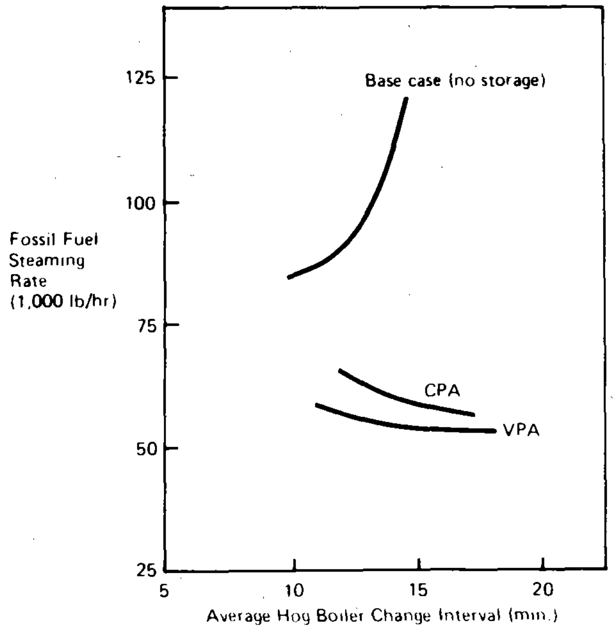


Figure 6. Fossil Fuel Boiler Steaming Rate Comparison

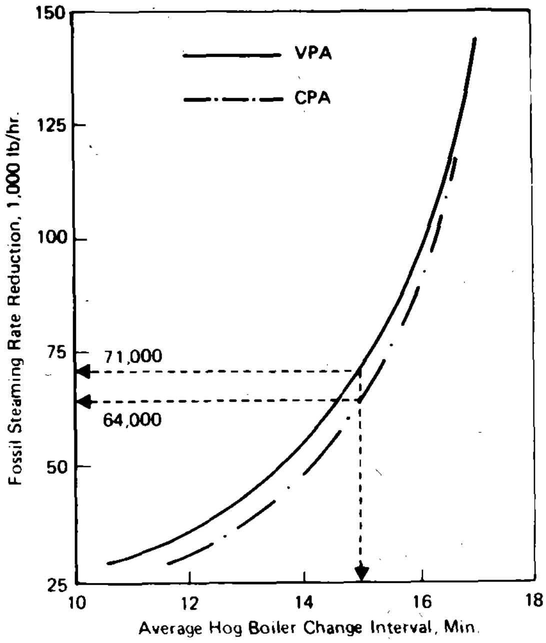
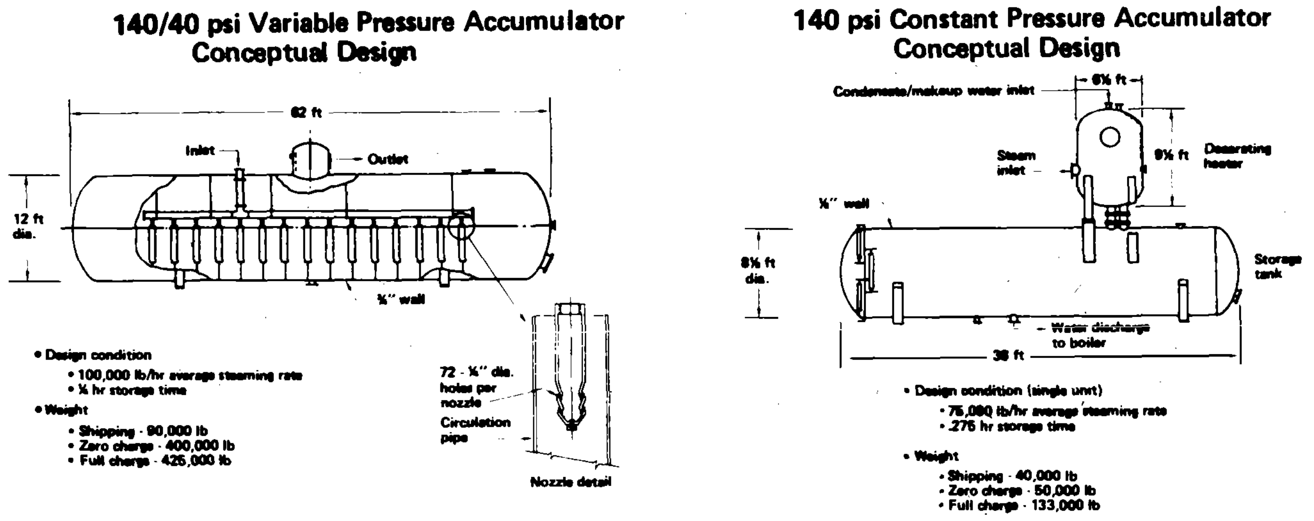


Figure 7. Steam Accumulator Performance



140/40 psi Variable Pressure Accumulator Conceptual Design

- Design condition
  - 100,000 lb/hr average steaming rate
  - ¼ hr storage time
- Weight
  - Shipping - 90,000 lb
  - Zero charge - 400,000 lb
  - Full charge - 425,000 lb

140 psi Constant Pressure Accumulator Conceptual Design

- Design condition (single unit)
  - 75,000 lb/hr average steaming rate
  - .275 hr storage time
- Weight
  - Shipping - 40,000 lb
  - Zero charge - 50,000 lb
  - Full charge - 133,000 lb

Figure 8. TES Conceptual Design Summaries

Cost Account	140/40 psi Variable Pressure	140 psi Constant Pressure
Mechanical system		
Vessel & internal piping (1)	$ 72,000	$ 22,000
Deaerating heater (2)	N/A	52,000
Insulation (3)	20,000	8,000
Valves (3)	12,000	19,000
Feedwater pump (3)	N/A	7,000
Subtotal	$104,000	$108,000
10% Contingency	10,000	11,000
Total (FOB costs)	$114,000	$119,000
Field installation (typical) (4)		
Direct material	75,000	77,000
Direct labor	73,000	75,000
Freight, insurances, taxes, other indirects	114,000	118,000
Total mechanical systems	$376,000	$389,000
Control system (5)	$172,000	$172,000
Grand Total	$548,000	$561,000

(1) Based on vendor quotations (2) Based on vendor information (3) Engineering estimates
(4) Based on Guthrie's estimating factors for pressure vessel installations (5) Includes installation and test

Figure 9. Accumulator System Cost Estimates

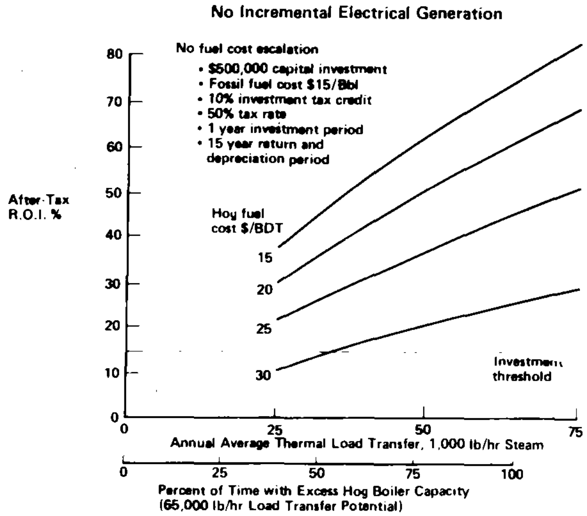


Figure 10. Return on Investment

U.S. DEPARTMENT OF ENERGY

THIRD ANNUAL

THERMAL ENERGY STORAGE CONTRACTOR'S INFORMATION EXCHANGE MEETING

PROJECT SUMMARY

Project Title: Applications of Thermal Energy Storage to Process Heat and Waste Heat Recovery in the Iron and Steel Industry

Principal Investigator: L. B. Katter and D. J. Peterson

Organization:

Rocket Research Company
York Center
Redmond WA 98052

Project Objectives: Identify Application of High Temperature Energy Storage Techniques in the Iron and Steel Industry which are Energy Conservative and Cost Competitive. Quantify the Projected Savings from these Applications upon a Nationwide Basis.

Project Status:

The system identified in this study operates from the primary arc furnace evacuation system as a heat source. Energy from the fume stream is stored as sensible energy in a solid medium (packed bed). A steam-driven turbine is arranged to generate power for peak shaving (either internal company load peaks or utility area demand peaks can be smoothed with the system). A parametric design approach is presented since the overall system design, at optimum payback, is strongly dependent upon the nature of the electric pricing structure. Results of this program are reported in CONS/5081-1 issued October, 1978.

Contract Number: EC-77-C-01-5081

Contract Period: August 30, 1977 through October 30, 1978

Funding Level: $91,000

Funding Source: Department of Energy, Division of Energy Storage Systems

RRC-79-H-231

APPLICATION OF THERMAL ENERGY STORAGE TECHNIQUES TO PROCESS HEAT AND WASTE HEAT RECOVERY IN THE IRON AND STEEL INDUSTRY

The study was performed by Rocket Research Company, with support from team members: Bethelehem Steel Company (Seattle plant) and the Lighting Department of the City of Seattle (Seattle City Light).

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The scope of the project was limited to consideration of currently available technology so that industry-wide application could be achieved by 1985. Slight additional scope limitations were found from the additional criterion that concepts and equipment must be compatible with the heavy industrial environment.

A search of the literature, coupled with interviews with representatives of major steel producers, served as the means whereby the techniques and technologies indicated for the specific site are extrapolated to the industry as a whole and to the 1985 time frame. The conclusion of the study is that by 1985, a national yearly savings of 1.9 million barrels of oil could be realized through recovery of waste heat from primary arc furnace fume gases on an industry-wide basis.

Economic studies indicate that the proposed system has a plant payback time of approximately 5 years. Due to the favorable economic and technical results in the program, additional work leading to a full-scale demonstration is recommended. This program would be carried out in five phases to prove the overall feasibility of the concept and provide industry with the necessary data for nationwide implementation.

STEEL ARC FURNACE ENERGY RECOVERY SYSTEM

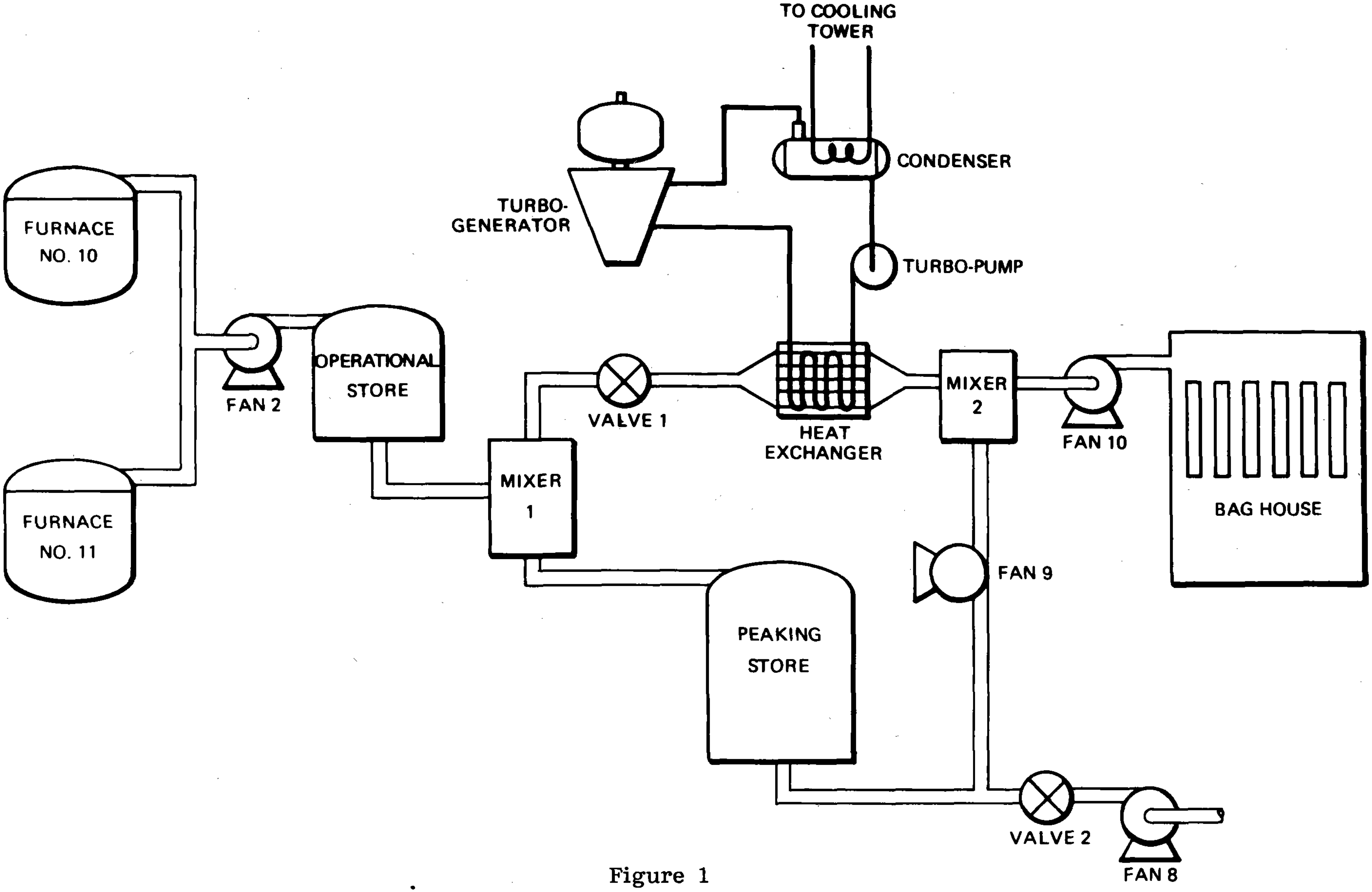

Figure 1

Figure 1 is a schematic of the total system with two thermal energy storage subsystems. The operational store, relatively small, buffers the temperature excursions to the turbo-generator and the peaking store is size dependent upon the time that "peaking power" is required.

An economic analysis was conducted to determine the value of storing thermal energy over a 16 hour charge cycle to displace grid peaking power. The least expensive capital costs for energy recovery is to use the energy when available to generate electrical power; however, the displaced energy is of smaller value. By storing energy to feedback at critical times (i.e., 8 hour duration during grid peaking condition) the system capital costs increase as shown in Figure 2. The peaking power system may be worth the additional investment if the displaced energy is of higher unit costs. Preliminary economic analysis have shown that for electrical time of day pricing where cost of 3/1 exists for 8 hour peaking, large storage systems as described in this program are economically attractive.

COMPONENT CAPITAL COST COMPARISON FOR SCRAP IRON SYSTEM

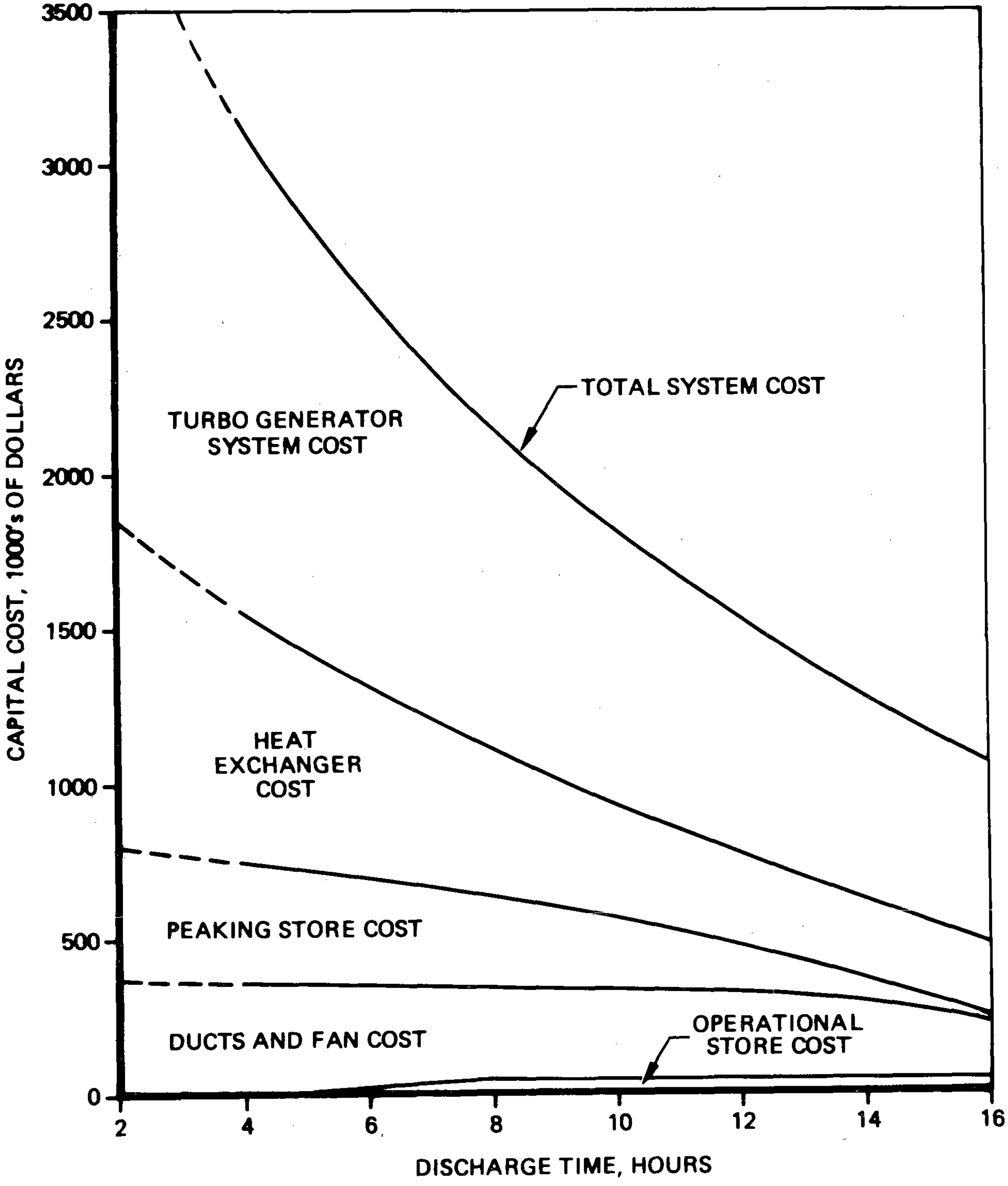

Figure 2

PROJECT SUMMARY

Project Title: Applications of Thermal Energy Storage in the Cement Industry.

Principal Investigator(s): F. A. Jaeger, D. G. Beshore and Dr. F. M. Miller (PCA).

Organization(s):

Martin Marietta Aerospace	Portland Cement Association
Denver Division	Skokie, Illinois
P. O. Box 179	(312) 966-6200
Denver, Colorado 80201	
(303) 973-3000	

Project Objectives: This contract includes a definition of the energy consumption by process; sources of waste heat; the amount, quality, and potential for recovery of that heat; and the in-process uses of stored thermal energy in the cement industry. Various energy storage systems and applications were compared. The most promising was selected for further technical and economic analyses. As a result of these analyses, a technology validation program and program plan was developed.

Project Status: This project was divided into various tasks which included the following effort:

1) Define the energy consumption by process, the sources of waste heat and corresponding amount and temperature, the potential for recovery, the in-process uses of stored thermal energy, typical plant equipment layouts, and potential energy savings. Select the most promising energy sources.

2) Review the various types of thermal storage techniques and identify those most suitable for use in the cement industry.

3) Select the candidate source/storage system/application. Prepare flow diagrams of each showing process flowrates, temperatures and pressures. Perform analyses to describe size and requirements for major items of equipment.

4) Evaluate the overall economics and technical feasibility of full-scale commercialization of cement plant waste heat usage.

5) Provide a detailed program plan for the required analysis, design, and development testing and system demonstration testing of the concept.

The current project status is as follows:

1) Project completed technical work April 1978.

2) Final report (CONS/5084-1) has been published.

Contract No.: EC-77-C-01-5084

Contract Period: September 1977 through November 1978

Contract Amount: $89,000

Funding Source: DOE, Division of Energy Storage Systems.

I. PROJECT SUMMARY

In the manufacture of cement, trillions of Btu's are rejected to the environment each year. The purpose of this study program was to determine whether thermal energy storage could be used to conserve or allow alternative uses of this rejected energy. This study identifies and quantifies the sources of rejected energy in the cement manufacturing process, establishes use of this energy, investigates various storage system concepts, and selects energy conservation systems for further study. Thermal performance and economic analyses are performed on candidate storage systems for four typical cement plants representing various methods of manufacturing cement. Through the use of thermal energy storage in conjunction with waste heat electric power generation units, an estimated 2.4×10^{13} Btu/year, or an equivalent of 4.0×10^{6} barrels of oil per year, can be conserved. Attractive rates of return on investment of the proposed systems are an incentive for further development.

II. PROJECT DESCRIPTION

A. Process Study

Two processes are used for manufacturing Portland cement, wet and dry. When rock is the principal raw material, the first step in both processes is primary crushing. Pieces of rock the size of an oil drum are fed through crushers that reduce the rock to about 5-inch size. Secondary crushers or hammer mills then reduce the material to about 3/4-inch size.

In the wet process, the crushed raw materials, properly proportioned, are ground with water, thoroughly mixed, and fed into the kiln in the form of "slurry." In the dry process, the raw materials are ground, mixed, and fed into the kiln in their dry state. In other respects, the wet and dry processes are essentially alike.

The raw material is heated to about 2700°F in cylindrical steel rotary kilns lined with firebrick. Some kilns have a diameter of as much as 25-ft and can be 750-ft long. The kiln axis is slightly inclined, and the raw material is fed into the higher end. At the lower end, an intensely hot flame is produced by the precisely controlled buring of coal, oil, or gas under forced draft.

As the raw material moves countercurrent to the flow of hot gases through the kiln, certain elements are driven off in the form of gases. The remaining elements combine to form a substance with raw physical and chemical characteristics. It is called "clinker" and usually takes the form of grayish-black pellets about the size of marbles. The hot clinker discharged from the kiln is cooled to manageable temperatures by one of the various types of coolers. The clinker is conveyed to a series of grinding mills where gypsum is added to form Portland cement.

Although wet process will continue to be used in many plants for the foreseeable future, the low gas temperatures and high moisture contents characteristic of exit gases from wet kilns make them much less attractive for heat recovery. Therefore, only dry process kilns were considered in this study.

The current energy consumption of cement plants is shown in Table 1. For dry process kilns only, the kiln consumes an average 4.94 million Btu/ton fuel energy and and 29.3 kWh/ton electrical requirements. The overall totals for all plants are 5,760,000 Btu/ton total fuel energy and 148.3 kWh/ton electrical energy.

Table 1. Present Energy Consumption

Department	Energy (Fuel + Electric) Equivalent Btu/ton Clinker	
	Average	Range
Quarry and Crushing	48,000	0 to 175,000
Drying	239,000	0 to 1,000,000
Raw Milling	117,000	
Kiln Operations	5,779,000	3,000,000 to 10,100,000
Grinding	307,400	150,000 to 525,000

Four specific existing plants were chosen as models for evaluation in this study. All four plants chosen had different kiln and heat recuperation systems as follows:

Plant 1 - Long, dry-process kiln with grate cooler.

Plant 2 - Intermediate length dry-process kiln plus a one-stage cyclone preheater and grate cooler.

Plant 3 - Short kiln with four-stage suspension preheater and grate cooler.

Plant 4 - Long, dry-process kiln with grate cooler. Waste heat boiler system is used for on-site power generation.

The significant sources of waste heat for the model plants are summarized in Table 2. Although all three sources appear to offer considerable quantities of waste heat suitable for recovery, the problems of capturing the heat lost from the kiln shell caused its elimination as a heat source from this study.

Table 2. Summary of Possible Heat Sources

Sources	Description	Plant No.	Maximum Temp. of Source, °F	Net Heat Available MBtu/ Ton of Clinker
Kiln Shell	Radiative and Convective Heat Losses	1	650	0.38
		2	700	0.50
		3	600	0.19
		4	700	0.62
Clinker Cooler	Waste Air	1	350	0.30
		2	450	0.66
		3	350	0.52
		4	350	0.22
Kiln System Exit Gas	Exhaust Gas from the Kiln or Preheater, Considered Before Entering the Precipitator	1	1150	1.41
		2	720	1.13
		3	800	0.81
		4	1500	2.96

B. Storage System Selection

Present thermal energy storage techniques or those under development were reviewed and storage systems most suitable for recovering and storing thermal energy in the cement industry were identified. Consideration was given to the uses of thermal energy in: (1) the cement process; (2) other off-site industrial processes; and (3) for district heating and for cooling. Preliminary economical evaluations led to the selection of on-site electricity generation as the application for the waste heat. Storage system technologies can be classifed under the broad categories of sensible heat storage, latent heat storage, and chemical heat storage. Eleven materials were selected from the sensible, latent, and chemical energy storage categories for high-temperature applications.

Based on capital costs, material compatibility with high temperature gases, ease of operation, and system reliability, sensible heat storage media were chosen for further analysis. Rockbeds consisting of either granite, limestone, or cement clinker were selected. Shown in Figure 1 is the incorporation of this system in the cement manufacturing process.

C. Economic Analysis

A preliminary economic analysis was conducted for the conceptual storage system designs. These analyses were used to determine the economic feasi-

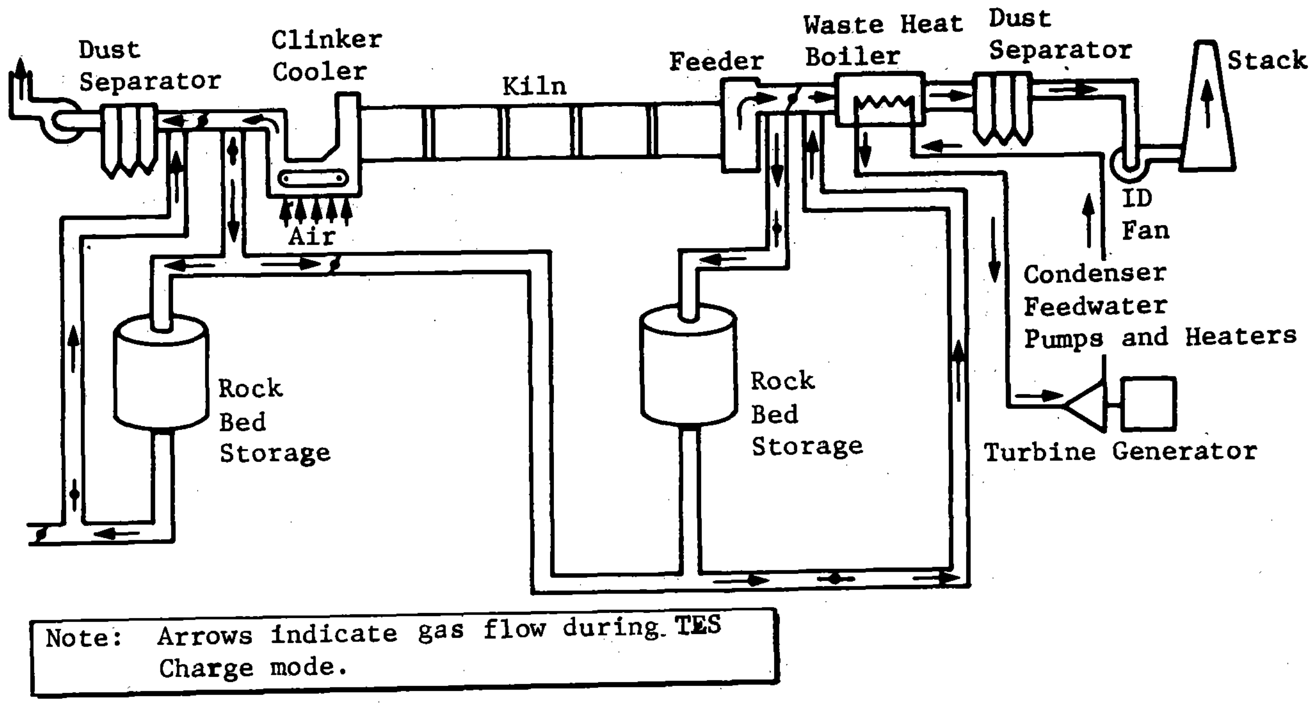

Figure 1 Rock Bed/Waste Heat Boiler/Power Plant System Diagram

bility of selected systems in terms of stored energy costs versus current and projected energy costs and the rate of return on investment. Costs were determined for thermal energy storage installation at each of the four model plants.

Return on investment methodology was developed under this phase of the study. The methodology involved in the use of calculated electrical power savings realized by producing the electrical energy on-site and the capital investment. Capital costs were estimated from literature references and vendor quotes. Investment for a waste heat recovery system, turbogenerator, and appropriate facilities (site-work, buildings, electrical, etc) amount to \$800 to \$1000/kW. With the present industry-wide average of 2.5¢ to 2.8¢/kWh, return on investment can be high as 80 to 90% considering an 11% escalation rate of electricity over a 30-year system life.

Return on investment calculations using on-site power generating costs with those utility costs likely to occur over cement plant life were performed. Rates of return were compared for waste heat power generation systems only and those having a thermal energy storage capability. Results of an analysis (Figure 2) performed on plant 4 indicate that a rockbed storage system is an economically viable investment.

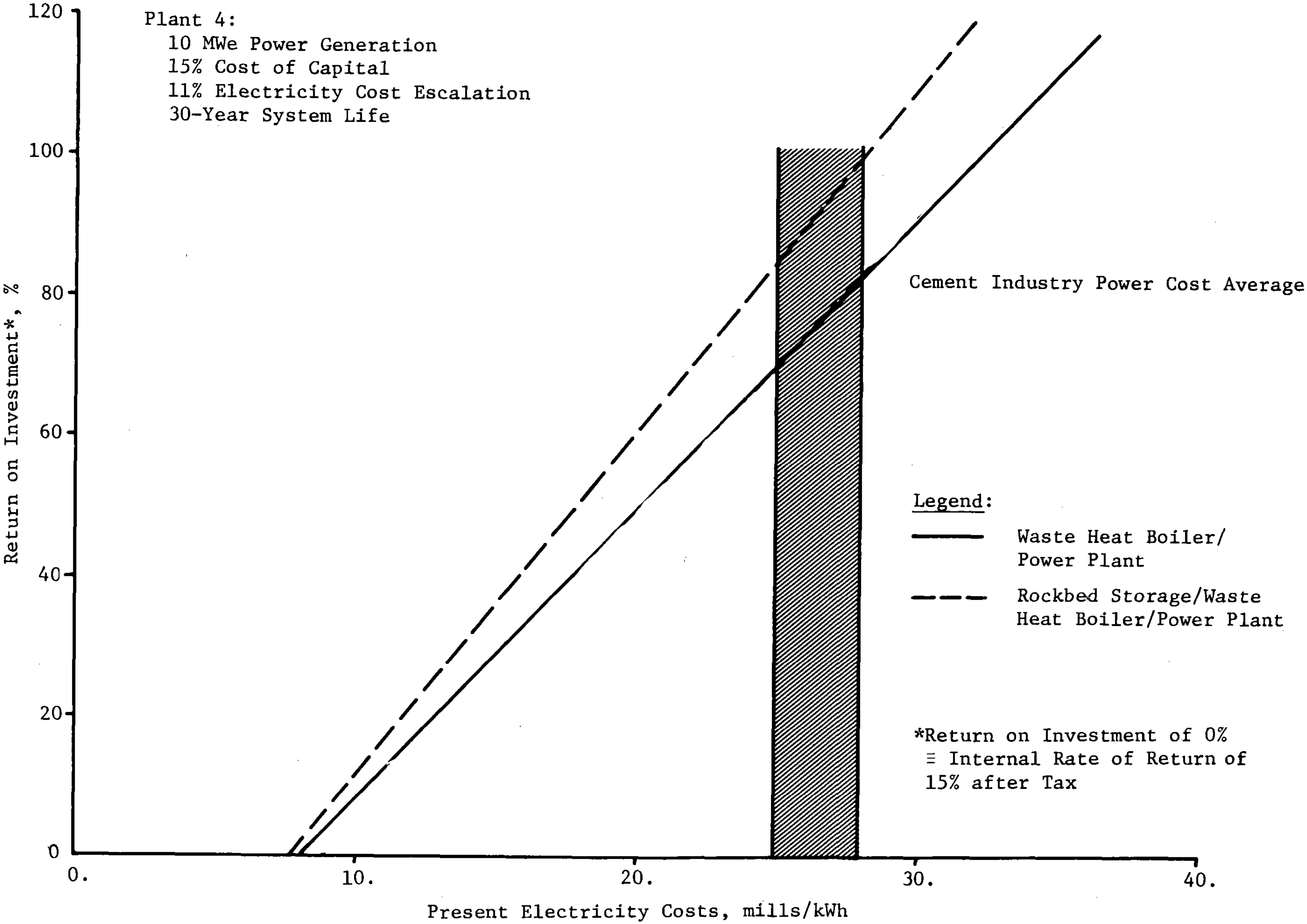

Figure 2. Return on Investment - Plant 4

III. CONCLUSIONS

This study has shown that the use of thermal energy storage in conjunction with waste heat power generation in the cement industry can save up to 6.7 million barrels of oil per year and provide an attractive rate of return on investment. Specific conclusions reached in each portion of study are discussed in the following paragraphs.

Sources of Waste Heat - The dry process kilns were determined to be the only practical sources of waste heat as opposed to the wet process kilns whose lost energy is at too low a temperature to be of major use within the plant. Of the types of dry process kilns, the long dry kilns have the highest quality and quantity of recoverable energy, followed by the single-stage suspension preheater, and the four-stage suspension preheater. Of the sources of waste heat in each plant, the kiln exit gas was the best source. It contains 80% of the waste heat and is the highest temperature source in the plant. The clinker cooler exhaust gas was also found to be a practical source of heat used in conjunction with the kiln exit gas system. The heat in each of these sources is concentrated and easily recoverable.

Uses for the Waste Heat - The use of the kiln exit gas and clinker cooler gas to generate electricity for use in the cement plant was found to be the most effective of the methods considered.

Storage System Selection - A rockbed-type storage system was found to be the most economical type of storage. This system could use granite, cement clinker or limestone as the storage medium.

System Size and Performance - System size and performance was determined for storage systems using the four typical plant models. The size of the equipment was within that normally fabricated for other uses and the performance can easily meet the requirements of the plant operation. No problems were encountered in physically locating and installing the system in any of the plants. The system could be installed with only a few days or weeks of halted production.

Economic Analysis - Generation of electricity using waste heat is economically attractive for long dry and single-stage preheater kilns. Assuming an 11% escalation rate in the cost of electricity, a 15% after tax cost of capital and a 25 mil/kWh of electricity, the ROI is 50% for the long dry kiln (Plant 1) and 35% for the single-stage preheater kiln (Plant 3).

Development Program - Some technical questions exist relative to the feasibility of the rockbed. It is recommended that a development program be undertaken to answer those technical questions pertaining to the rockbed system and then to demonstrate commercial operation with a ¼ scale system in a cement plant.

Thermochemical Energy Storage and Transport Overview

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Introduction:

Under the DOE's program to decentralize the implementation of its Energy Technology policy to field offices and national laboratories, Sandia Laboratories, Livermore, has been assigned program management responsibilities for the Thermochemical Energy Storage and Transport (TEST) Program. The TEST Program investigates reversible thermochemical reaction technologies as they apply to the storage and movement of thermal energy. All classes of reactions are considered with the exception of hydrogen generating and photochemical reactions. The objective of the program is to initiate and develop those concepts and reactions couples which can provide commercially viable solutions to energy storage and transport problems at the earliest possible date.

Program Structure

The TEST Program has been divided into four technology elements according to a Technical Breakdown Structure (Figure 1). The four TBS elements are: (1) thermal energy storage, (2.0) thermochemical pipelines, (3.0) chemical heat pump storage, and (4.0) generic research. Each of these major elements has been futher divided into subelements which represent specific concepts or applications being pursued.

Thermochemical energy technology (TBS 1.0) is being considered for both solar and nonsolar electric utility applications. Activities to date have consisted of both: (1) systems studies to establish the technical and economic viability of proposed concepts, and (2) parallel laboratory investigations of promising reactions for which more information is required to enable more detailed evaluations to be made.

Emphasis for the thermochemical pipelines portion of the program (TBS 2.0) have been on systems studies and component development. Studies of both open-loop and closed-loop pipelines have been conducted for a variety of energy sources including nuclear, fossil energy and solar. Promising reactions have been identified and applications requiring additional study have been noted. In one case where the reaction technology was well understood (methane steam reforming) a major hardware development activity has been initiated.

THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT PROGRAM

TECHNOLOGY BREAKDOWN STRUCTURE

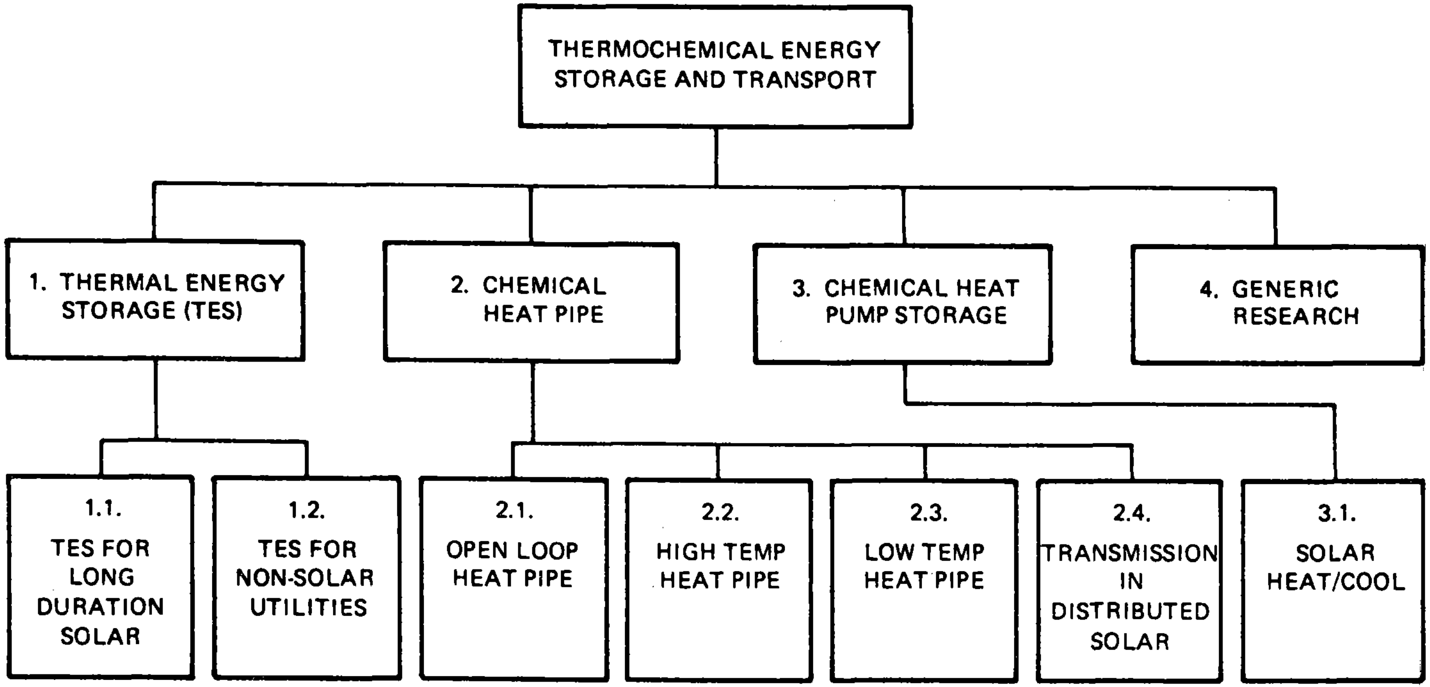


FIGURE 1

Following a preliminary analysis of the potential of chemical heat pump storage systems (TBS 3.0), experimental investigations of several attractive concepts were initiated. Closed-loop operation of a prototype configuration has been demonstrated for one concept, and laboratory results to date suggest the other concepts are viable alternatives.

Generic research (TBS 4.0) consists of catalyst development, heat transfer investigations, and laboratory investigations of promising reaction systems.

Project Activity

In this section, the objectives of each TBS subelement are discussed and the projects and schedules required to meet these objectives are described.

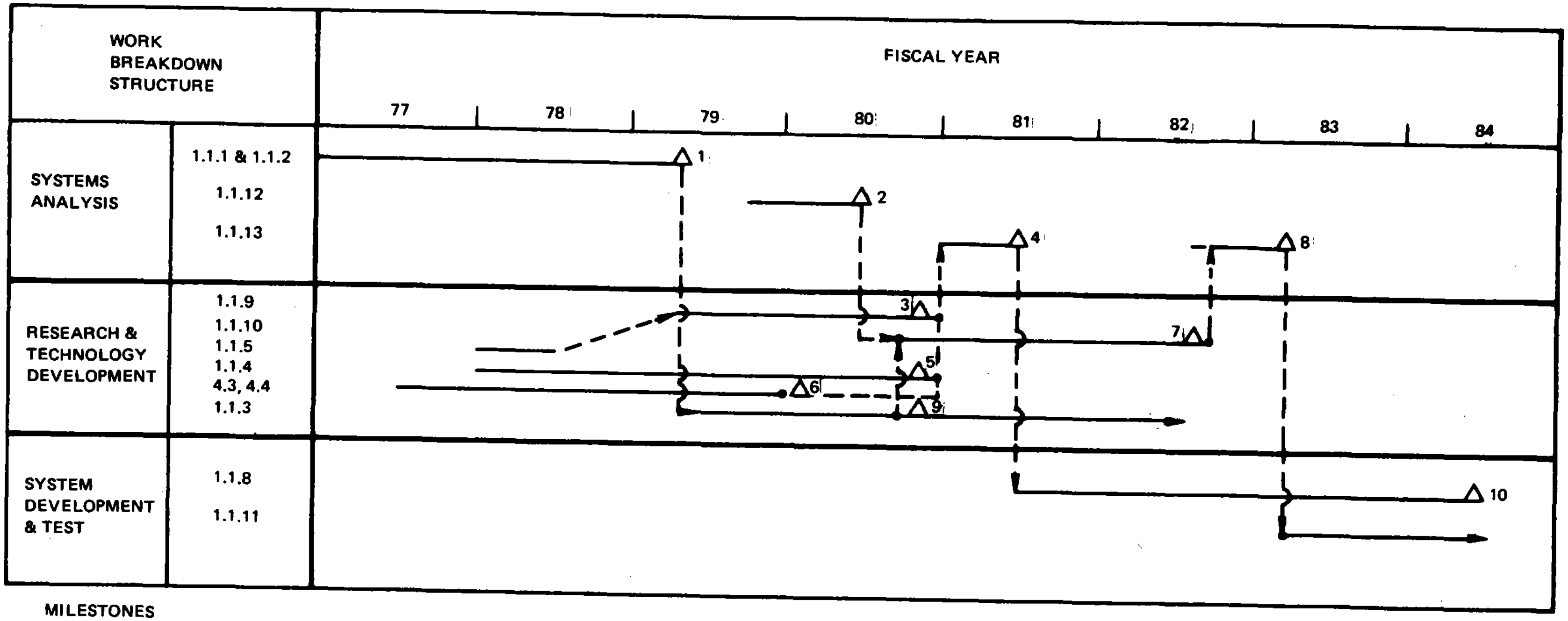
TES for Solar Utilities (TBS 1.1) -- The objectives of this subelement are to assess and develop thermochemical storage technologies on a schedule compatible with the development schedules for solar thermal electric conversion systems. Because the solar thermal electric conversion systems actually chosen for large scale demonstration will depend upon the results of a number of ongoing solar programs, it is essential to carry on a number of parallel investigations of promising thermal energy storage concepts. The coordination, interaction, and anticipated results of these various activities are depicted in Figure 2.

The systems analysis (1.1.1) of selected solar thermal electric power plants, and investigations of several first generation chemical reactions (1.1.4, 4.3, 4.5 and 1.1.9) will continue in FY79. New programs in FY79 are a systems analysis of more advanced solar thermal electric power plants (1.1.12) and initial laboratory investigations (1.1.3) of promising additional chemical reaction systems. Results from these two activities may lead to the initiation of a development activity for a second generation TES system (1.1.10) in mid FY80. In late FY80 results from (1.1.9, 1.1.4, 4.3 and 4.5) will be assessed (1.1.3), leading to a decision by mid FY81 of whether to proceed to a Subsystem Development and Test activity (1.1.9) for the first generation TES system. This activity will be completed in FY84. The schedule for second generation system lags behind the first generation program by approximately 1-1/2 years.

TES for Non-Solar Electric Utilities (TBS 1.2) -- The objectives of this subelement are to assess and develop energy storage and transport technologies for use in nonsolar electric utilities. The second phase of a systems study (1.2.1) which is identifying potential energy source/chemical reaction/end user combinations will continue in FY79. Depending upon the outcome of that study, development of appropriate concepts may be initiated in FY80. At that time, long-range plans consistent with the schedules of the selected users will be developed.

Open-Loop Thermochemical Pipelines (TBS 2.1) -- This subelement is concerned with the development of open-loop energy transport systems. Initial work in FY79 will be conducted as part of the Sandia in-house research program, and will consist of a reassessment of previous work (2.1.1)

TES FOR SOLAR UTILITIES TBS 1.1



MILESTONES

1 – TECHNICAL & ECONOMIC FEASIBILITY OF TES FOR 3 SOLAR THERMAL SYSTEMS; IDENTIFICATION OF 1 OR MORE REACTIONS FOR FURTHER INVEST
2 – SAME AS 1, BUT FOR ADVANCED SOLAR THERMAL SYSTEMS
3 – LAB SCALE INVESTIGATIONS COMPLETED FOR SELECTED REACTIONS; INFORMATION REQUIRED FOR MORE REFINED SYSTEMS MODELING AVAILABLE
4 – DETAILED ANALYSES COMPLETE; DECISION TO PROCEED TO SYS. DEV. & TEST
5 – LAB SCALE INVESTIGATIONS FOR AHS COMPLETE
6 – SO_2/SO_3 CATALYST DEVELOPMENT COMPLETE
7 – LAB SCALE INVESTIGATIONS FOR SECOND GENERATION TES SYSTEMS COMPLETE
8 – MORE DETAILED SYSTEMS MODELING; DECISION TO PROCEED TO SYS. DEV. & TEST
9 – POTENTIAL REACTIONS IDENTIFIED FOR SECOND GENERATION SYSTEMS

Figure 2

in light of current DOE guidelines. Research and technology development of a coal gasification based system (2.1.3) could be demonstrated on a large scale by late FY83, as indicated in Figure 3, in ample time to provide an alternative to other coal gasification schemes.

In mid FY79 to early FY80 a study (2.1.4) to determine the possibility of interfacing open-loop thermochemical pipelines and advanced solar systems will be initiated. System identification and development could begin in early FY81 with large scale demonstration by late FY84.

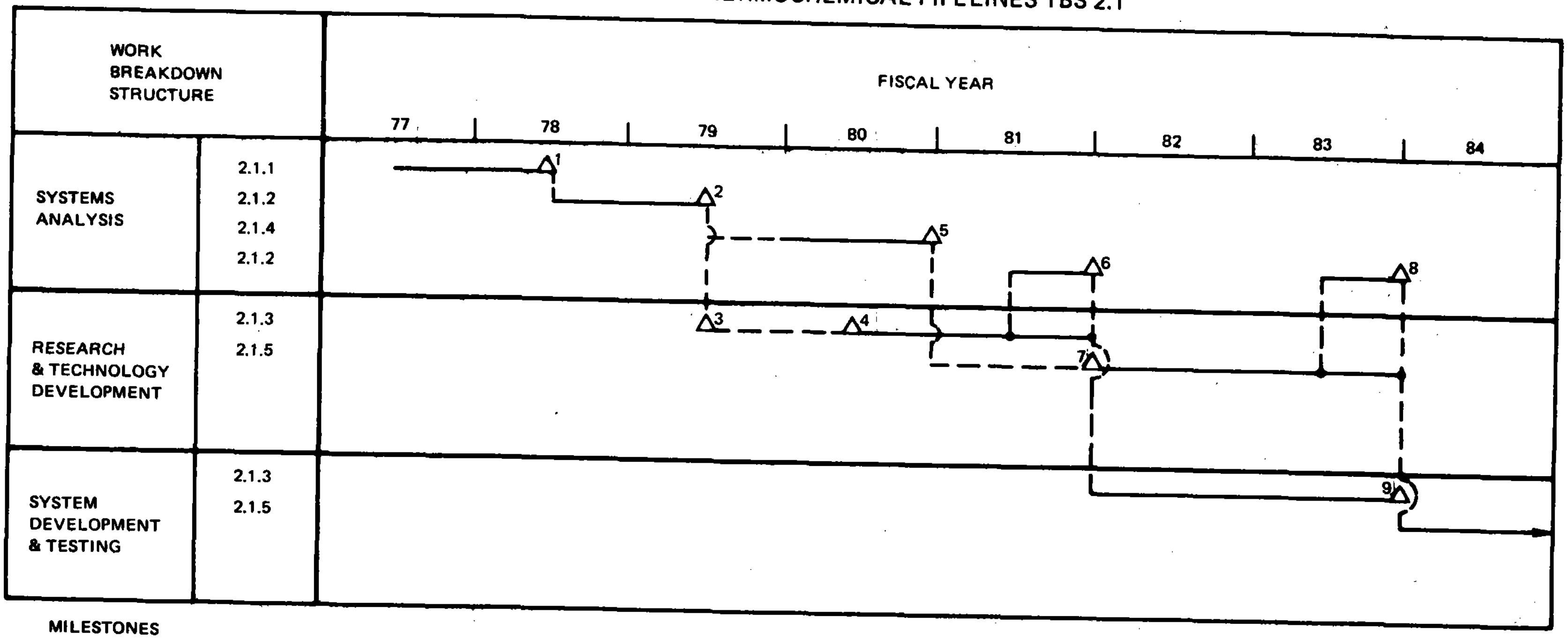
High Temperature Thermochemical Pipelines (TBS 2.2) -- FY79 activities in this subelement are addressing two areas. The first of these is the development of a duplex steam reformer (2.2.2) for interfacing a thermochemical pipeline with a high temperature gas cooled reactor. This activity, which is being supported jointly by the United States and Germany, will be completed in FY80.

The second activity (2.2.5), which will be addressed initially in the Sandia in-house research program will assess the feasibility and desirability of interfacing a high temperature thermochemical pipeline with a solar central receiver energy source. Assuming positive results from this study, an RFQ will be prepared in FY80. Although development is feasible by FY84, (see Figure 4) the actual schedule will be established following the completion of 2.2.5. This program will be in parallel with the development of the solar interfaced open-loop thermochemical pipeline (2.1.4). Depending on the systems identified, the two programs could be combined into one.

Low-Temperature Thermochemical Pipelines (TBS 2.3) -- The objective of this subelement is to develop low-temperature technologies for energy transport systems which may be interfaced with nuclear or solar energy sources. Activities in FY79 and 80 will establish the feasibility of using the benzene/cyclohexane reaction (2.3.1) for energy transport. In FY80, a detailed characterization of the potential market will be initiated (2.3.4), and preliminary investigations of alternate reactions will begin (2.3.5). A critical reassessment of the concept will be conducted in FY80, and this, in conjunction with the results from (2.3.1), (2.3.4), and (2.3.5) will provide the information required to reach a decision regarding large scale system development and test (2.3.2). The target for large scale demonstration is FY83, subject to re-evaluation as the early studies are completed (see Figure 5).

Transmission in Distributed Solar Systems (TBS 2.4) -- The objective of this subelement is to develop energy transport systems for distributed solar systems. Activities in FY79 will be conducted in-house, and will consist of a preliminary analysis of the concept, the identification of required research, and the preparation of an RFQ for a more detailed systems analysis (2.4.1). In FY80, a more detailed analysis (2.4.1) will be performed in parallel with laboratory investigations of potential reaction systems (2.4.2). In FY81, a comparison of the various concepts will be made (2.4.3) and, if warranted, the project will proceed to the System Development and Test stage (2.4.4). Figure 6 presents the schedule for this TBS. This schedule is quite tentative, with considerable interaction between Sandia, JPL and SERI envisioned.

OPEN LOOP THERMOCHEMICAL PIPELINES TBS 2.1

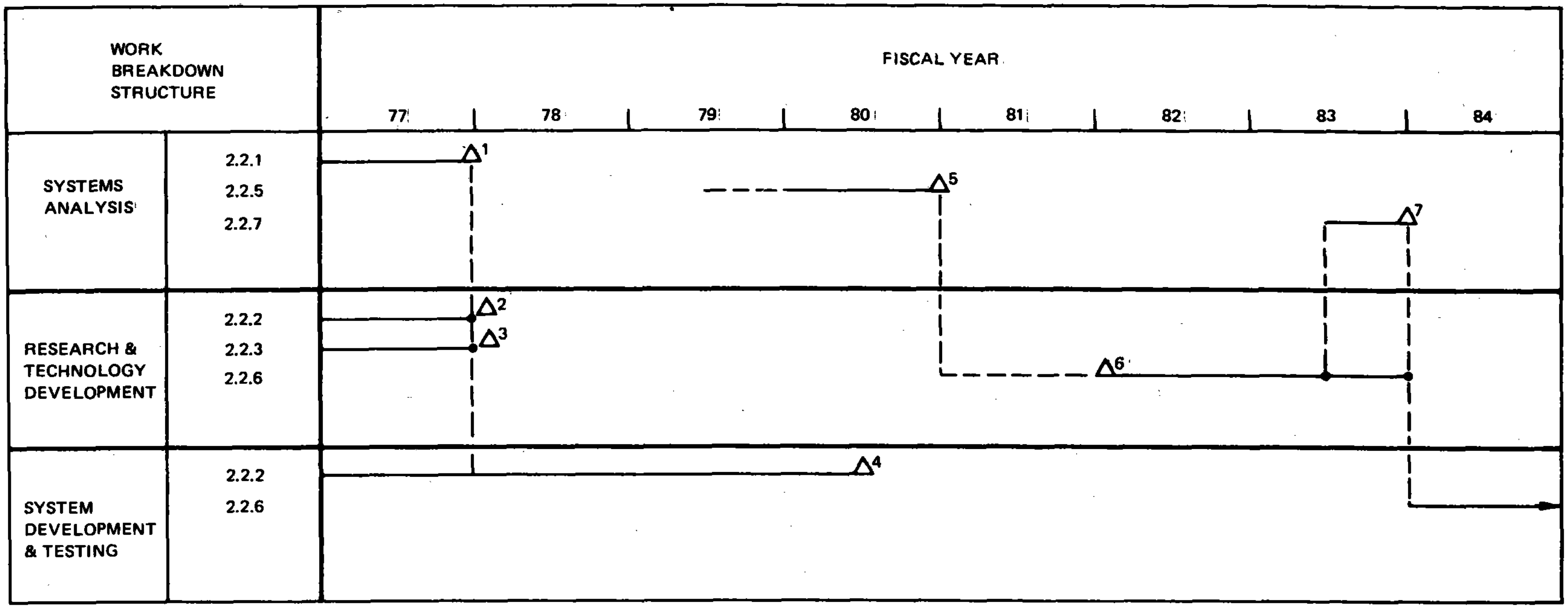


MILESTONES

1 – TECHNICAL AND ECONOMIC FEASIBILITY OF OPEN-LOOP THERMOCHEMICAL PIPELINE CONCEPT ESTABLISHED
2 – 2.1.1 REASSESSED, AND, IF WARRANTED, RFQ PREPARED
3 – RFQ ISSUED
4 – CONTRACT AWARDED FOR RESEARCH AND TECHNICAL DEVELOPMENT OF METHANE-BASED SYSTEM
5 – INTERFACE OF OPEN-LOOP THERMOCHEMICAL PIPELINES AND SOLAR SYSTEMS EVALUATED, RFQ ISSUED, IF WARRANTED
6 – RE-EVALUATION OF METHANE-BASED SYSTEM AND DECISION TO PROCEED WITH SYSTEM DEVELOPMENT
7 – CONTRACT AWARDED FOR SOLAR INTERFACED SYSTEM TECHNOLOGY DEVELOPMENT
8 – RE-EVALUATION OF SOLAR INTERFACED SYSTEM AND DECISION TO PROCEED WITH SYSTEM DEVELOPMENT
9 – METHANE-BASED OPEN-LOOP THERMOCHEMICAL PIPELINE CONCEPT READY FOR COMMERCIALIZATION

Figure 3

HIGH TEMPERATURE THERMOCHEMICAL PIPELINES TBS 2.2



MILESTONES

1 – FEASIBILITY OF THERMOCHEMICAL PIPELINE ESTABLISHED

2 – DECISION TO PROCEED WITH SYSTEM DEVELOPMENT

3 – ALTERNATE CATALYST DESIGN COMPLETED AND EVALUATED

4 – TEST EVALUATION REPORT ISSUED

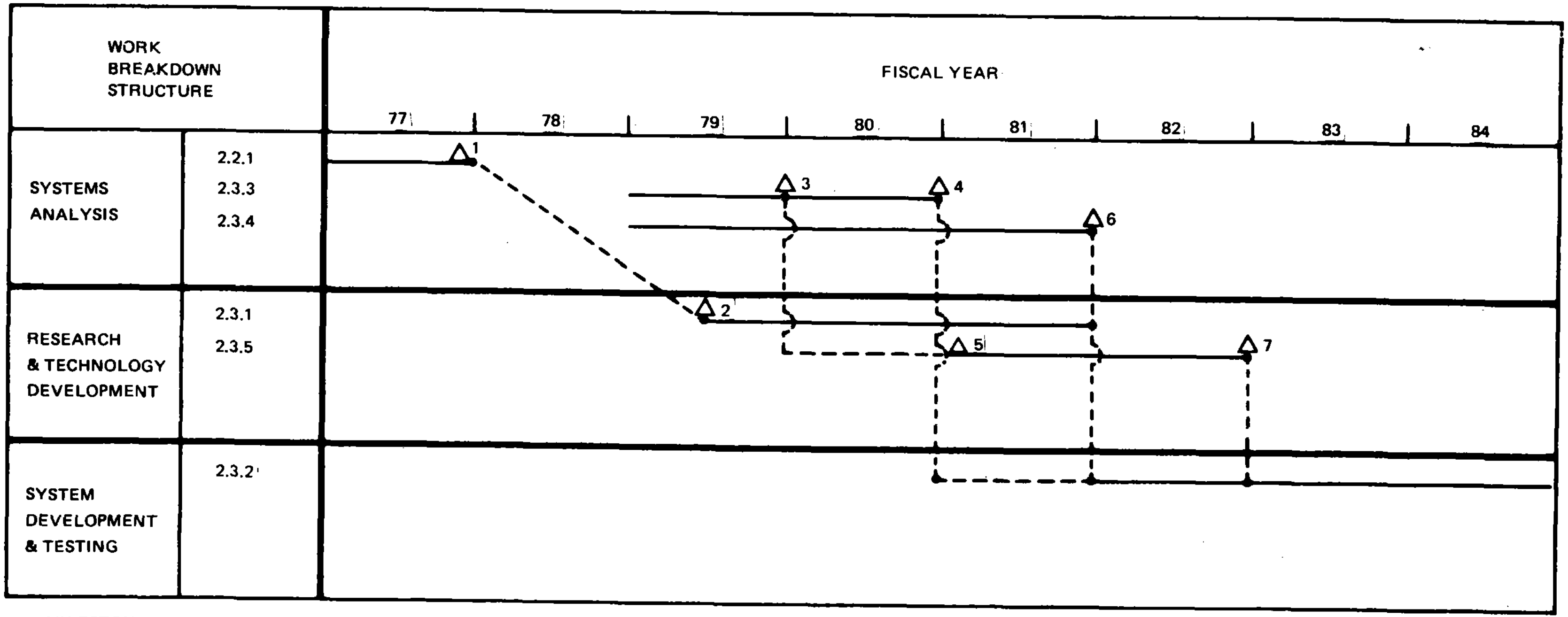
5 – SOLAR INTERFACED HIGH TEMPERATURE THERMOCHEMICAL PIPELINE EVALUATED, RFQ ISSUED, IF WARRENTED

6 – CONTRACT AWARDED FOR SOLAR INTERFACED HIGH TEMPERATURE THERMOCHEMICAL PIPELINE TECHNOLOGY DEVELOPMENT

7 – RE-EVALUATION OF SOLAR INTERFACED SYSTEM AND DECISION TO PROCEED WITH SYSTEM DEVELOPMENT

Figure 4

LOW TEMPERATURE THERMOCHEMICAL PIPELINES TBS 2.3

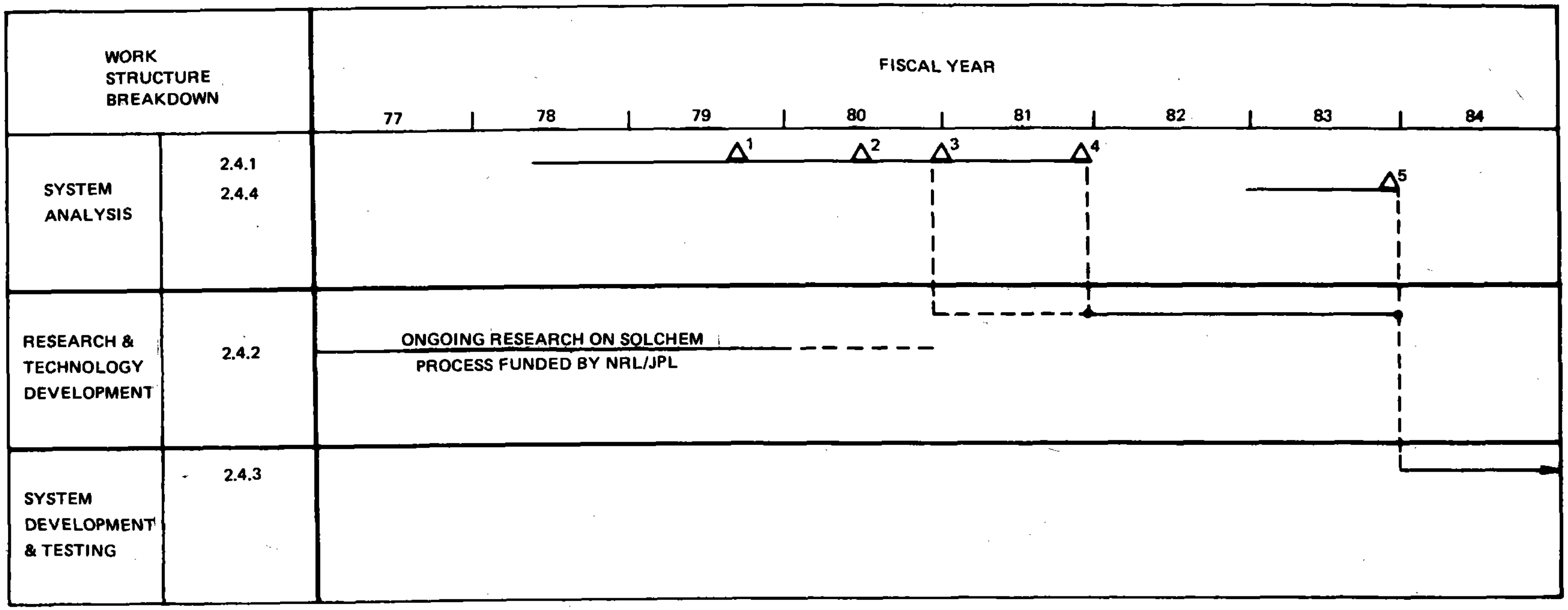


MILESTONES

1 – TECHNICAL AND ECONOMIC FEASIBILITY OF THERMOCHEMICAL PIPELINE ESTABLISHED
2 – CONTRACT AWARDED FOR BENZENE/CYCLOHEXANE TECHNOLOGY DEVELOPMENT
3 – RFQ ISSUED FOR ALTERNATE REACTION(S) TECHNOLOGY DEVELOPMENT
4 – RFQ ISSUED FOR LOW TEMPERATURE THERMOCHEMICAL PIPELINE SYSTEM DEVELOPMENT
5 – CONTRACT AWARDED FOR ALTERNATE REACTION(S) TECHNOLOGY DEVELOPMENT
6 – MARKET ANALYSIS COMPLETE, DECISION TO PROCEED WITH SYSTEM DEVELOPMENT
7 – ALTERNATE REACTION(S) ASSESSED AND FINAL SYSTEM FOR DEVELOPMENT SELECTED

Figure 5

TRANSPORT IN DISTRIBUTED SOLAR SYSTEMS TBS 2.4



MILESTONES

1 – RFQ ISSUED FOR DETAILED SYSTEMS ANALYSIS AND REACTION(S) IDENTIFICATION
2 – CONTRACT AWARDED FOR SYSTEMS ANALYSIS
3 – RFQ ISSUED FOR RESEARCH AND TECHNOLOGY DEVELOPMENT OF ALTERNATE REACTION SYSTEMS
4 – CONTRACT AWARDED
5 – DECISION TO PROCEED WITH SYSTEM DEVELOPMENT TO PROTOTYPE STAGE

Figure 6

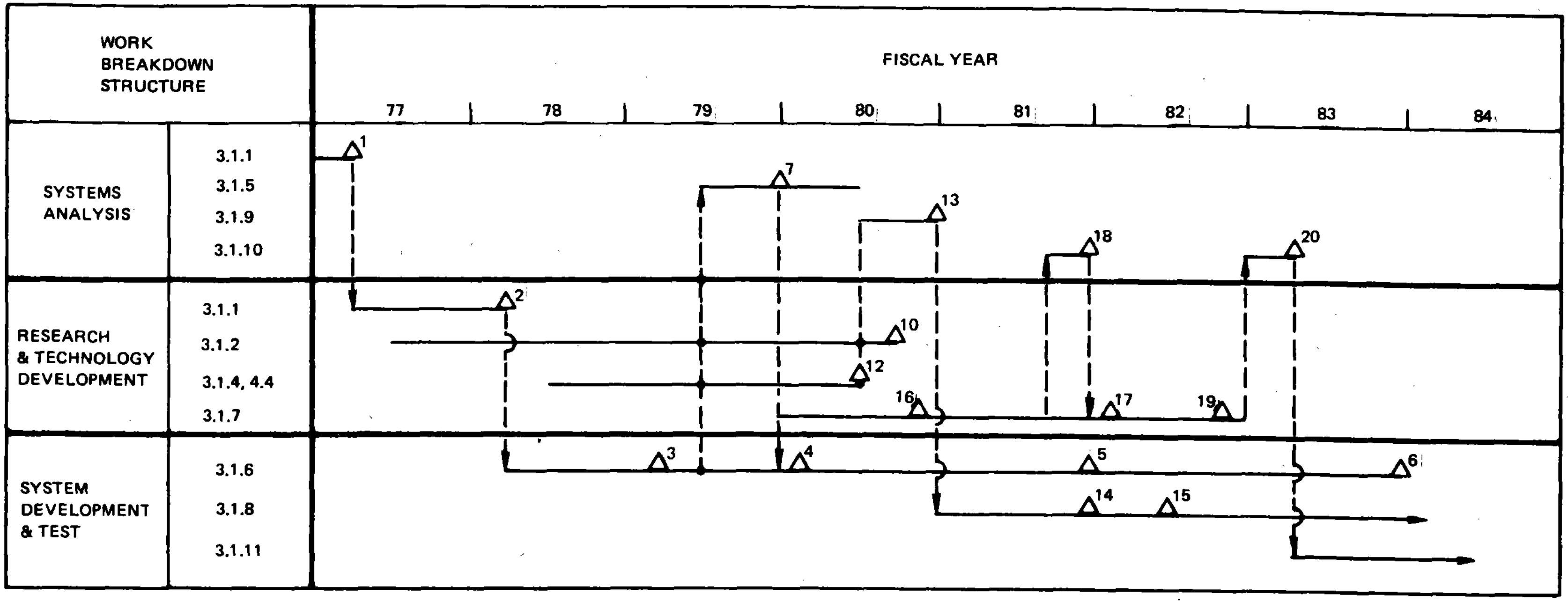
Chemical Heat Pump Storage (TBS 3.1) -- The objective of the subelement is to develop chemical reaction systems for use as chemical heat pump storage systems. In FY79, experimental activities will concentrate on the sulfuric acid (3.1.1), methanolate (3.1.2), and ammoniate (3.1.4, 4.4) systems. Systems analyses conducted in FY79 (3.1.4) will assess the potential of the sulfuric acid system and, coupled with the initial results of (3.1.6), will determine whether (3.1.6) is carried to the large scale development phase. Also part of (3.1.5) will be an evaluation of 3.1.2 and 3.1.4 which may lead to a demonstration project (3.1.8). The results of a workshop held in the first quarter of FY79 will be used to formulate an RFQ for advanced systems (3.1.7). This work will be conducted in FY80 and 81, and examined in detail in later FY80 (3.1.9). If warranted, closed loop demonstration will be conducted in FY82 and analyzed in FY82 (3.1.10). Figure 7 presents the schedule for this activity.

Generic Research (TBS 4.0) -- Long range activities in the program subelement depend upon the evolution of the program. In FY79, they consist of a study of the fundamental processes occurring in gas/solid TGS systems (4.12), SO_2/SO_3 catalyst development (4.3), and research on ammoniated salts (4.4).

Project Status:

Table I gives a brief description of each of the current TEST projects and provides a listing of the contractors and documentation status. Activities summarized include systems studies, basic research, and large scale component development projects for a number of chemical reaction systems and a variety of energy sources and applications. It is anticipated that as more information is obtained regarding the reaction systems, energy sources, and applications, the emphasis of the TEST program will shift from studies of this type to the large scale demonstration of the more promising concepts.

CHEMICAL HEAT PUMP STORAGE TBS 3.1



MILESTONES

1 – H_2SO_4 CHEMICAL HEAT PUMP CONCEPT IDENTIFIED
2 – COMPONENT DEVELOPMENT COMPLETE; CLOSED-LOOP OPERATION DEMONSTRATED
3 – COMP. OPTIMIZATION & TRANSIENT TESTING COMPLETE
4 – PROTOTYPE DESIGN COMPLETE
5 – PROTOTYPE FABRICATION & TEST COMPLETE; SECOND GENERATION SYSTEM DESIGNED
6 – SECOND GEN. FAB. & TEST COMPLETE
7 – MARKET POTENTIAL FOR H_2SO_4 ESTAB.; TECH. EVALUATION OF GAS/SOLID SYSTEMS COMPLETE
8 – CANDIDATE METHANOLATES IDENTIFIED
9 – METHANOLATE CHARACTERIZATION & HEAT TRANSFER EXPMTS. COMPLETE
10 – CLOSED-LOOP SYSTEM DEMONSTRATION
11 – AMMONIATE CHARACTERIZATION & HEAT TRANSFER EXPMTS. COMPLETE
12 – CLOSED-LOOP DEMONSTRATION
13 – COMPARATIVE EVALUATION OF GAS/SOLID HEAT PUMPS
14 – COMPONENT OPTIMIZATION COMPLETE
15 – DETAILED PROTOTYPE DESIGN COMPLETE
16 – ALTERNATIVE CHEMICAL SYSTEMS IDENTIFIED
17 – CHEMISTRY OF ALTERNATIVE SYSTEMS CHARACTERIZED
18 – SELECTION OF ADVANCED SYSTEMS FOR CLOSED-LOOP DEMONSTRATION
19 – CLOSED-LOOP DEMONSTRATION COMPLETE
20 – SELECTION OF ADVANCED SYSTEM FOR SYSTEM DEV. & TEST

Figure 7

Table I TEST Project Status

TBS	Project	Contractor	Documentation
1.1.1	Extended Storage Feasibility - a system study to evaluate the technoeconomic feasibility of thermochemical storage concepts in solar energy systems	RRC	Several technical papers; final report due January 1979
1.1.2	Extended Storage Feasibility - an activity complementary to activity 1.1.1	SLL	Several technical papers
1.1.4	Ammonium Hydrogen Sulfate Decomposition - to develop an energy storage concept based upon the decomposition of ammonium hyrogen sulfate	U of H	Several technical papers; draft final report due
1.1.5	$Ca(OH)_2/CaO$ Reaction - to develop an energy storage concept based upon the hydration and dehydration of CaO and Ca(OH) respectively	AI	Draft report received February 78
1.1.6	High Temperature Storage and Heat Pipe Analysis - system studies to formulate and evaluate operational chemical cycles	LBL	Final draft report expected October 78
1.2.1	TES for Non-Solar Electric Utilities - a system study to evaluate the technoeconomic potential of thermochemical storage concepts in current and near near electric utilities	Gilbert Associates	Draft final report received and reviewed August 78

Table I TEST Project Status (Con't)

TBS	Project	Contractor	Documentation
2.1.1	Open Heat Pipe Feasibility - a system study to determine the technoeconomic feasibility of the open-loop methane-based heat pipe	IGT	Final report approved August 78
2.2.1	Heat Pipe Feasibility - a systems study to determine the technical and economic feasibility of chemical heat pipes	GE/CRD	Final report approved August 78
2.2.2	Duplex Steam Reformer - to test and evaluate the duplex steam reformer concept at the very high temperature reactor at the Kernforschungsanlage facility in Germany	GE/ESPD	Several interim reports
2.2.4	CH_4/CO Heat Pipe Solar - a system study to assess the potential of using solar central receivers as the thermal energy source for a methane based heat pipe	U of H	Draft final report past due

Table I TEST Project Status (Con't)

TBS	Project	Contractor	Documentation
3.1.1	Sulfuric Acid Concentration/Dilution - a chemical heat pump system based on the concentration/dilution of sulfuric acid will be developed	RRC	Draft final report for Phase 2 received and reviewed March 78. Revision expected November 78
3.1.2	Methanol-Salt System - a chemical heat pump storage system using methanolated salt reactions will be developed	EIC	Draft final report for Phase I received and reviewed August 78. Revision expected November 78
3.1.3	Hydrated Salt Heat Pump - a chemical heat pump storage system based on hydrated salts, $MgCL_2 \cdot XH_2O$ in particular will be pursued	CES	Final report received January 78
3.1.4	Ammoniated Salt Heat Pump - to develop a chemical heat pump system based upon the use of coupled ammoniated salt reactions	MM	---

Table I TEST Project Status (Con't)

TBS	Project	Contractor	Documentation
4.1	Heat Transfer - experimentally obtain heat transfer correlations in packed beds	MM/CSU	Final report received and approved
4.2	Thermal Decomposition Kinetic Studies - an investigation of fundamental processes occurring in gas/solid systems	UCD	Interim report past due
4.3	SO_3/SO_2 Catalyst Development - assess the applicability of current catalysts for use in the SO_3/SO_2 system, and develop new catalyst if required	RRC	--
4.8	In-House R&D	SLL	--

PROJECT SUMMARY

Project Title: Chemical Energy Storage for Solar Thermal Conversion

Principal Investigator: Richard D. Smith

Organization:
Rocket Research Company
York Center
Redmond, Washington 98052
(206) 885-5000

Project Goals: Evaluation from a total system point-of-view of the concept of thermal energy storage by reversible chemical reaction for Solar Thermal Electric Conversion (STEC) applications.

Project Status: The purpose of this study is: (1) to identify potential chemical reactions capable of operating at one of three nominal temperatures (588, 783, or 1310°K), and to tabulate their physical, thermochemical, and kinetic properties; (2) to conceptually design storage subsystems for specified solar thermal electric power plants for selected reactions; and (3) to establish the technical and economic feasibility of using thermal energy storage subsystems to extend solar thermal electric systems to baseload capability.

Fourteen attractive systems were identified by the reaction screening. Preliminary estimates of the associated power and energy costs and system performance were made to arrive at this selection. Storage subsystems based upon the reactions have been designed to provide more accurate cost and performance data for use in a computer model of a stand-alone, or grid independent, power plant.

A final report is being prepared for review.

Contract Number:
SLL 18-2563
NSF AER 75-22176

Contract Period: July 1, 1976 through January 31, 1979

Funding Level:
SLL 149,816
NSF 120,900

Funding Source:
Sandia Laboratories, Livermore, California
National Science Foundation

CHEMICAL ENERGY STORAGE FOR SOLAR THERMAL ELECTRIC CONVERSION

Principal Investigator: Dr. Richard D. Smith
Rocket Research Company
Redmond, WA 98052

OBJECTIVES

The overall objective of this program is the evaluation on a total system basis of the concept of chemical energy storage for Solar Thermal Electric Conversion (STEC) applications. Included in this overall objective are:

i) Determination of performance and cost requirements for chemical energy storage subsystems used in STEC power plants

ii) Examination of the technical and economic feasibility of extending STEC operation to baseload power generation by use of long-term chemical energy storage

iii) Identification of promising chemical reactions for such storage applications, and preliminary design and evaluation of storage subsystems based on these reactions.

APPROACH

The first part of the original NSF contract (Fig. 1) involves selection of promising reactions, tabulation of thermodynamic and kinetic properties for these reactions, and division of the reactions selected into a low-temperature group (400 to 950°K) and a high-temperature group (950 to 1,500°K), according to the estimated operating temperature range of each reaction. Part 2 of the NSF effort involves more detailed study and evaluation of the two most promising reactions.

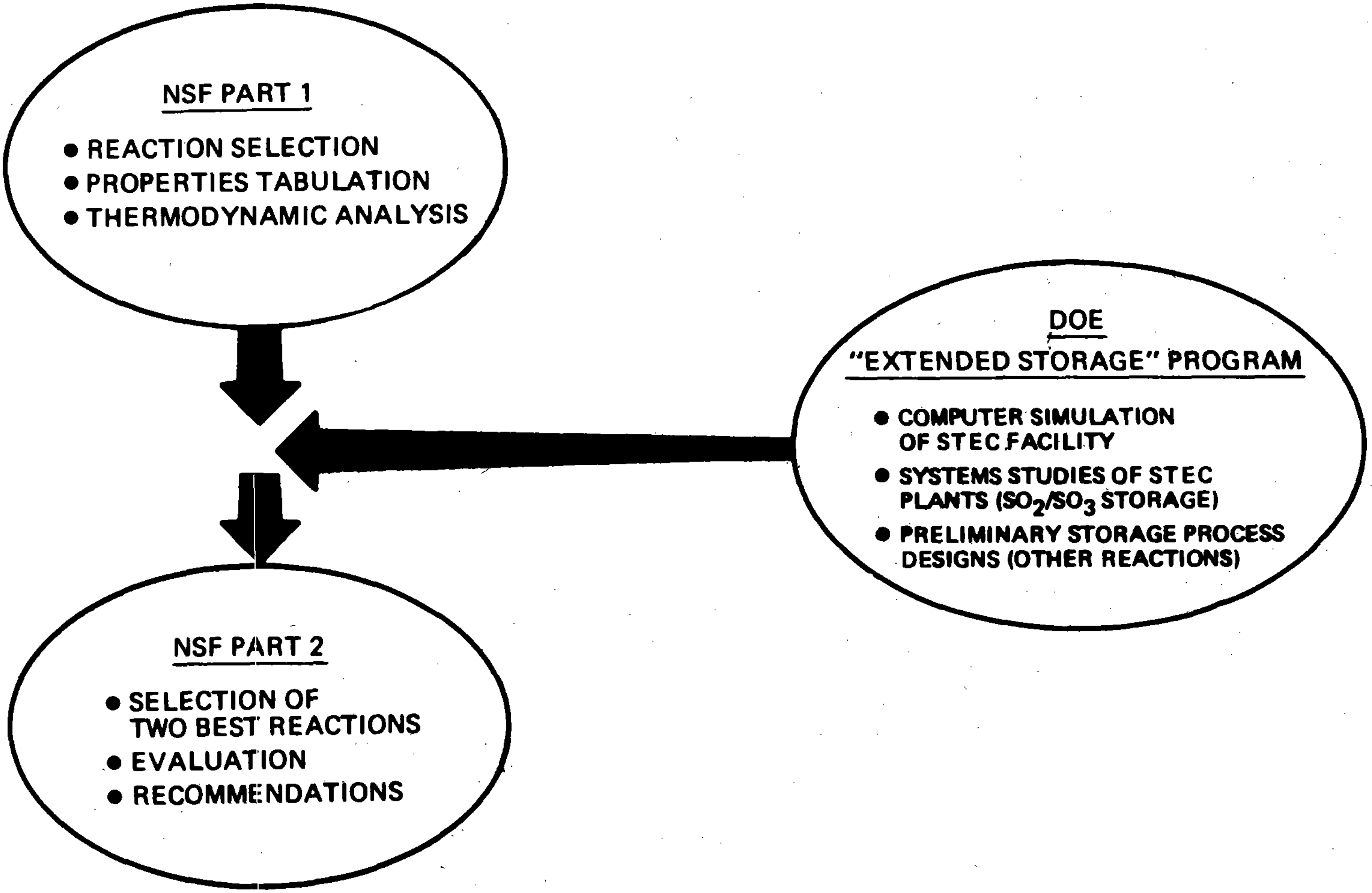
To examine the performance capabilities, size and cost of STEC facilities using long-term, chemical energy storage and to provide a more system-oriented basis for selecting the most promising reactions for further study, the add-on contract (SLL 18-2563) was inserted between parts 1 and 2 of the original NSF effort. The add-on effort involves creation and use of a computer simulation of a STEC facility for systems studies of STEC plants with storage subsystems based on the reversible oxidation of SO_2. In addition, preliminary process designs of chemical energy storage subsystems based on other promising reactions are to be developed.

ACCOMPLISHMENTS

At present, the second part of the NSF effort is about half completed, with the selection of the two most promising reactions having been made during the preceding month. Part 1 of the NSF effort and the entire add-on effort are complete.

The simulation code (Fig. 2) is based on an hour-by-hour energy balance on the entire STEC facility and can model autonomous (100 percent solar) as well as hybrid (solar with alternate energy backup) STEC operation. In the case of the hybrid model, the code automatically finds the optimum solar/alternate mix, based on minimum busbar energy cost (BBEC). Important outputs of the code include busbar energy cost, optimum collector area and storage capacity necessary to satisfy a specified demand, and storage operating requirements.

INTEGRATION OF "EXTENDED STORAGE" PROGRAM WITH NSF "CHEMICAL ENERGY STORAGE FOR SOLAR THERMAL CONVERSION" PROGRAM



NSF PART 1

- REACTION SELECTION
- PROPERTIES TABULATION
- THERMODYNAMIC ANALYSIS

DOE
"EXTENDED STORAGE" PROGRAM

- COMPUTER SIMULATION OF STEC FACILITY
- SYSTEMS STUDIES OF STEC PLANTS (SO_2/SO_3 STORAGE)
- PRELIMINARY STORAGE PROCESS DESIGNS (OTHER REACTIONS)

NSF PART 2

- SELECTION OF TWO BEST REACTIONS
- EVALUATION
- RECOMMENDATIONS

Figure 1

STEC COMPUTER SIMULATION

- OPERATING MODES
    - AUTONOMOUS (100% SOLAR)
    - HYBRID (SOLAR/ALTERNATE BACKUP)
- STEC SYSTEM MODELS
    - CENTRAL RECEIVER/STEAM RANKINE
    - CENTRAL RECEIVER/BRAYTON
    - DISTRIBUTED/STEAM RANKINE
- INSOLATION/DEMAND
    - INSOLATION – YEARLY, HOUR-BY-HOUR
        - MIAMI, FLORIDA (SE)
        - MADISON, WISCONSIN (NC)
        - ALBUQUERQUE, NEW MEXICO (SW)
        - NEW YORK, NEW YORK (NE)
    - DEMAND – YEARLY, HOUR-BY-HOUR, SAME LOCATIONS
- OUTPUT INCLUDES
    - BUSBAR ENERGY COST (BBEC)
    - COLLECTOR AREA/STORAGE CAPACITY
    - STORAGE AND FRONT-END OPERATING REQUIREMENTS

Figure 2

A series of systems studies of STEC facilities (with storage oxidation of SO_2) have been conducted as part of the add-on effort. These studies, as well as the STEC simulation itself, have been described in detail in a previous paper [1] and will not be discussed here. However, several important results of these systems studies directly influenced the preliminary storage process designs discussed below and therefore bear mentioning:

- Optimum storage requirements for autonomous operation of STEC power plants which satisfy continuous baseloads are in the range of 150 to 300 hours.
- Hybrid operation of STEC power plants appears to be an economically attractive alternative where maximum fossil fuel displacement is not a criterion, and requires storage capacities of 15 to 30 hours.
- Maximum storage charge rate is greater than maximum storage discharge rate in all autonomous and most hybrid cases of interest.

The reaction evaluation and selection procedure has been described in detail elsewhere [2]. Suffice it to say that systematic evaluation of approximately 550 candidates yielded a list of the 12 most promising reactions for further study under the add-on contract. Table 1 presents a summary of the disposition of the 12 reactions originally considered for design studies. Preliminary storage process designs and cost estimates for 9 of the 12 reactions have been developed, with the cost and efficiency estimate for the NH_4HSO_4 system pending publication of the results of other workers. Each of the nine reactions for which process designs were developed may be classified as either solid gas/catalytic (catalyst is the solid phase) or solid-gas/noncatalytic. The reactor designs for the catalytic reactions consisted of a series of standard packed bed, adiabatic reactors with inter-bed heat exchangers. The noncatalytic reactions presented a perplexing reactor design problem since in all cases one of the reactants was a solid. The process design finally settled upon was a continuous one in which the solid phase is stored and reacted in different vessels (as opposed to a batch process in which the solids storage vessel is also the reactor.). The reactor train generally consisted of four moving bed reactors (Fig. 3) with the solid passing through them in series and the gas phase passing through them in parallel flow in order to reduce the pressure drop. To further reduce the pressure drop through the reactor train, the moving bed reactors were designed for radial-flow in the gas phase.

Table 2 presents capital cost estimates and round-trip efficiencies for the nine reactions studied to date. The capital cost estimates were developed from the process designs according to the module cost estimation method of Guthrie [3] except where more reliable or more current information was available. Capital requirements are divided into energy- and power-related costs; energy-related costs account for storage vessels and chemicals, and power-related costs account for the rest of the storage facility. These unit costs are "raw" numbers in that they are for use directly in the STEC simulation code described above and are not intended to be used out of the context of this code. Nonetheless, they do offer a cost comparison of the reactions listed.

Round-trip efficiency is defined as that fraction of the energy charged to storage which actually leaves the storage subsystem as usable thermal energy. No availability penalty or credit is incorporated in this value; differences in availability between storage input and output streams are accounted for by the STEC simulation code.

$CaO/Ca(OH)_2$ ENERGY STORAGE SYSTEM PRELIMINARY PROCESS FLOWSHEET ENDOTHERMIC MODE ($Ca(OH)_2 \rightarrow CaO + H_2O$)

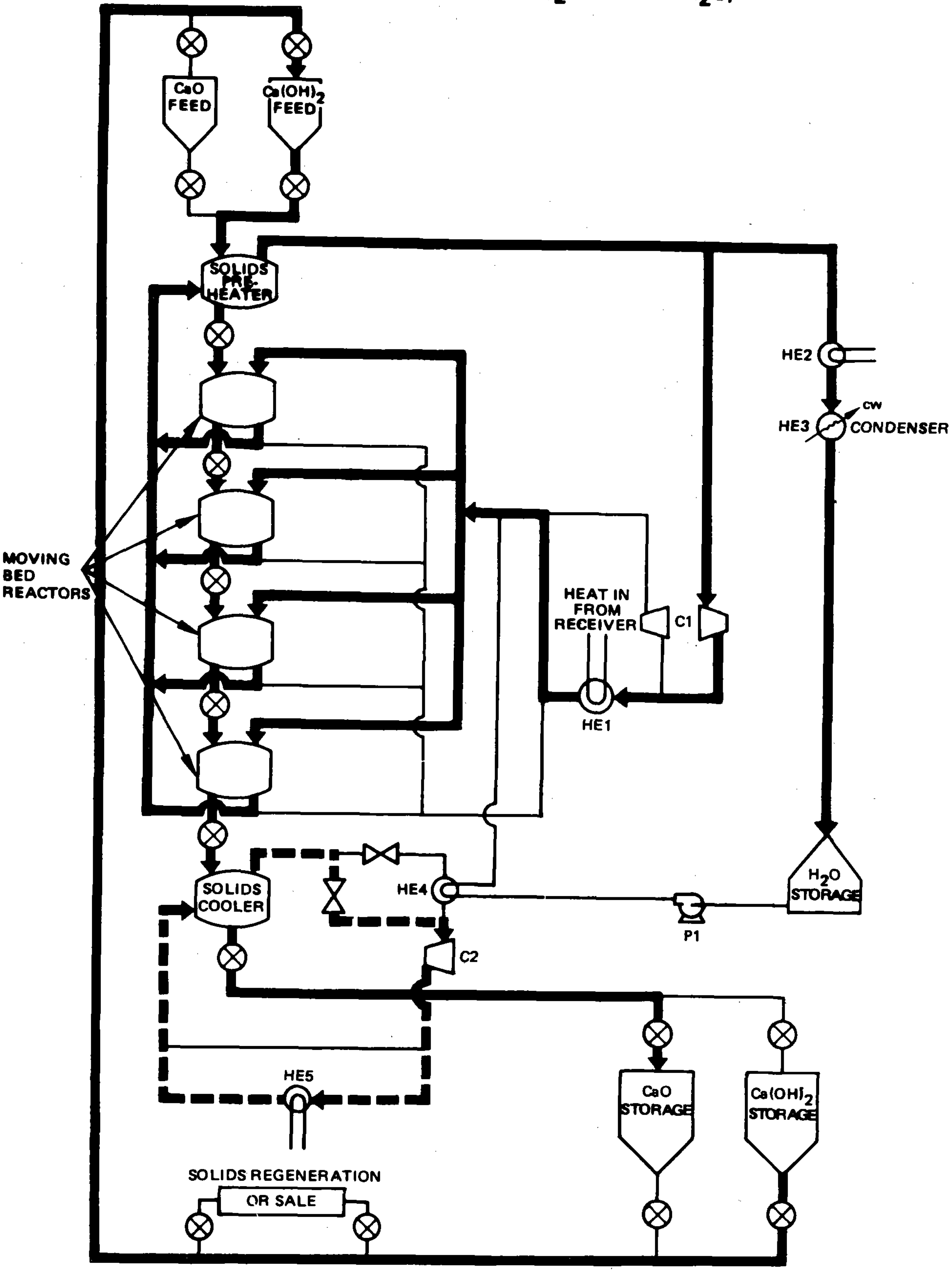


Figure 3

Table 1

CHEMICAL REACTIONS CHOSEN FOR PRELIMINARY PROCESS DESIGN STUDIES

$CaO + H_2O = Ca(OH)_2$	Solid-gas noncatalytic	Preliminary process designs complete
$CaO + CO_2 = CaCO_3$		
$MgO + CO_2 = MgCO_3$		
$ZnO + SO_3 = ZnSO_4$		
$CS_2 = C + 2S$		
*$MgCl_2 \cdot NH_3 + NH_3 = MgCl_2 \cdot 2NH_3$		
$2SO_2 + O_2 = 2SO_3$	Solid-gas catalytic	
$C_2H_4 + H_2 = C_2H_6$		
$C_6H_6 + 3H_2 = C_6H_{12}$		
$NH_3 + SO_3 + H_2O = NH_4\ HSO_4$	Design pending results of other workers	
$MgO + H_2O = Mg(OH)_2$	Discarded based on experimental results of other workers	
$FeCl_2 \cdot NH_3 + NH_3 = FeCl_2 \cdot 2NH_3$		
$MgCl_2 + NH_3 = MgCl_2 \cdot NH_3$		

*Substituted for discarded mono-ammoniate of $MgCl_2$

Table 2

CAPITAL COST AND EFFICIENCY OF ENERGY STORAGE SUBSYSTEMS (1978 DOLLARS)

Chemical Reaction	Power Related Cost ($\$/MW_t$*) x 10^5	Energy Related Cost ($\$/MW_t$**-Hr) x 10^3	Round-Trip Efficiency
$2SO_2 + O_2 = 2SO_3$	1.2	6.7	0.41
$CaO + H_2O = Ca(OH)_2$	1.8	0.2	0.42
$CaO + CO_2 = CaCO_3$	3.8	4.7	0.27
$MgCl_2 \cdot NH_3 + NH_3 = MgCl_2 \cdot 2NH_3$	3.6 - 5.2	3.3	0.28
$MgO + CO_2 = MgCO_3$	24.5	9.7	0.40
$C_6H_6 + 3H_2 = C_6H_{12}$	1.7	11.1	0.48
$C_2H_4 + H_2 = C_2H_6$	2.7	12.4	0.38
$CS_2 = C + 25$	0.5	0.5	0.62
$ZnO + SO_3 = ZnSO_4$	4.7	3.3	0.30

*Maximum charging power converted to MW_t at storage exit.
**MW_t - Hr at storage exit.

The chemical reactions in Table 2 are listed in three groups containing four, three, and two reactions, respectively. These groupings are based roughly on kinetic data availability; reliable data on reaction rates was available for the four reactions in the first group; rough approximations or severe extrapolation were required to estimate endothermic reaction rates for the second group; and no endothermic reaction rate data was found for the two reactions in the third group. These groupings serve mainly to indicate the relative reliability of the cost and efficiency estimates.

The composite results presented in Table 2, together with the design studies themselves, lead to the following general conclusions:

i) Storage systems based on solid/gas noncatalytic reactions (with the exception of the $CS_2/S/C$ system) generally require higher power-related capital investment and exhibit lower round-trip efficiency than the catalytic reactions considered.

ii) Reactions involving "noncondensible" constituents result in higher energy-related capital costs and relatively low round-trip efficiencies due to work required to compress the gases for storage.

iii) Major design difficulties are efficient heat transfer into and out of the reactor and efficient heat transfer between reactant and product streams.

iv) Suggested solid/gas noncatalytic reactor design includes moving bed, direct heat transfer, and radial flow in the gas phase.

v) Solid/gas noncatalytic reactions require high gas recycle rates. High compression work for gas circulation lowers efficiency significantly, and required receiver temperatures are higher than expected in all cases.

vi) C_6H_6/C_6H_{12} is the only reaction studied which is compatible with low-temperature distributed systems (parabolic trough collectors).

vii) $CS_2/C/S$ reaction offers prospect of most efficient energy storage, provided the dissociation kinetics (presently unknown) are favorable.

It is the implicit intent of the work statement for this contract that two of the nine reactions in Table 2 be chosen for further study under the remaining parts of the NSF effort. Originally the two reactions chosen were to include one "low" temperature reaction ($400^oK < \Delta H^o/\Delta S^o < 900^oK$) and one "high" temperature reaction ($900^oK < \Delta H^o/\Delta S^o < 1{,}500^oK$.) The objectives and scope of the present contract have evolved over its course, and both the contract monitor and the contractor now agree that the two most promising reactions should be chosen without regard to their operating temperature.

The most important criteria to use in choosing the most promising reactions are round-trip efficiency, capital investment requirements, and technical feasibility. It would be desirable to have the first high, the second low, and the third promising. The third criterion recommends strongly that the two final reactions be chosen from among the first group of four in Table 2. The relatively low round-trip efficiencies of the ammoniated $MgCl_2$ and $CaO/CaCO_3$ systems will have far greater effect on total system capital cost (and thus on busbar energy cost) than will the generally small differences between the storage system unit costs.

The designation of the SO_2/SO_3 and $CaO/Ca(OH)_2$ reactions for further study under Part 2 offers the prospect of direct comparison of long- and short-term storage using storage systems which are best suited to each of these options. Previous comparisons used the SO_2/SO_3 storage system in all cases. Its relatively high energy-related unit cost undoubtedly led to optimum STEC configurations with lower storage capacities than those which would result if the extremely low $CaO/Ca(OH)_2$ energy-related costs were used. Systems studies paralleling those already completed, but using the $CaO/Ca(OH)_2$ storage system model, should provide an interesting contrast to the systems studies performed with the SO_2/SO_3 system.

FUTURE PLANS

The project described herein is nearing completion, and the time remaining will be spent on the evaluation phase of the second part of the NSF contract. More detailed performance and cost estimates of the SO_2/SO_3 and $CaO/Ca(OH)_2$ storage systems will be made, transient behavior of these systems will be examined, and life-cycle estimates will be made. A general safety assessment of each system will be made, and an instrumentation and control study will be carried out to identify critical control features of each system and their interaction with the rest of the system.

REFERENCES

[1] J. J. Iannucci, R. D. Smith and C. J. Swet, "Energy Storage Requirements for Autonomous and Hybrid Solar Thermal Electric Power Plants," presented at the International Solar Energy Congress, New Delhi, India, January 1978 (to be published in the Proceedings).

[2] Interim Report No. 2, prepared by Rocket Research Company for NSF contract AER 75-22176.

[3] Guthrie, K. M., "Process Plant Estimating Evaluation and Control, "Craftsman Book Company of America, Solana Beach, CA (1974).

PROJECT SUMMARY

Project Title: Chemical Energy Storage for Solar Thermal Conversion/Extended Storage Studies

Principal Investigator: J. J. Iannucci

Organization:
Sandia Laboratories
P. O. Box 969
Livermore, California 94550
(415) 422-2140; FTS 532-2140

Project Goals: Assess the economic and performance impact of chemical energy storage on solar thermal electric conversion plants, especially for extended duration storage.

Project Status: A computer model developed performs an hour-by-hour simulation of the solar plant as it attempts to meet a specified demand with available solar insolation, energy from storage, energy from a fossil-fuel backup system, or from some combination of these sources. For a plant required to meet all of the specified load with solar input, the optimization code conducts tradeoffs between collector, receiver, and storage subsystems to arrive at the design which minimizes busbar energy cost.

Thus far, three central receiver systems have been simulated with the model: one based upon a Rankine cycle using steam as the working fluid, and the other two based upon open and closed Brayton cycles using air and helium, respetively, as the working fluids.

The conclusions drawn from the work performed to date are: (1) large solar contributions are achievable with modest amounts of storage (20-50 hours, depending on location) since this "first" part of storage is used frequently, whereas the seasonal storage segment is not, (2) inexpensive storage is much more important in regions with poor insolation characteristics, (3) variations in insolation from year to year can alter significantly the storage requirements and busbar energy costs for 100% solar plants, and (4) a hybrid plant with a fossil fuel backup system is a more economical way to provide the desired electrical load.

A final report is being drafted.

Contract Number: AD-03-01

Contract Period: October 1977 - October 1978

Funding Level: $50,000.00

Funding Source: Department of Energy, Advanced Solar Thermal Power Systems

SYSTEMS IMPACT OF THERMOCHEMICAL ENERGY STORAGE FOR SOLAR APPLICATIONS

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In order to investigate the potential impact of chemical storage on solar electric plants, DOE initiated the contract: "Chemical Energy Storage for Solar Thermal Conversion/Extended Studies." As part of this task, Sandia, Livermore, initiated an applications analysis of chemical storage to determine its value, especially in seasonal (autonomous operation) storage applications where chemical storage is most likely economically competitive. Rather than review the complete analysis which has been reported previously [1,2,3], the essence of this work has been synthesized to provide cost and performance goals that chemical storage research must point toward.

Goals for any new technology can be stated in many ways depending on one's point of view. In this paper, goals are described as hurdles which the technology must overcome in order to become viable in widespread utility usage. If any one of these goals is not met, chemical storage may not be viable at all. A preliminary screening analysis now in progress has examined a host of reactions in light of these hurdles.[4]

There are first certain indigenous goals which are almost completely independent of any consideration of competitive storage modes. First, such a chemical storage system must simply work. If a chosen endothermic/exothermic reaction sequence yields appreciable side products or is not almost completely reversible, such a system can never make sense for a solar plant, no matter what the economics may look like for the first cycle of operation. A similar hurdle is that of compatibility with some receivers in terms of temperature and thermodynamic compatibility and perhaps material properties; even if a reaction were otherwise acceptable, it would be unlikely that an entire solar plant would be designed around it if any other storage option were available. Another goal of chemical storage has to be operational ease. A utility is likely to put a large premium on the simplicity of inclusion of any storage subsystem; design complexity not only will lead to higher capital expenses, but also sizable operations and maintenance costs. If a process requires many steps and constant attention to minute pressure changes (for example), such a system may not be robust enough to be viable.

The other goals of chemical energy storage are those relating to economics: capital cost and performance. These cannot be evaluated logically without direct comparison to some competition. While it may occur that chemical storage is the only system which can satisfy the above indigenous goals for a given solar electric technology approach (making cost/performance comparison impossible), this is not currently the case. In fact, these two criteria cannot really be evaluated separately. In the remainder of this work, the assumption is made that chemical storage systems will be available which have met the first three goals. The competition is assumed to be a sensible (i.e., thermal) storage system.

Although there has been considerable interest recently in chemical energy storage, completely reliable and accurate estimates of their costs and efficiencies must await at least small scale pilot projects. However cost ranges and efficiency estimates are being generated [4] which will be of sufficient accuracy to provide at least a preliminary guidance as to what may be feasible. Sensible storage systems are not all that well characterized either, but the currently planned Barstow technology provides a cost upper bound and probably an efficiency lower bound.

Chemical and sensible system costs differ most dramatically in the balance between power (rate) and energy (hours of capacity) related costs. Chemical systems are burdened with relatively high buy-in costs for reactors, product separators, heat exchangers, and possibly compressors to drive a working fluid; these are all power related components, i.e., as one increases the charge rate, these components must be enlarged. (For most envisioned chemical energy storage systems, charge rates dominate discharge rates.) The energy related costs, however, can be very low, consisting of the cost of tankage of some type to hold the products and reactants and the cost of these chemicals. Most designs need no costly insulation since storage can be at ambient temperature. Most sensible storage costs cannot be easily or meaningfully divided into power and energy related parts, as both components tend to increase somewhat linearly as the number of hours of storage capacity increase. The costs of both types of storage subsystems are shown conceptually in Figure 1. If efficiency were not an issue, it is clear that at some number of hours of storage, chemical storage will be preferred on economic grounds; its lower energy related costs give a more gentle slope to the cost. This economic break-point depends on the cost of the competition.

Efficiency is an issue, however, and its effect must be included in order to obtain believable goals for chemical energy storage. Sensible storage will probably have higher efficiency than any conceivable chemical storage subsystem. (Efficiency is defined herein as the fraction of the energy remaining for electrical production after a round trip through storage. Availability losses are also included in this roundtrip efficiency.) Some of the advanced sensible storage concepts are approaching high efficiencies and for convenience all the sensible systems compared herein are assumed to have a 100% roundtrip efficiency. This assumption will not affect the chemical goals appreciably since they are much less efficient (probably less than 60% when all losses are taken into account) and an additional few percent efficiency difference will be a minor perturbation.

The lower chemical efficiencies are used to determine a modified economic break-point as shown in Figure 2. The way that the lower than 100%

efficiency affects the economics is by efficiency leveraging the storage attributable portion of all of the upstream components, such as the receiver, tower, and most important, the collector area. As the efficiency drops, the portion of these front end components attributable to storage must be oversized to collect enough extra energy to charge storage. Thus, depending on the roundtrip efficiency and number of hours of storage, the capital investment will vary. As the chemical storage subsystem efficiency decreases, the number of hours at which chemical and sensible storage compete increases.

Using this methodology, the economic break-point for chemical storage has been computed. Costs for sensible storage ranging from 10 to 40 dollars per kilowatt hour electric were used. The costs for chemical storage were parameterized in terms of a "storage cost multiplier" [3] applied to published estimates [5] for chemical storage based on the SO_2/SO_3 reaction. These normalizing costs of $412/Kwe and $15.50/Kwhe correspond to the power and energy related costs respectively at a storage cost multiplier of one. It is assumed for convenience and as a first cut that future chemical storage technologies may have lower cost, but that their relative power and energy related costs will not vary appreciably. The efficiency of the potential chemical storage mode is varied between 20 and 100 percent. Component sizings are for Albuquerque, New Mexico. Front end costs have been assumed to be proportional to the number of collectors required at $60 per square meter and an additional 25 percent has been added on for receiver and tower costs.

Figures 3 through 5 show the economic break-point for chemical storage versus sensible storage, for three different costs of the latter. The significance of this break-point is that beyond it, chemical storage is economically superior to sensible, including what may be rather severe front end penalties due to inefficiency. To determine desirable goals for the costs and efficiency of chemical energy storage, one chooses an estimate for the sensible competition cost and select the mode of plant operation. Daily mode operation of storage (diurnal cycling) will require no more than 10 to 20 hours of daily and seasonal storage, while the seasonal storage mode may need as many as 100 to 200 hours. These daily and seasonal storage bands should be examined in these figures to determine the cost goals for chemical energy storage, depending on the competitive sensible cost, chemical efficiency, and selected mode of operation.

For example, if sensible storage costs $10/Kwhe (see Figure 3), chemical storage must have a storage cost multiplier of less than .25 and greater than 60% efficiency to compete with sensible for diurnal operation (10 to 20 hours). Seasonal chemical storage (100 to 200 hours) may compete with a storage cost multiplier of up to about .5 depending on efficiency. If, on the other hand, the closest competition for a given system were sensible storage at $40/Kwhe, Figure 5 tells us that for daily storage (e.g., 12 hours) chemical may be attractive at 60% efficiency and a storage cost multiplier of .5, but that this competitive break-point is very dependent on efficiency. Beyond 60 hours of storage, chemical storage will be economically superior to sensible even for 20% efficiency. Sensible costs assumed at $20/Kwhe give results intermediate to these extremes as can bee seen in Figure 4.

The competitiveness of 20% efficient storage for seasonal usage at first seems counter-intuitive. But for seasonal applications, storage costs (mostly energy related) dominate the economics. Most of the front end leverage penalties are incurred as the first 10 or so hours of storage are added to a plant. Beyond this point, the front end size must grow, but not nearly as fast as the number of hours of storage increases. For example, a plant with no storage might have a solar multiple of 1.2, with 12 hours of storage, perhaps a solar multiple of 3, but for 120 hours of storage a solar multiple of 6 will be sufficient (not 30 as might be gotten by extrapolation). Since the energy cost of storage (and not the front end leveraging) dominates for hundreds of hours of storage, chemical modes will be economically superior to sensible for any reasonable efficiency.

The cost of producing baseload solar electricity is dominated by the costs of both storage and heliostats. It is interesting to note that for a busbar energy cost optimized solar plant, the busbar cost in Albuquerque is about equally sensitive to these two costs. This can be seen in Figure 6. Here iso-cost curves are presented for heliostat costs ranging from 60 to 120 dollars per square meter, and the full range of storage costs. For less favorable solar locations, the busbar cost becomes higher and more sensitive to storage costs than to heliostat costs.[3]

CONCLUSIONS

The goals or hurdles for chemical storage have been qualitatively and quantitatively described. A potential reaction sequence must be: (1) free of side products and completely reversible, (2) compatible in terms of temperature and perhaps materials with an otherwise viable receiver concept, and (3) not unduly complex to incorporate, operate or maintain in its solar application. The cost/performance goals are found to be very sensitive to the mode of storage operation (diurnal vs. seasonal) and to the cost of the sensible competition. Since seasonal storage operation requires a proportionally larger investment in energy capacity over collector area than does diurnal storage, lower efficiencies can be tolerated in the seasonal case. To make chemical preferable to sensible for diurnal cycling, chemical costs will have to be reduced and efficiency improved dramatically from current technology if sensible costs are in the 10 to 20 $/Kwhe range.

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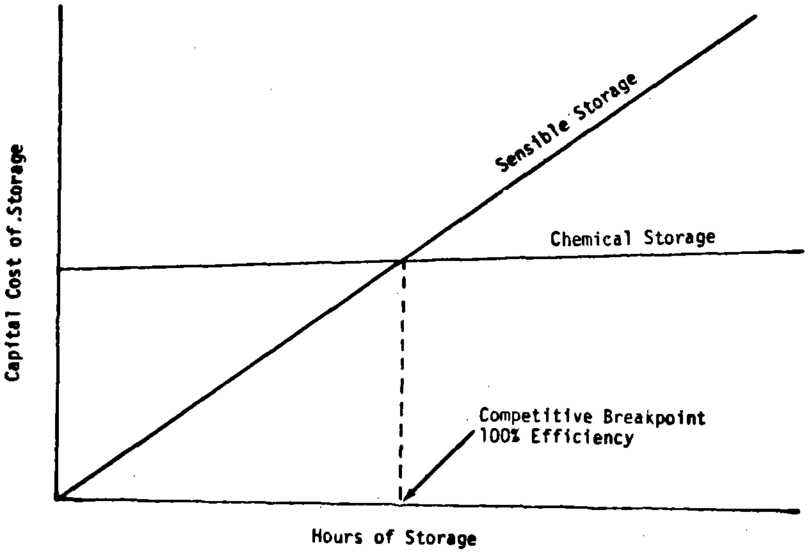

Figure 1. Economic Break-point Definition for Sensible and Chemical Storage Efficiencies Equal to 100%

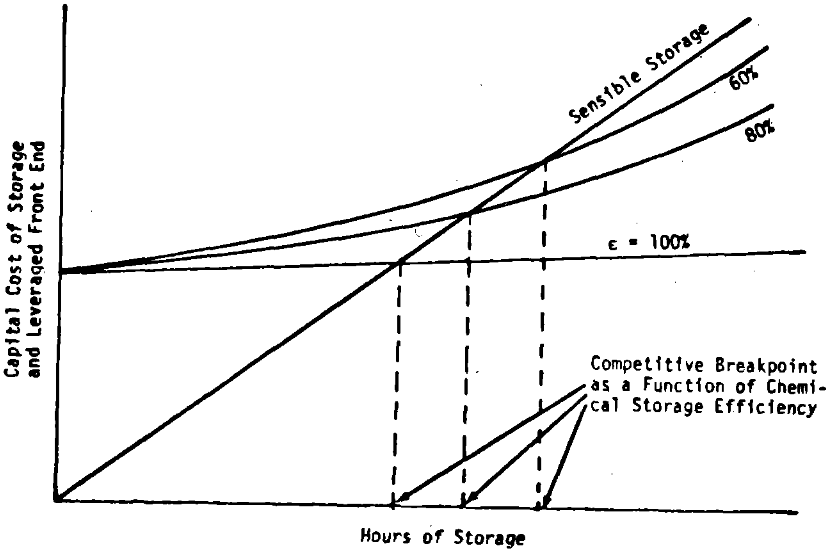

Figure 2. Economic Break-point Definition for Varying Chemical Storage Efficiencies

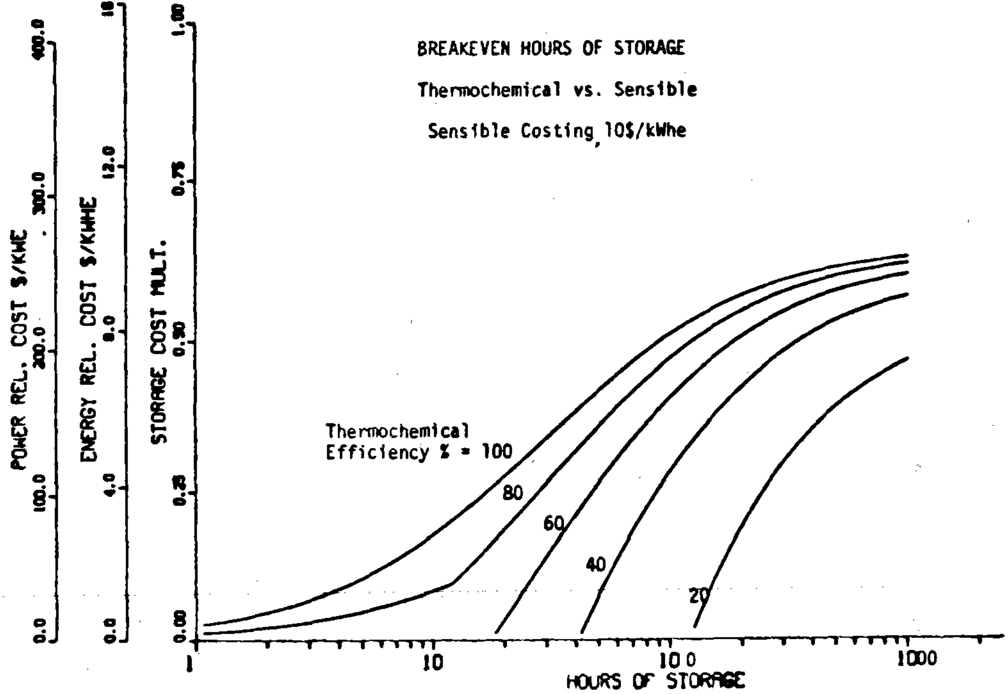

Figure 3. Breakeven Hours of Storage, Thermochemical vs. Sensible

Sensible Costing 20$/kWhe

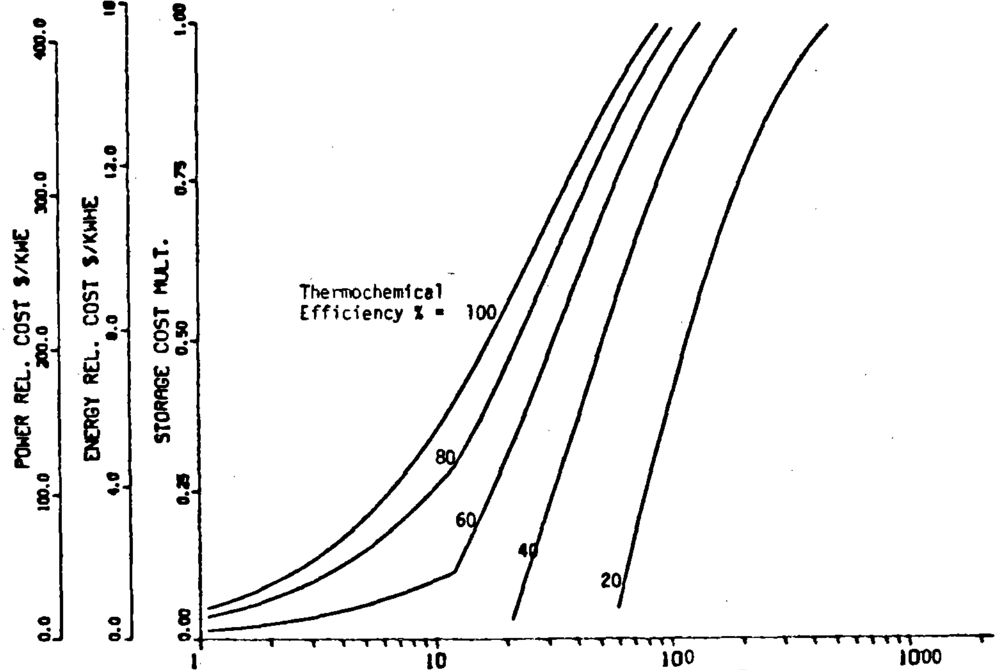

Figure 4. Breakeven Hours of Storage, Thermochemical vs. Sensible

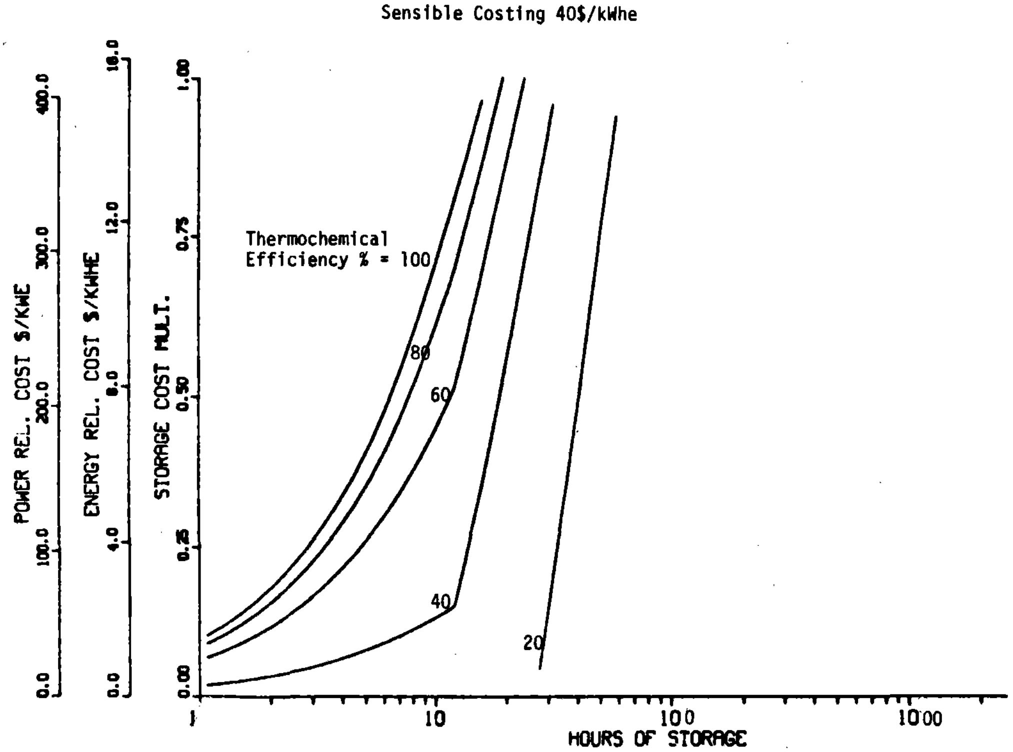

Figure 5. Breakeven Hours of Storage, Thermochemical vs. Sensible

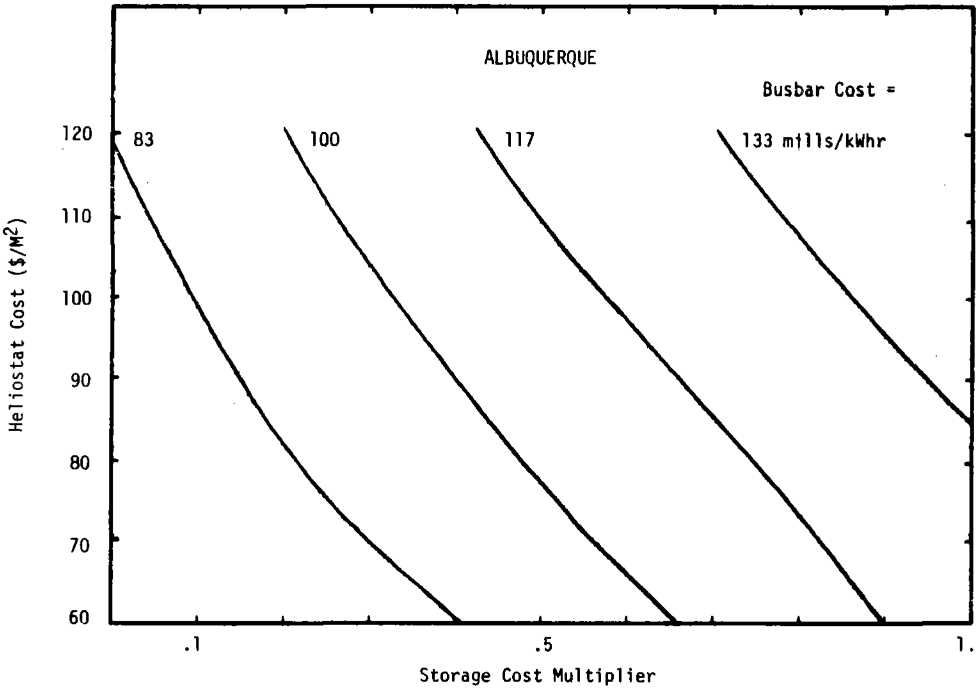

Figure 6. Tradeoff Between Storage Costs and Heliostat Costs for Autonomous Solar Baseload Operation (1978 dollars)

PROJECT SUMMARY

Project Title: Development of Operational Chemical Cycles for the Storage of Energy

Principal Investigator: Wayne E. Wentworth

Organization: University of Houston - Central Campus
Department of Chemistry
Houston, Texas 77004
(713) 749-2627

Project Goals: To identify, develop and demonstrate a chemical reaction cycle for thermal energy storage and regeneration in the temperature range of 400-500°C. The proposed cycle is based on the net thermal decomposition of ammonium hydrogen sulfate (NH_4HSO_4).

Project Status: Chemical Reaction Fundamentals - Two reaction mechanisms have been identified which are equivalent to the net thermal decomposition of NH_4HSO_4 and which allow separation of NH_3 and H_2O from the sulfur oxide product at high temperature by formation of an intermediate compound. Twenty-four different intermediate formers have been screened. Nine have been selected for detailed experimental evaluation. The energy regeneration reaction has been investigated and temperatures in excess of 400°C have been achieved.

Process and Engineering Configurations - A bench scale flow reactor has been designed and is now operational. The unit is being used to study the energy storage reactions identified as promising. A conceptual NH_4HSO_4/cogeneration cycle has been developed, costed, and performance is being calculated.

Solar Energy Input Configuration - Optical and thermal analyses of parabolic dish solar collector systems have been completed. Experiments to study the effect of high temperature on solar components are being formulated. A preliminary economic analysis of the NH_4HSO_4 storage system and solar component cost has been made.

Contract Number: EG-77-C-01-3974

Contract Period: FY78, continuing

Funding Level: $227,300

Funding Source: Department of Energy, Advanced Solar Thermal Power Systems

GENERAL PRINCIPLES OF REVERSIBLE CHEMICAL REACTION CYCLES - In principle such a cycle would use thermal input (eg. concentrated solar flux) to provide the heat required for an endothermic decomposition reaction. This effectively converts the thermal input to chemical potential energy. Separation of the decomposition reaction products at the decomposition temperature would allow the products (and the energy of decomposition) to be stored at ambient temperature. Thermal energy could then be regenerated upon demand by recombining the stored products according to the reverse exothermic reaction. The maximum temperature available from the solar concentrator and the minimum operating temperature of the power generating facility determine a temperature range within which the reaction must be cycled. The success of such a cycle depends critically upon a high reaction yield on both directions, the ability to separate the products of the decomposition reaction at the decomposition temperature, and a long term reversibility for the net reaction, all within a closed system.

THE AMMONIUM HYDROGEN SULFATE CYCLE - In particular, the net thermal decomposition of ammonium hydrogen sulfate (NH_4HSO_4) into ammonia (NH_3), water (H_2O) and sulfur trioxide (SO_3 or $SO_2 + O_2$) is being investigated for the energy storage step and the reverse recombination of these products to reform NH_4HSO_4 for the energy regeneration step. (Figure 1) Values for the standard enthalpy of reaction, $\Delta H° = 336.5$ kJ mole^{-1} (80.4 kcal mole^{-1}) and for the standard entropy of reaction, $\Delta S° = 455.8$ J deg^{-1} (108.9 cal deg^{-1}) have been used to calculate the approximate temperature, $T^* = 467°C$, at which the thermodynamic equilibrium constant, K_{eq}, for this reaction is equal to one under standard conditions. The value of T^* is an approximation of the temperature at which this reaction cycle can be turned. According to this approximation, decomposition (energy storage) will be favored at temperatures above T^* and recombination (energy regeneration) will be favored at temperatures below T^*. The actual temperature required for the energy storage step (T_1) and provided by the energy regeneration step (T_2) will depend on the reaction conditions necessary to obtain high yields for these reactions.

The decomposition products are gases at temperatures in the vicinity of T^* under standard conditions, but each can be liquified at modest pressures, < 10 atm, at ambient temperature, < 40°C. Condensation, and thus storage, of these products will be simplified if reaction conditions can be found such that the partial pressure of each product in the decomposition step is in excess of its liquid vapor pressure at ambient temperature. Using the thermodynamic data available for the decomposition reaction, calculations show that this self-condensation can be achieved at $T_1 = \sim 500°C$, and that the energy storage density provided by this process (storage of H_2O, NH_3 and SO_3 as liquids at ambient temperature) would be approximately 3,100 MJ m^{-3} (740 kcal ℓ^{-1}). These calculations assume complete loss of the heat of condensation of each product to an ambient heat sink. The practical storage density will be less by the amount of heat which must be added to the stored products to satisfy the conditions required for recombination and greater by that part of the heat of vaporization of these products which can be recovered from the ambient heat sink.

Two reaction mechanisms have been identified which are equivalent to the net thermal decomposition of NH_4HSO_4 and which in principle allow separation of the NH_3 and H_2O products from the sulfur oxide at high temperature. The mechanisms differ in the type of reaction intermediate formed by reaction with the product SO_3. One mechanism (Figure 2) depends on the selection of appropriate metal sulfates (M_2SO_4) for formation of intermediate pyrosulfates ($M_2S_2O_7$), the other (Figure 3) depends on selection of appropriate metal oxides (MO) for formation of intermediate metal sulfates (M_2SO_4). These mechanisms will allow product separation if intermediate formers (M_2SO_4 or MO) can be found such that the intermediate is formed below the decomposition temperature of pure NH_4HSO_4 and is decomposed below the maximum thermal input temperature. Energy storage thus becomes a two step process. The success of this process requires that it be possible to achieve a high yield from each step by controlling the reaction mixture temperature.

PROPOSED RESEARCH - The selection of appropriate intermediate forming compounds, the characterization (kinetics and thermodynamics) of the reactions of these compounds with NH_4HSO_4 for energy storage and of the recombination of the reaction products for energy regeneration, the optimization of reaction conditions, and the materials problems associated with handling these reactions have been undertaken by a research group whose work is classified as Chemical Reaction Fundamentals (Phase IA).

The design and construction of a bench scale flow reaction, the use of such a reactor for the study of flow reaction kinetics and heat transfer characteristics for each step of the cycle, and the eventual design (including economics and technical feasibility) of a pilot scale reaction unit have been undertaken by a second research group whose work is classified as Process and Engineering Configurations (Phase IB).

The experimental evaluation of the effects of high temperatures on solar components, the evaluation of high temperature concentrator-receiver designs developed by other research facilities, and the use of this information for the conceptual design (including cost estimates) of a full scale demonstration solar to electric power plant including the NH_4HSO_4 storage cycle have been undertaken by a third reseach group whose work is classified as Solar Energy Input Configuration (Phase IC).

The progress of each research group during the first 18 months of this contract is discussed separately below.

CHEMICAL REACTION FUNDAMENTALS - During the first twelve months of this contract, fifteen metal sulfates and nine metal oxides were screened experimentally as intermediate formers for the two step energy storage reaction. Only nine of these, three metal sulfates and six metal oxides, gave the desired two step decomposition when mixed with NH_4HSO_4 and heated. During the past six months, four of these nine (K_2SO_4, Rb_2SO_4, Cs_2SO_4, and ZnO) have been studied in greater detail.

A laboratory reactor system and a chemical analysis procedure were developed for the study of NH_3 and SO_3 yields from reaction mixtures. Preliminary results indicated that product yield is a function of reaction temperature (T_{1a}) and reaction mixture mole (n) ratio. Experiments were done to optimize these variables separately for the first step of the decomposition reaction occurring in a mixture of NH_4HSO_4 with each intermediate former. The criterion for optimization was a maximum $NH_{3(g)}$ yield and a minimum $SO_{3(g)}$ yield.

Results for mixtures of NH_4HSO_4 with each of the three metal sulfates show that the thermal decomposition of such mixtures at temperatures below 425°C results in the evolution of a high yield of free $NH_{3(g)}$ and only a small yield of $SO_{3(g)}$. This is in good agreement with the measured stability of the metal pyrosulfate intermediate and with the assumed reaction. For each of the three mixtures maximum $NH_{3(g)}$ yield is obtained when the starting mixture consists of

1.2 moles of metal sulfate per mole of NH_4HSO_4. When this mole ratio is used, the optimum temperature is ~ 415°C for each mixture. Under these conditions, the $NH_3(g)$ yield is greatest for the mixture containing Cs_2SO_4 and lowest for the mixture containing K_2SO_4, and the product separation ($NH_3(g)$ yield/$SO_3(g)$ yield) is greatest for the mixture containing Cs_2SO_4 and least for the mixture containing K_2SO_4. Above 415°C the $NH_3(g)$ yield remains essentially constant while the amount of NH_3 left in the mixture residue continues to decrease. In no case does the volatile NH_3 reach 100%, and in no case is there 100% recovery of the available NH_3. This suggests that some of the available NH_3 is lost by reactions which produce nitrogen containing products other than NH_3. In no case is the total recovery of SO_3 equal to 100%, but in general it is 98% or greater. These results are summarized in Figure 2.

It is important to note that these conclusions are based on experiments in which the temperature and mole ratio were optimized independently. Experiments to optimize these variables simultaneously are now in progress. It is also important to note that these results were obtained by heating the mixtures in a helium atmosphere. Additional experiments have shown that $NH_3(g)$ yield and total NH_3 recovery from the thermal decomposition of a mixture of NH_4HSO_4 plus K_2SO_4 can both be increased when water vapor is added to the helium atmosphere above the reaction mixture. The influence of this variable must also be evaluated in detail for each of the three intermediate formers.

Similar experiments were done to independently optimize T_{1c} and n for the reaction mixture consisting of NH_4HSO_4 plus ZnO. Results show that the thermal decomposition of such mixtures at temperatures below 420°C results in the evolution of a high yield of free $NH_3(g)$ and only a small yield of $SO_3(g)$. This is in good agreement with the calculated stability of the $ZnSO_4$ intermediate and with the assumed reaction. Maximum $NH_3(g)$ yield is obtained when the starting mixture consists of ~ 1.5 moles of ZnO per mole of NH_4HSO_4. When this mole ratio is used the optimum temperature is ~ 400°C. Under these conditions, the $NH_3(g)$ yield is 99.3%. This is significantly higher than the yield obtained from mixtures of NH_4HSO_4 with any of the three metal sulfates. Product separation ($NH_3(g)$ yield/$SO_3(g)$ yield) is not complete but is as good as that obtained with any of the metal sulfates. These results are summarized in Figure 3. Experiments to optimize these variables simultaneously must also be done.

A second laboratory reactor system has been developed for measurement of the vapor pressure developed above a particular reaction mixture as a function of time at a given temperature. From this data it is possible to calculate the time required to reach one half the total equilibrium pressure developed at that temperature. This "half life" ($t_{1/2}$) gives an estimate of relative reaction rates. Experiments have been done for mixtures of NH_4HSO_4 + 1.2 M_2SO_4 for each of the three metal sulfates over the temperature range of the first step in the thermal decomposition reaction. In general $t_{1/2}$ decreases as reaction temperature is increased. Results obtained at the value of T_{1a} which gave a maximum $NH_3(g)$ yield (~ 415°C) are summarized in Figure 2. At this temperature, the reaction is most rapid for the mixture containing Cs_2SO_4 and least rapid for the mixture containing K_2SO_4. In principle it should be possible to calculate a rate constant and an activation energy for each reaction from this data. Such calculations depend upon the correct choice of a rate equation. Various plausible rate equations are being examined to determine which best fits the data. Additional experiments may be required to test these choices.

From the total equilibrium pressure data at each temperature, it is possible to extract the equilibrium partial pressures of the product gases (NH_3 and H_2O).

In principle these partial pressures may be used to calculate an equilibrium constant, K_{eq}, and values of ΔH and ΔS for this reaction step. These calculations depend on the correct choice of a mathematical expression for the equilibrium constant, which in turn requires assumptions concerning the details of the actual reaction mechanism. The data is currently being analyzed to determine what assumptions best fit the data. The only conclusion at this time is that the schematic mechanism shown in Figure 2 is an incomplete description of the actual process.

Finally, an experimental apparatus has been designed and constructed for the laboratory study of the energy regeneration reaction at a total pressure of one atmosphere. Preliminary experiments produced a reaction temperature of ~ 410°C. The reaction product was ~ 90% NH_4HSO_4 and ~ 10% $(NH_4)_2SO_4$. We expect that optimization of reactant flow will give an even higher NH_4HSO_4 yield and that reaction at higher pressure will give higher temperatures.

PROCESS AND ENGINEERING CONFIGURATIONS - A bench scale flow reactor has been designed, fabricated, and put in operation. This unit is being used to study the two step thermal decomposition reactions which have been identified as promising for the energy storage step of the proposed cycle. A computer model has been developed for the design of such tubular flow reactors. This model has been used to predict heat transfer, conversion, and pressure drop for several test cases. An investigation has been started to determine the maximum heat flux through the wall of a tube. This information will be used in future reactor designs.

Calculations have been made of the flux distributions inside furnaces of various shapes when heated by a Cassegrainian solar concentrator. This configuration is being considered as a means for providing the thermal input for the flow reactor.

A conceptual design has been developed which combines the NH_4HSO_4 storage cycle with the cogeneration of steam for producing electric power and for other mechanical and chemical uses. This design is shown in Figure 4. Water is pumped through a preheater to a tower where it is heated by concentrated sunlight and converted to superheated steam. The steam goes to heat two reactors, R_2 then R_1, in series. The cooled steam is then split, part going to drive the large turbine (LT) to produce an output shaft work (W_{s2}) for electrical power generation, and part going to preheat the tower feed water. The exhaust steam from LT may be condensed by water from a cooling tower to give up heat (Q_0) or be recombined with the preheat steam. This recombined steam with enthalpy (H_0) goes to industrial processes, from which it returns to storage as water with enthalpy (H_I). When the tower cannot supply steam (night or cloudy day), water passes through R_3, takes energy from storage, and becomes fully rated steam to drive LT. Even on a sunny day, a small amount of energy is constantly taken from storage to assure that the storage system is always ready to become immediately operational if the tower becomes inoperable because of an emergency or cloud cover.

On the storage side, NH_4HSO_4 undergoes a controlled decomposition when heated by steam from the tower. At the lower temperature reactor (R_1) ammonia gas and water vapor are produced, and at the higher temperature reactor (R_2) sulfur trioxide gas is produced. The two product gas streams are separately cooled by expansion in two small turbines (ST), producing shaft work (W_{s1}) for electrical power generation or for mechanical power such as may be required to drive pumps. Each gas stream is separately condensed to a liquid by removing heat (Q_L) with water from a cooling tower. The ammonia water is stored as ammonium hydroxide, and then sulfur trioxide is stored above its melting temperature (slightly above room temperature. When energe is needed from storage, NH_4OH and SO_3 are mixed in R_3 to liberate heat at a temperature high enough to produce fully rated steam for LT. The NH_4HSO_4 produced by this reaction is recycled.

A preliminary cost estimate has been made for such a cogeneration cycle and performance calculations have been made for over a hundred variations of the basic configuration.

SOLAR ENERGY INPUT CONFIGURATION - Work on this phase has been planned to provide technoeconomic backup data on solar components compatible with the chemical reaction cycles and reactor designs developed by phase IA and phase IB, and to design a solar concentrator configuration suitable for interfacing with the proposed storage system. The work has been divided into the following major subtasks: a) to evaluate flux profiles inside receivers (furnaces) heated by parabolic dishes, b) to specify, purchase and install a parabolic dish, c) to conduct, with this dish, heat transfer experiments applicable to mental solar component costs for high temperature receivers, and e) to make a conceptual design for a full scale solar to electric power plant including storage. Work on each task is essentially on or ahead of schedule.

The optical and thermal analysis of parabolic dishes has lead to simplified techniques for evaluating flux profiles inside and thermal losses from cavities (see [1] and [2] for details).

A six meter parabolic dish was purchased during the first year of the contract, and installation was begun late in August 1978. The installation is now complete except for some fine tuning of the control electronics. At present the dish is being fitted with a heat transfer loop (Figure 5). Preliminary heat transfer experiments will begin as soon as this is complete. A simple coiled external receiver (Figure 6) will be used for the first series of experiments.

Cost estimates, using chemical plant costing techniques, have been made for a 100 MWe (with 1.7 solar multiple) power plant in which the turbine works solely from NH_4HSO_4 storage. For six hours of storage, the calculated cost of the NH_4HSO_4 portion of this plant alone is $570/KWe. However, the add-on cost for NH_4HSO_4 storage (i.e. the cost for replacement of a rock-oil storage system in an existing solar to steam to electric plant with an NH_4HSO_4 storage system) is only $310/KWe. This is only 14.5% of the estimated cost of the first commercial solar to steam to electric power plant [3]. All costs are in 1977 dollars. It is to be noted that the above costs are for an arbitrarily chosen, non-optimized flow scheme. Refinements of the flow scheme and other concepts like cogeneration are now being analyzed by the engineering group (phase IB).

The solar component costs also have been evaluated to reflect the increased losses which will result from use at the high receiver temperatures required by the proposed storage cycle. Using scaling laws derived from the continuing field optimization studies at the University of Houston, we estimate that the heliostats, land, wiring, tower, and vertical piping will cost a minimum of $227/KWth (absorbed power). This can be compared to about $210/KWth for the steam receiver [3]. The full scale receiver design is not yet complete and therefore has not been costed.

FUTURE PLANS - For phase IA, future activities will include: yield measurements on the first step of the energy storage reaction for the five metal oxides not yet investigated; optimization of reaction conditions for each reaction which appears promising; yield measurements and reaction condition optimization for the second step of each energy storage reaction which appears promising; extention of vapor pressure measurements to other reactions which appear promising, analysis of vapor pressure measurement results to determine reaction mechanism details, thermodynamic constants, and kinetic constants where possible; yield and vapor pressure experiments at higher total reaction pressures for the most promising reactions; extention of the experiments on the energy regeneration (recombination) reaction to higher total reaction pressures and optimization of reaction conditions; a continuing consideration of the materials problems associated with containing these reactions; and finally laboratory scale recycling of the most promising cycles.

For phase IB, future activities will include: flow reaction and heat transfer experiments in both steps of selected energy storage reactions; the design, and fabrication of a bench scale flow reactor for the energy regeneration (recombination) reaction; flow and heat transfer studies on the recombination reaction; the design of a pilot scale reactor; and the evaluation of the process cycle economics.

For phase IC, future activities will include: parabolic dish experiments with the goal of achieving temperatures of about 18000°F in prototype receivers; and the completion of a conceptual design for a full scale receiver.

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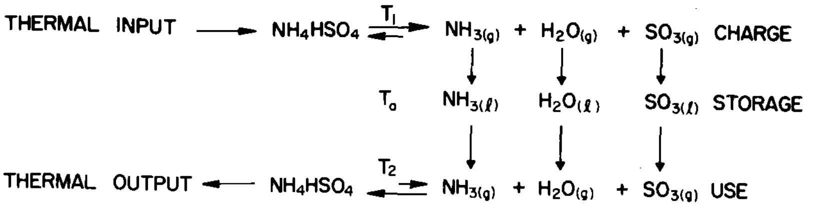
FIGURE 1

SCHEMATIC REPRESENTATION OF NET CYCLE



TEMPERATURE

$T_1 > T^* > T_2$

$900°C > T^* > 400°C$

THERMODYNAMICS

$\Delta H° = 80.4$ kcal mole^{-1}

$\Delta S° = 108.9$ cal deg^{-1}

$K = 1$ at $T^* \sim 467°C$

STORAGE

NH_3 LIQUID $P_{NH_3} > 15$ atm

H_2O LIQUID $P_{H_2O} > .07$ atm

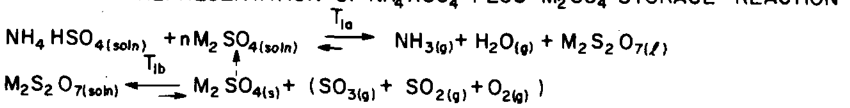
SO_3 LIQUID $P_{SO_3} > 1.5$ atm

Requires $K \sim 1.6$ $T_1 \sim 487°C$

$\Delta H/V = 740 - 980$ kcal ℓ^{-1}

FIGURE 2

SCHEMATIC REPRESENTATION OF NH_4HSO_4 PLUS M_2SO_4 STORAGE REACTION



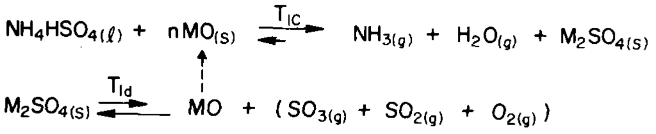
$$NH_4HSO_{4(soln)} + nM_2SO_{4(soln)} \overset{T_{1a}}{\rightleftharpoons} NH_{3(g)} + H_2O_{(g)} + M_2S_2O_{7(\ell)}$$

$$M_2S_2O_{7(soln)} \overset{T_{1b}}{\rightleftharpoons} M_2SO_{4(s)} + (SO_{3(g)} + SO_{2(g)} + O_{2(g)})$$

MEASURED REACTION DATA	K_2SO_4	Rb_2SO_4	Cs_2SO_4
MAXIMUM $NH_{3(g)}$ YIELD	93.6 %	95.4 %	96.1 %
OPTIMUM T_{1a}	~ 415 °C	~415 °C	~ 415 °C
OPTIMUM n	1.2	1.2	1.2
$SO_{3(g)}$ YIELD AT T_{1a}	0.6 %	0.1 %	0.3%
TOTAL NH_3 RECOVERY AT T_{1a}	97.7%	99.1 %	98.0%
TOTAL SO_3 RECOVERY AT T_{1a}	98.5%	99.8 %	98.5 %
$t_{1/2}$(minutes)	12.4	7.5	6.2

FIGURE 3

SCHEMATIC REPRESENTATION OF NH_4HSO_4 PLUS MO STORAGE REACTION



$$NH_4HSO_{4(\ell)} + nMO_{(S)} \overset{T_{1C}}{\rightleftharpoons} NH_{3(g)} + H_2O_{(g)} + M_2SO_{4(S)}$$

$$M_2SO_{4(S)} \overset{T_{1d}}{\rightleftharpoons} MO + (SO_{3(g)} + SO_{2(g)} + O_{2(g)})$$

MEASURED REACTION DATA	ZnO	NiO
MAXIMUM $NH_{3(g)}$ YIELD	99.3 %	
OPTIMUM T_{1C}	~400 °C	
OPTIMUM n	1.5	
$SO_{3(g)}$ YIELD AT T_C	.3	
$t_{1/2}$(minutes)	9.7	

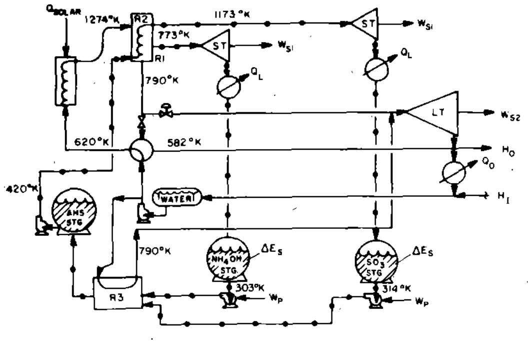


FIGURE 4. SIMPLIFIED AHS ENERGY STORAGE / COGENERATION CYCLE

[—•— PROCESS; —— WATER / STREAM]

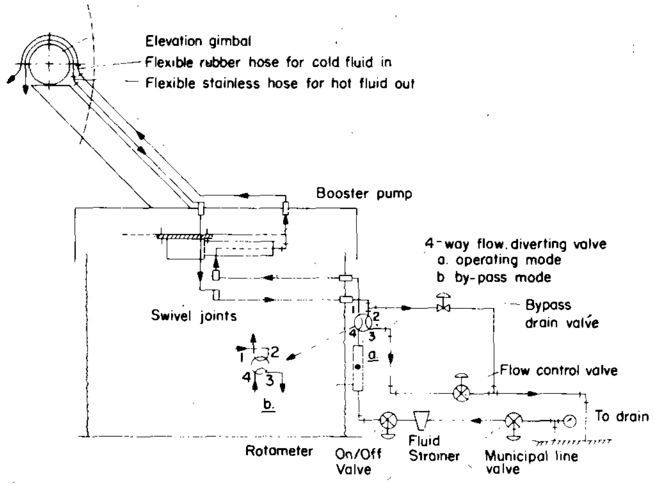


FIGURE 5
COOLANT FLOW SCHEME

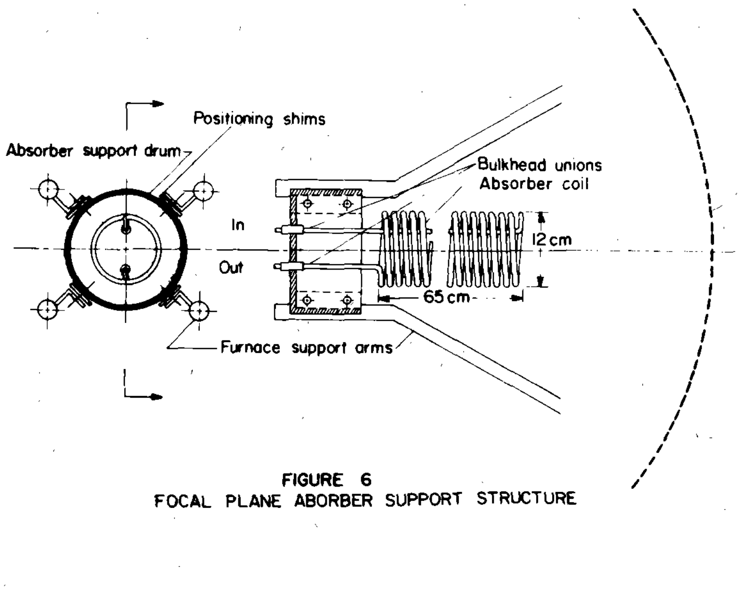


FIGURE 6
FOCAL PLANE ABORBER SUPPORT STRUCTURE

PROJECT SUMMARY

Project Title: Solar Energy Storage by Reversible Chemical Processes

Principal Investigator: T. H. Springer

Organization: Rockwell International Corporation
Energy Systems Group
8900 DeSoto Avenue
Canoga Park, California 91304
(213) 341-1000, x1325

Project Goals: Verify the technical feasibility and economic attractiveness of the $CaO/Ca(OH)_2$ reversible chemical solar energy storage concept.

Project Status: A draft final report for this project has been written and submitted for review. In the conclusions, the report states that a very substantial amount of information about the $CaO - Ca(OH)_2$ reaction has been developed to date: the reaction is completely reversible, the rates of reaction are acceptable, the heat of reaction is as expected, and the material can be cycled at least 1000 times without inherent degradation.

Thus, although uncertainties remain at this time, inorganic oxide-hydroxide thermal storage appears to be very attractive, especially since the materials are inexpensive. The products of reaction are basically very safe (one of the products is water which is, of course, universally available), the energy density can potentially be very high, the energy can be transported, and the energy can be stored indefinitely.

Contract Number: FAO-92-7671

Contract Period: August 1977 through January 1978

Funding Level: $96,800

Funding Source: Sandia Laboratories
Livermore, California

Introduction

The Energy Systems Group of Rockwell International has been investigating solar energy storage using reversible chemical reactions of inorganic salts, particularly the inorganic oxides/hydroxides, since early 1974. Early work was sponsored by NSF and DOE and, more recently, by Sandia Laboratories. The work reported here was carried out under contract with Sandia Laboratory, Livermore, California, and consists of systems studies and experimental work with $CaO/Ca(OH)_2$, the most promising of the inorganic materials that have been investigated to date.

Task 2

Task 2 consists of three subtasks, all of which deal primarily with the experimental verification of the properties of $CaO/Ca(OH)_2$ under conditions typical of a fixed-bed reactor system. In the fixed-bed concept, the $CaO/Ca(OH)_2$ remains in a vessel or several vessels and the heat energy required to dehydrate is transported to the material by a suitable heat transport fluid. Heat generated by the reverse reaction is carried away by the same fluid at a later time. The basic questions to be answered by the experimental work on this task were (1) in what way, if at all, do the properties (surface area, particle size, etc.) of the $CaO/Ca(OH)_2$ particles in the bed change as a result of thermal cycling up to one thousand cycles or so, (2) how do the bulk bed characteristics change upon repeated cycling in terms of gas evolution, utilization, gross reaction rate, and agglomeration, and (3) what are some of the fundamental properties of the $CaO/Ca(OH)_2$ materials, properties that govern the inherent reaction rate, heat evolution, etc.?

The apparatus that was designed and constructed for performing multiple cycles is shown schematically in Figure 1. The furnace consists of sheathed, MgO insulated heater wire surrounding an annular sample space containing about 8 grams of $CaO/Ca(OH)_2$ powder. Power is applied to the furnace to raise the temperature of the powder to about 550°C. The water vapor driven off is condensed in the graduated cylinder where the volume is measured as a function of time.

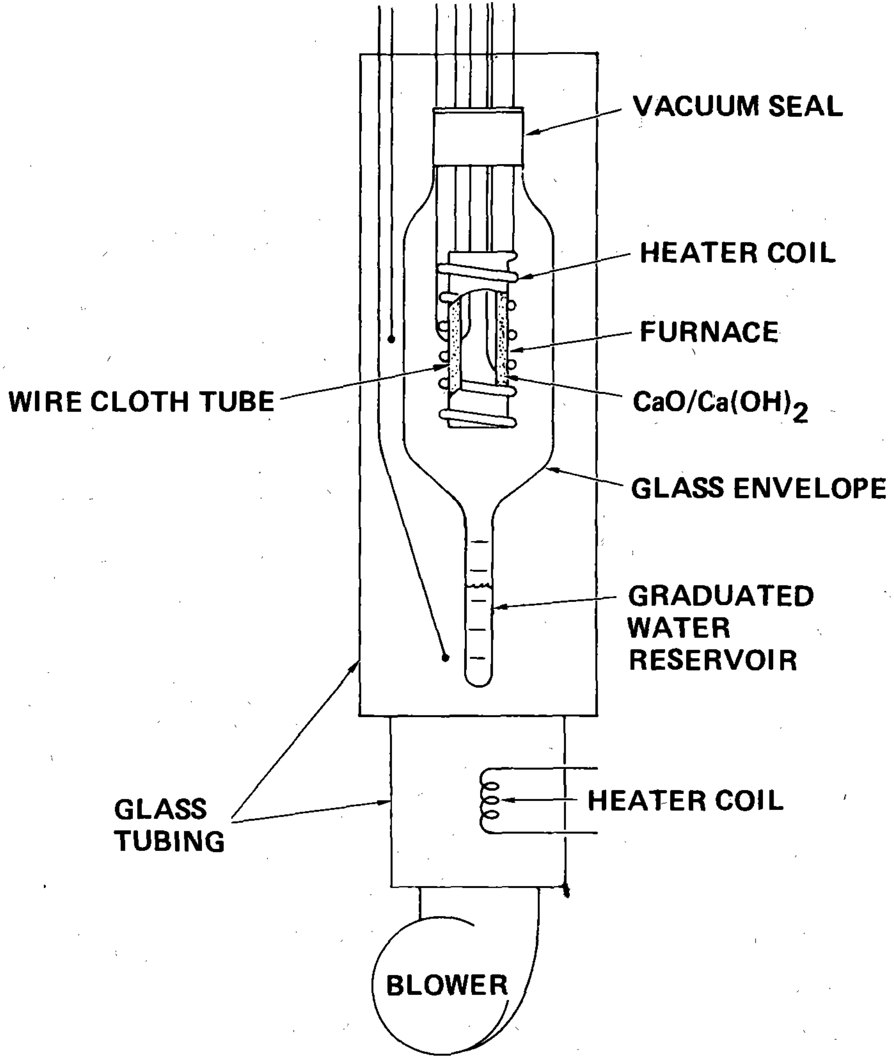


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Figure 1. Materials Cycling Apparatus

Table 1 shows the results of cycling one of the three units to 1,171 cycles. Gradual losses of utilization were observed at intervals during the course of the experiment, but it was found that a rapid re-evaluation of the glass envelope immediately restored the utilization of the material to the 90% level or greater. This behavior is hypothesized to be the result of the generation of noncondensables, some of which may be generated from a corrosion reaction. A typical analysis of the gas recovered from the apparatus at Cycle 1,148 is shown in Table 2.

Table 2

GAS ANALYSIS FROM UNIT I

Species	Vol % (Dry Basis)
H_2	49.8
N_2	47.8
O_2 + Ar	1.6
CO_2	0.4
CH_4	0.4

It is concluded that, in a full-scale operating system, periodic evacuations could be used to maintain utilization at acceptable levels or the source of the noncondensable could be eliminated.

Gross reaction rates were not observed to change drastically during the cycling, and no significant change in the bulk powder properties was observed except that a slight tendency to light sintering was noted. This phenomenon did not appear to grow worse with time; the powder could be readily scooped out regardless of the number of cycles over which it had been carried, at least up to 1171.

TABLE 1
CYCLING RECORD FOR UNIT I

Cycle	Dehydration (% in 44 min)	Hydration (% in 14 min)
1	>95	>95
119	-	88
165	91 (vac)*	100
166	100	88
188	96	94
212	95	82
281	- (vac)	-
288	100	91
353	- (vac)	100
354	100	100
381	-	91
382	84	-
449	-	48
450	45	-
496	51	-
521	-	32
522	32	-
616	-	30
617	- (vac)	94
618	-	100
641	-	95
1000	-	39
1001	39	39 (cold evac.)**
1002	73	88
1003	87	-
1023	-	63
1055	-	64
1119	-	61
1148	-	57**
1149	85	65
1150	-	66
1151	66	100
1167	89	89
1171	-	85

*(vac) indicates that a 5-15 sec evacuation was applied near the end of dehydration

**Evacuated 10 sec with reactant and water reservoir below 50°C Generator tube malfunction. Temperature was only 88°C. Corrected prior to Hydration 1151.

Analyses of the powdered material from each of the three cycled units (Unit I: 1,171 cycles, Unit II: 837 cycles, and Unit III: 484 cycles) were obtained, were compared with the starting material, and are shown in Table 3. Some in-leakage of CO_2 into the apparatus during cycling seems to have occurred in Units I and III. In Table 4, are shown the results of measurements of specific surface areas and average particle size for each of the powders from the three units relative to other materials, including uncycled feed material.

TABLE 4

SURFACE AREA AND PARTICLE SIZE MEASUREMENTS

Sample	Specific Surface Area (m^2/g)	Average Particle Size (μ) (At 44% Theoretical Density)
Feed Bottle 1 (New)	16.5	1.83
Feed Bottle 1 After 3-Month Storage	17.0	1.71
Feed Bottle 2	16.9	1.65
Aged Sample from Feed Bottle 2	15.4	1.68
Material from Unit I (1,171 Cycles)	6.42	1.70
Material from Unit II (837 Cycles)	5.33	2.68
Material from Unit III (484 Cycles)	7.16	20.5
Material Cycled Six Times	13.40	1.06

Decreases in surface area have taken place, but do not appear to affect reaction rates, nor did an increase in particle size as observed in the case of the sample taken from Unit III.

The conclusions drawn from these and several other characterization tests are that a fixed-bed concept is technically feasible, although some additional confirmation work is recommended. Since some corrosion in the material in contact with the $CaO/Ca(OH)_2$ was observed, some additional consideration of materials of construction may be necessary.

TABLE 3

CONTAMINANT CONTENTS AND MATERIAL COMPOSITIONS

	Starting Material	Cycled Materials		
Contaminant	(Reagent $Ca(OH)_2$ wt-%	Unit I wt-%	Unit II wt-%	Unit III wt-%
$CaCO_3$	1.36	11.41	1.48	8.05
H_2O (moisture)	0.70	0	0	0
SiO_2	0.47	0.66	0.68	0.51
$Mg(OH)_2$	0.69	0.72	0.60	0.65
Fe_2O_3	0.06	0.10	0.12	0.08
NiO	0.00	0.02	0.02	0.01
Cr_2O_3	0.00	0.01	0.01	0.01
Al_2O_3	0.08	0.11	0.34	0.10
Subtotal(a)	3.36	13.03	3.25	9.41
Constituent				
Combined H_2O(b)	23.40	18.08	22.95	20.46
H_2O in $Mg(OH)_2$	0.21	0.22	0.19	0.20
H_2O for $Ca(OH)_2$	23.19	17.86	22.76	20.26
Equivalent $Ca(OH)_2$	95.44	73.50	93.67	83.38
$Ca(OH)_2$ + Subtotal(a)	98.80	86.53	96.92	92.79
$Ca(OH)_2$ by difference (100% - Subtotal(a))	96.64	86.97	96.75	90.59

(a) Subtotal of measured contaminants

(b) By ignition loss less CO_2 content determined by acidic evolution of CO_2 and gravimetric absorption in Ascarite

Relative to fundamental reaction rate studies, the heating rate/temperature correlation for $Ca(OH)_2$ decomposition was measured using a pressure differential scanning calorimeter (PDSC) and is shown in Figure 2. The activation energies derived from Figure 2 are shown in Table 5. These values are approximately twice those observed by other investigators. A possible reason for the deviation is related to the fact that the particle size used in the PDSC was very small relative to the "large" single crystals used in some cases by other experimenters.

Tasks 3 and 4

System application studies using the $CaO/Ca(OH)_2$ thermal storage concept were conducted under Tasks 3 and 4. A commercial solar power plant with a generating capacity of 100 net megawatts when operating using direct solar energy and 70 net megawatts when operating using the stored energy was analyzed. Figures 3 and 4 illustrate the principles of operation using fluidized-bed reactors. Liquid sodium is used as an intermediate heat transfer medium. For a reference design point, the solar receiver was sized so that 6 hours of energy could be stored during a winter solstice day simultaneously with the plant generating 100 net megawatts. System and economic comparisons were developed for three storage concepts (fixed-bed, fluidized-bed, and rotating drum reactor) using the $CaO/Ca(OH)_2$ hydration/dehydration reaction and a hot rocks/HT-43 thermal storage concept similar to the type selected for the Barstow 10-MWe Central Receiver. The overall station efficiency (at the reference design point) of the fixed-bed CaO system was 33.7 percent compared to 32.3 percent for the fluidized-bed CaO system and 31.1 percent for the HT-43/hot rocks system. The levelized busbar energy cost (6 cents/kilowatt-hour) for the fixed-bed CaO system was the lowest of the different concepts for storage times of about 12 hours or less. Figure 5 shows the levelized busbar cost trend of the concepts as a function of E_d/E_n, where E_d equals the total annual direct energy production and E_n equals the total annual energy production from storage. For storage times of 12 hours or greater, the fluidized bed appears to be the most cost effective. The rotating drum concept did not seem to be economically viable.

TABLE 5

ACTIVATION ENERGIES FROM PDSC, NON-ISOTHERMAL RUNS

CONVERSION (%)	E KCAL/MOLE
80	34.0
50	35.1
30	36.8
20	37.0
10	37.7

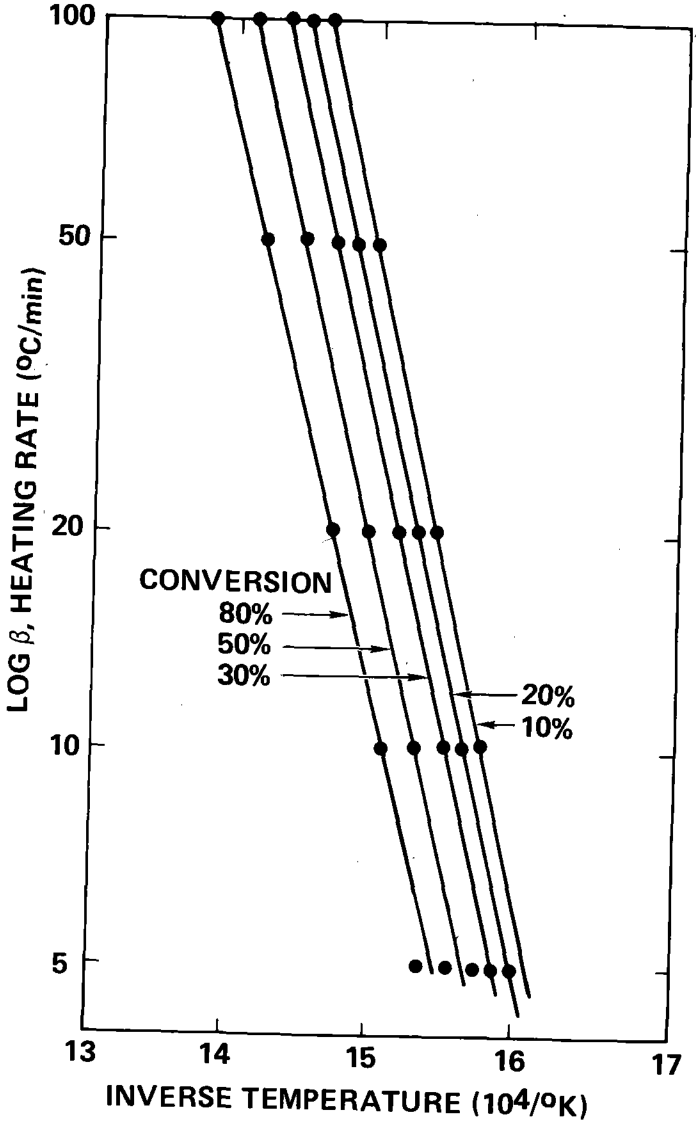

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Figure 2. Heating Rate-Temperature Correlation for $Ca(OH)_2$ Decomposition

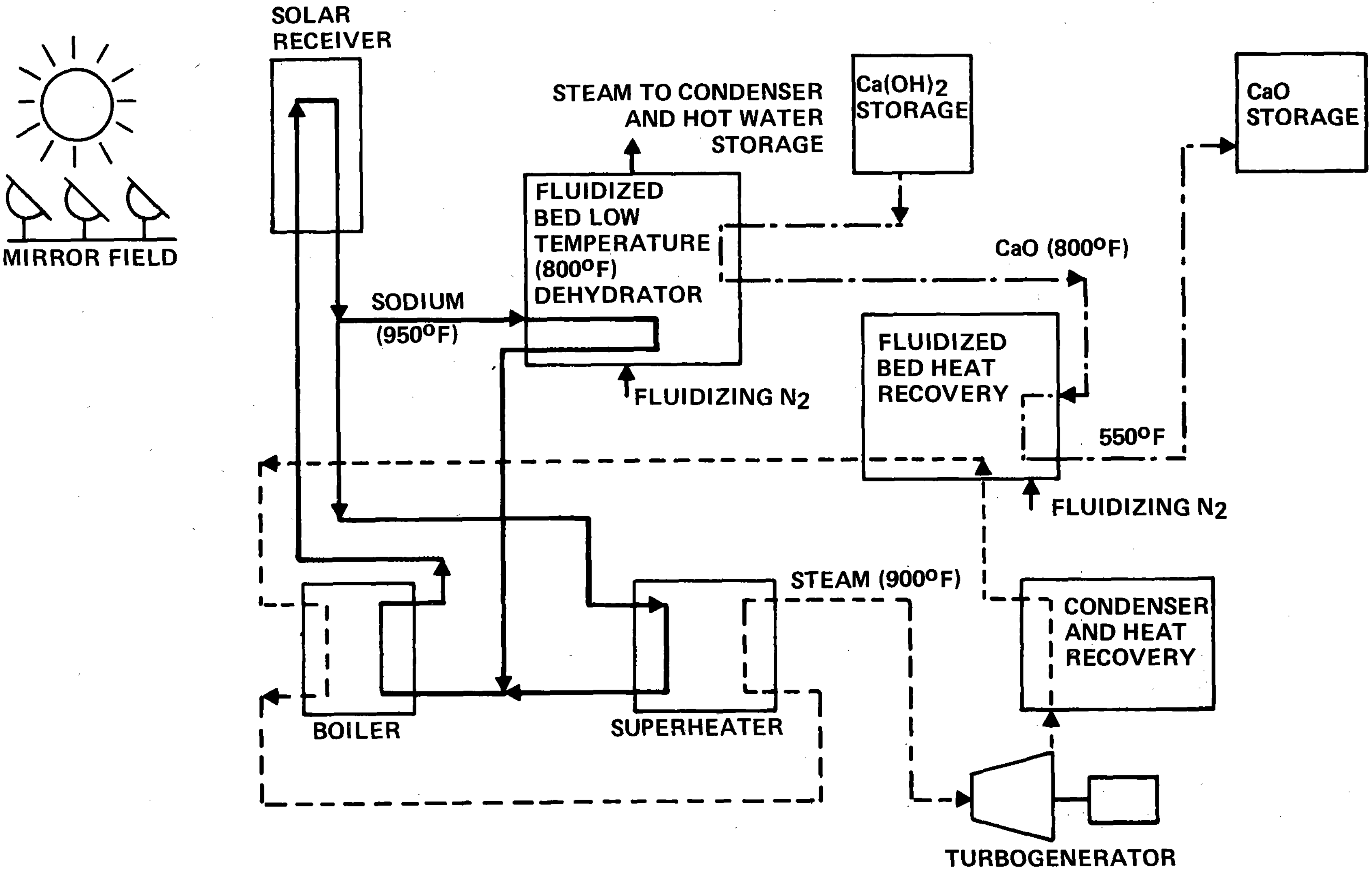

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Figure 3. Central Solar Power Station with $CaO/Ca(OH)_2$ Heat Storage Day Operation

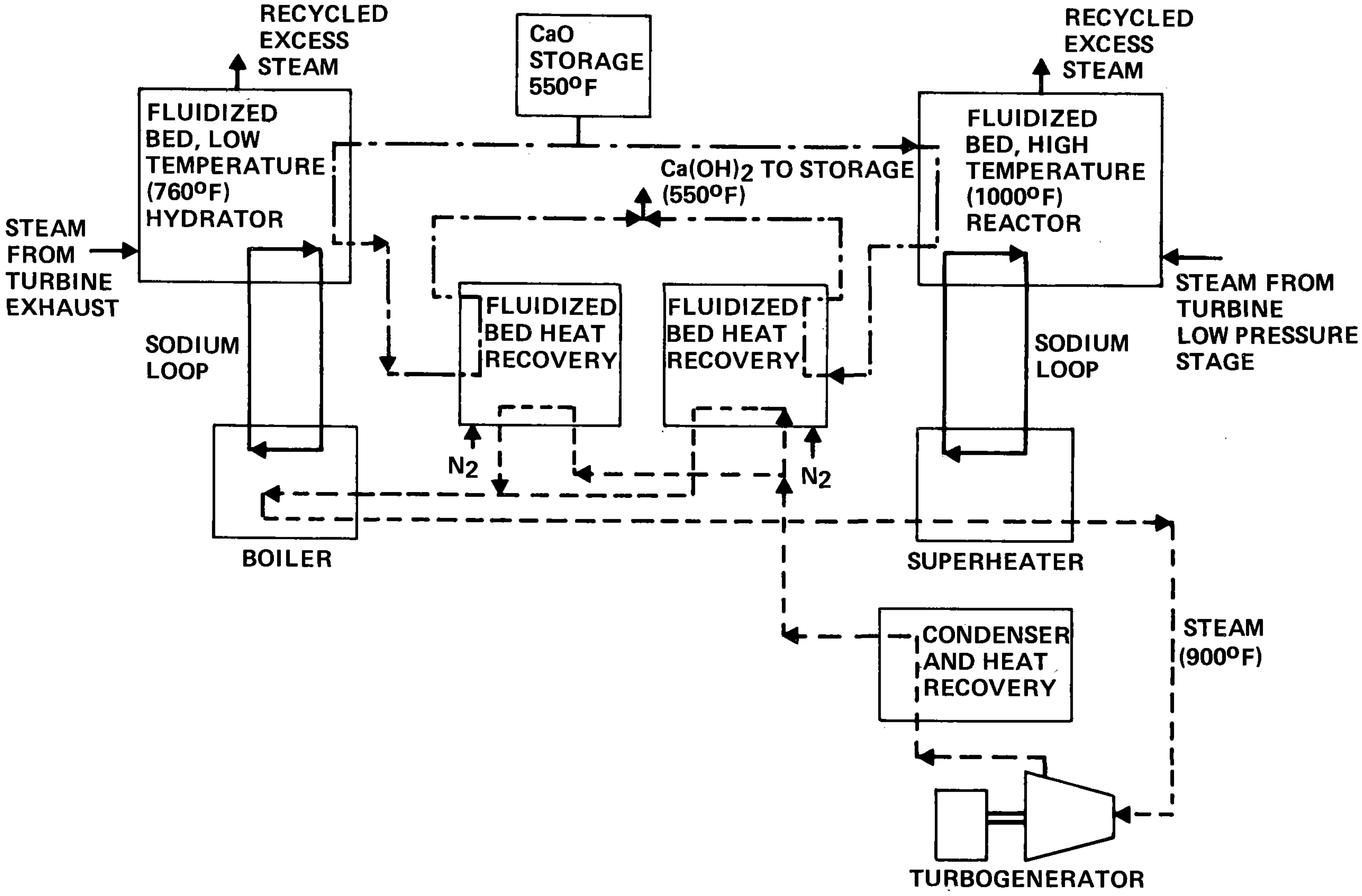

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Figure 4. Central Solar Power Station with CaO/Ca(OH)$_2$ Heat Storage Night Operation

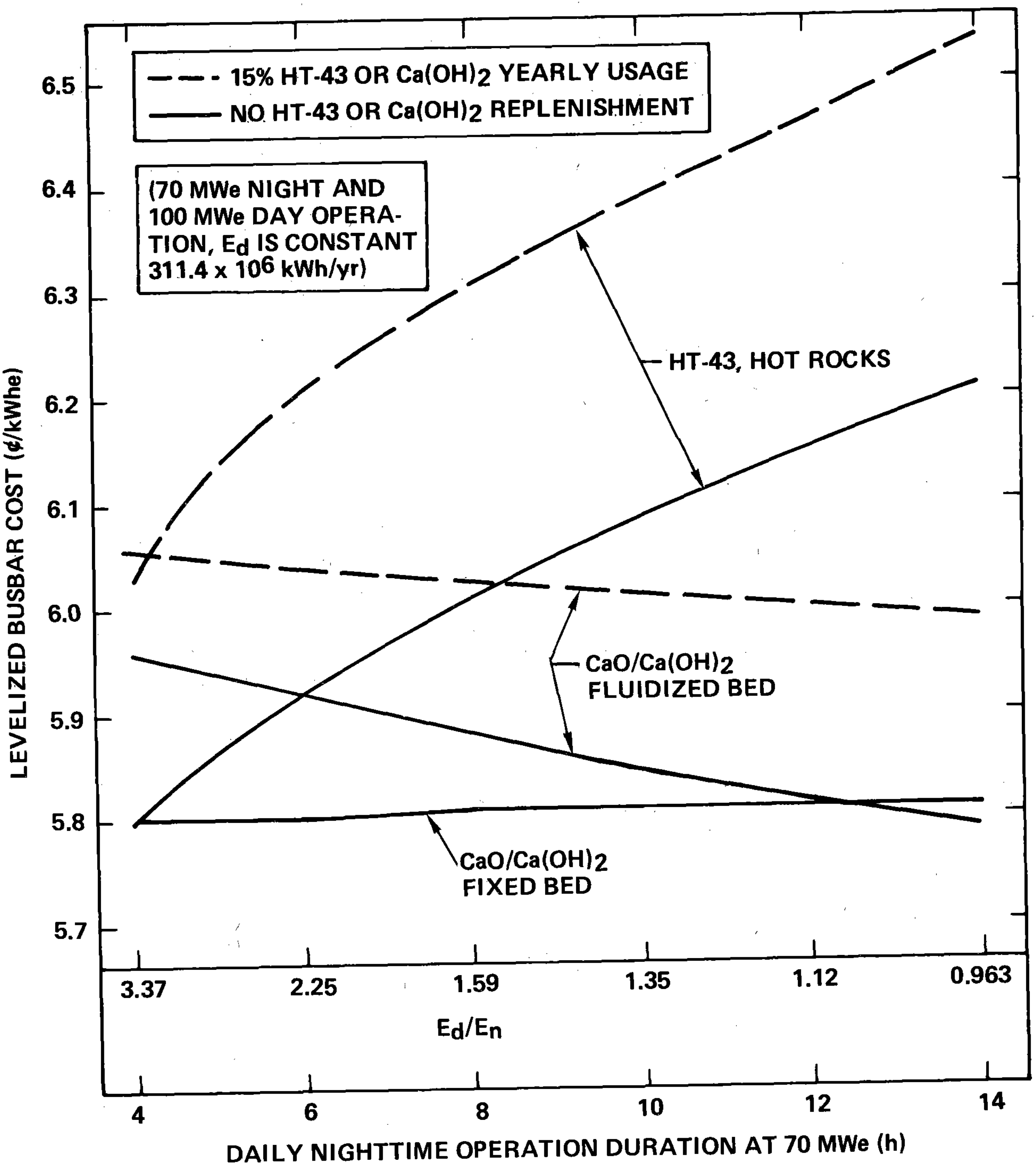

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Figure 5. Levelized Busbar Cost of Electricity

PROJECT SUMMARY

Project Title: Chemical Storage of Thermal Energy

Principal Investigators: A. S. Foss, S. Lynn

Organization: Lawrence Berkeley Laboratory
Berkeley, California 94720
(415) 642-1634

Project Goals: To develop and evaluate process flowsheets that integrate the operation of a solar steam-cycle power plant and a chemical storage system utilizing the reaction $SO_3 \rightleftarrows SO_2 + 1/2\ O_2$.

Project Status: To design and evaluate a sensible heat storage system using comparable bases as an additional means of determining the potential of chemical energy storage.

A technically feasible flowsheet has been developed that maximizes the efficiency of the combined steam-cycle power plant and energy storage system through energy interchange between the two. A computer program has been developed by which the chemical storage system heat and material balances are calculated. Equipment for the storage system flowsheet has been sized and costed. The sensitivity of the efficiency of the system to changing several of the key parameters has been determined.

A sensible heat storage system has been designed that uses magnesia brick cycling between 300° and 800°C. The storage system is operated in series with a steam-cycle power plant. A computer program has been developed to simulate the cyclic operation of the storage unit. A base-case flowsheet for the entire process has been sized and costed.

In addition, a short-term study of the use of a gas turbine for power production from the SO_3-SO_2-O_2 system has been initiated.

Contract Number: W-7405-ENG-48

Contract Period: FY1978, terminating FY1979

Funding Level: FY1978 - $100,000; FY1979 - $25,000

Funding Source: Sandia Laboratories
Livermore, California

Process Description

A simplified flowsheet for the storage process is shown in Figure 1. Liquid sulfur trioxide from storage is pumped to 40 atm, vaporized, and heated by the reactor effluent. The reactor tubes are mounted in a solar receiver of the type designed by Boeing. The interior tube walls are coated with a suitable catalyst such as iron oxide. Mass transfer within the flowing gas and heat transfer to the tube wall are assumed to be the rate-limiting factors for the decomposition of SO_3 to SO_2 and O_2.

Upon exiting the reactor the gas exchanges heat with the reactor feed and then heats the reboiler of the distillation column. The gas is further cooled to condense SO_2 and unreacted SO_3, and is then stored. The SO_2-SO_3 liquid is distilled; SO_3 is recycled to the solar reactor and the SO_2 is stored as a liquid until needed.

Heat for the vaporization of SO_3 is obtained from extraction steam from the parallel steam-cycle power plant. Part of the cooling of the reactor effluent, on the other hand, is used to preheat boiler feed water for the power plant. This integration is intended to maximize the energy efficiency of the system.

Energy is recovered from storage by recombining the SO_2 and O_2. Liquid SO_2 is vaporized, added to the O_2 stream, and heated to a temperature high enough to activate the catalyst, about 400°C. As reaction proceeds the temperature rises until the equilibrium composition is reached. The hot gas stream then passes through heat exchangers, forming superheated steam for the power plant. Three reactor stages are needed to convert about 97% of the SO_2 and O_2 back to SO_3. The SO_3 vapor then exchanges heat with the feed gas, and is condensed in the SO_2 vaporizer.

High-Temperature Reactor

Figure 2 shows typical temperature and composition profiles for a single tube of the solar-heated reactor. A single effective source temperature was chosen such that a specified average thermal flux for the whole tube was obtained. The temperature rise of the gas was also specified, and a gas flow rate was determined such that a specified maximum wall temperature for the reactor would not be exceeded. In this example about 76% of the energy flux through the tube wall is absorbed by the endothermic reaction and the remainder increases the sensible heat of the gas stream. The bulk temperature of the gas stream closely approaches the tube wall temperature at the outlet end whereas the outlet bulk SO_3 conversion is significantly less than the conversion at the wall, which is assumed to be at equilibrium. Mass transfer is thus shown to be the limiting factor for this case.

Energy Efficiency

The overall second-law efficiency of the process is simply the sum of the net electrical outputs from operation of the daytime power plant and of storage divided by the sum of the thermal inputs to the power plant and the storage reactor:

$$E_{oA} = \frac{P_{Day} \cdot \Theta_{Day} + P_{Sto} \cdot \Theta_{sto}}{(Q_{PR} + Q_{SR})\, \Theta_{Day}}$$

where

P_{Day} = Net power produced by daytime power plant (MW_e)

P_{Sto} = Net power produced from storage (MW_e)

Θ_{Day} = Time of daytime operation (HR)

Θ_{Sto} = Time of storage discharge operation (HR)

Q_{PR} = Rate of thermal input to power plant receiver (MW_t)

Q_{SR} = Rate of thermal input to storage receiver (MW_t)

In this simplified expression the thermal inputs and power outputs are assumed constant for the time periods of operation. If these rates are not constant, appropriate integrals would be used.

Low-and intermediate-temperature heat is exchanged between the power plant and the storage system. In discussing the energy efficiencies of the two separately one must therefore arbitrarily "credit" and "debit" the two operations for the heat that is supplied by the one to the other. The power plant efficiency then becomes

$$E_{PP} = \frac{P_{Day} \cdot \Theta_{Day}}{(Q_{PP} + Q_{BFW} - Q_{VAP})\, \Theta_{Day}}$$

where

Q_{BFW} = Rate of heat transfer to boiler feed water (MW_t)

Q_{VAP} = Rate of heat transfer to SO_3 vaporizer (MW_t)

The thermal storage efficiency is defined as the ratio of usable heat delivered by the storage system to the heat input to the storage system

$$E_{TS} = \frac{\Sigma\, Q_{Sto} \cdot \Theta_{Sto}}{(Q_{SR} + Q_{VAP} - Q_{BFW})\, \Theta_{Day}}$$

where

ΣQ_{Sto} = Sum of rates of heat transfer to power plant system from storage discharge (MW_t)

Sensitivity Analysis

Figure 3 shows the effect on E_{OA}, E_{PP}, and E_{TS} of the maximum allowable tube-wall temperature, $T_{W\ max}$. As this temperature is increased a larger fraction of the SO_3 can be converted to SO_2 and O_2. As a result, a larger fraction of the heat absorbed by the gas stream results in chemical reaction and a smaller fraction increases the sensible heat of the gas. The ratio Q_{PR}/Q_{SR} drops with increasing $T_{W\ max}$ because a smaller stream of SO_3 is needed to absorb the heat in the solar reactor and hence there is less heat to transfer to boiler feed water. E_{OA} increases slightly and E_{TS} increases substantially because there is relatively less low-temperature heat to dissipate to the environment per unit of chemical heat stored.

The maximum tube-wall temperature is only one of the system parameters being studied. The sensitivity of the system behavior has also been determined for variations in the solar reactor pressure, the temperature rise in the reactor, and the temperature at which heat can be rejected to the environment.

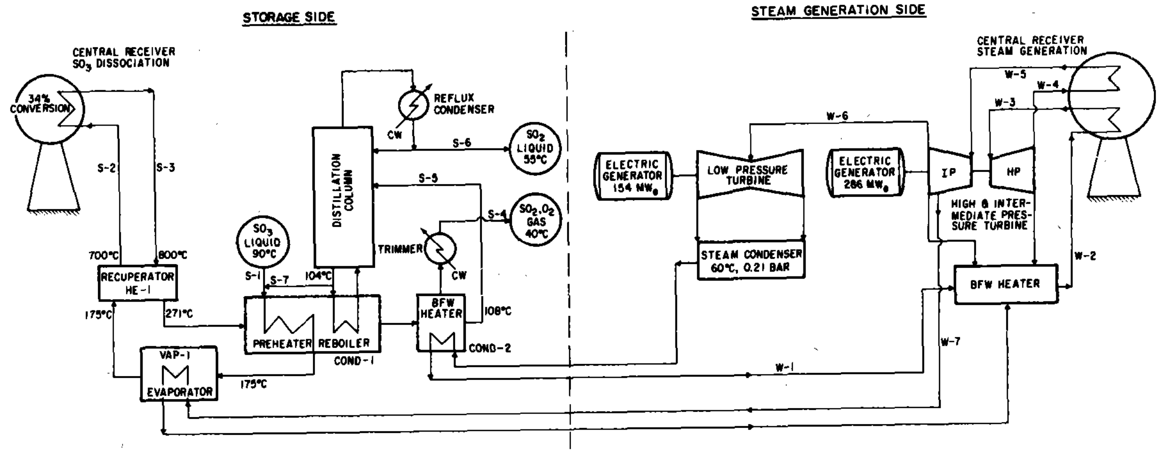
Sensible-Heat Storage

For purposes of comparison with chemical-heat storage a sensible-heat storage system was designed for use with a steam-cycle power plant. The system utilizes a checker-work of magnesia brick. A heat-transfer medium such as helium or nitrogen is circulated through the solar receiver to bring heat to the power plant superheater, reheater, and boiler. The storage system is placed between the receiver and the power plant heat exchangers. It cycles between the temperatures of about 816° and 327°C. In this way the energy stored loses little effective thermodynamic potential since it is at all times hotter than the highest temperature in the steam cycle. The behavior of this system has been simulated by computer; the flowsheet is being compared in cost and energy efficiency to the chemical storage system. The use of pre-stressed cast iron vessels to contain the magnesia bricks appears to offer attractive cost advantages.

Gas Turbine Cycle for Chemical Heat Storage

As was also recognized by Carl Hiller of Sandia Laboratories, a typical chemical energy storage system can be utilized in an unusual thermodynamic cycle. Such systems have in common that the endothermic reaction yields an increase in the number of molecules. The hot gas from the reactor can thus be expanded through a gas turbine with a high yield of work. After the gas stream is cooled it can be recompressed. With interstage cooling condensation occurs, reducing the work required to reach storage pressure. Discharge of storage can also be effected with a gas turbine. The gas is preheated before entering the first-stage reactor, where it attains a temperature approaching that in the dissociation reactor. It is then expanded through the gas turbine and is thereby cooled. Passage through the second-and third-stage reactors provides the heat required to preheat the first-stage reactor feed. A flowsheet for this energy system is currently being simulated by computer to allow evaluation of the system's potential.

DAYTIME OPERATION SCHEME (CHARGE MODE)

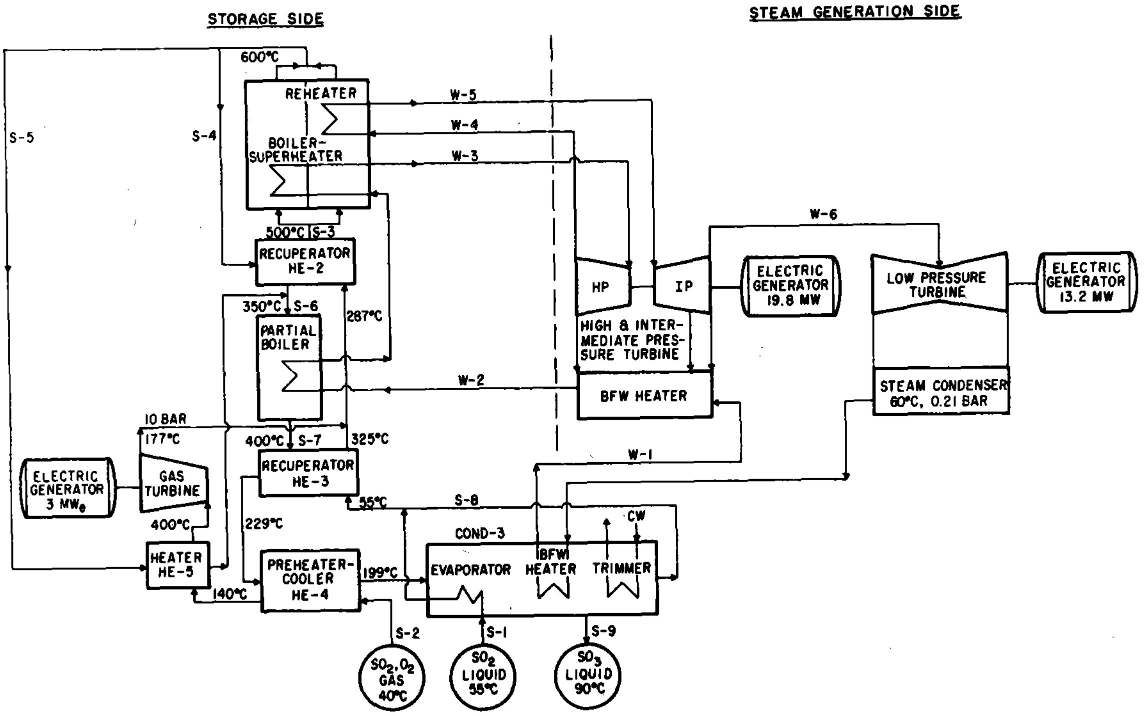


MAIN STREAM DATA - SULFUR (S) SYSTEM							
Stream	S-1	S-2	S-3	S-4	S-5	S-6	S-7
Flow (kmole/sec)	1.94	5.76	6.72	1.06	5.66	1.84	3.82
Composition* (mole%)							
SO_2	1.0	1.0	28.7	8.2	32.1	99.0	1.0
SO_3	99.0	99.0	56.8	1.2	67.9	1.0	99.0
Temperature (°C)	90	700	800	40	108	55	104
Pressure (bar)	10	40	40	40	40	10	10
State (L-liquid; G-gas)	L	G	G	G	L	L	L

*Oxygen content makes the balance.

MAIN STREAM DATA - WATER (W) SYSTEM							
Stream	W-1	W-2	W-3	W-4	W-5	W-6	W-7
Flow (kg/sec)	287	426	426	374	374	287	66
Temperature (°C)	140	243	538	316	538	349	427
Pressure (bar)	4	208	167	37	33	8	15
State (W-water; S-steam)	W	W	S	S	S	S	S

NIGHT TIME OPERATION SCHEME (DISCHARGE MODE)



MAIN STREAM DATA - SULFUR (S) SYSTEM									
Stream	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9
Flow (kmole/sec)	0.96	0.53	1.50	0.80	0.26	1.06	1.00	0.007	0.993
Composition* (mole%)									
SO_2	99	8.2	66	11	11	11	1.3	1	1.4
SO_3	1	1.2	1	83	83	83	98	9	98.6
Temperature (°C)	55	40	500	600	600	350	400	40	90
Pressure (bar)	10	40	10	10	10	10	10	10	10
State (L-liquid; G-gas)	L	G	G	G	G	G	G	G	L

*Oxygen content makes the balance.

MAIN STREAM DATA - WATER (W) SYSTEM						
Stream	W-1	W-2	W-3	W-4	W-5	W-6
Flow (kg/sec)	24	29	29	26	26	24
Temperature (°C)	140	243	538	316	538	349
Pressure (bar)	4	208	167	37	33	8
State (W-water; S-steam	W	W	S	S	S	S

FIGURE 1: FLOWSHEET FOR CHEMICAL STORAGE OF THERMAL ENERGY

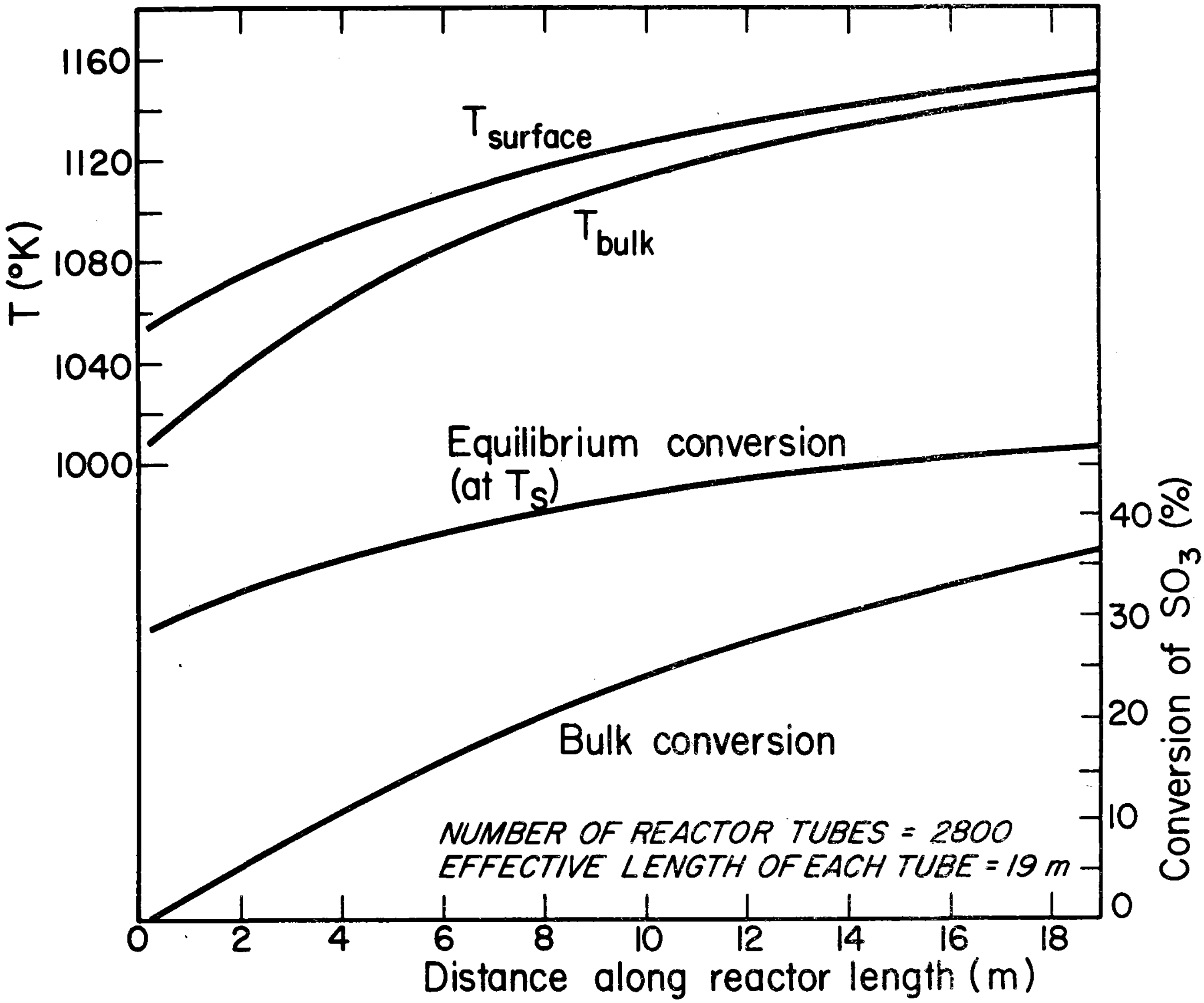


FIGURE 2 - TEMPERATURE AND COMPOSITION PROFILES IN SOLAR REACTOR

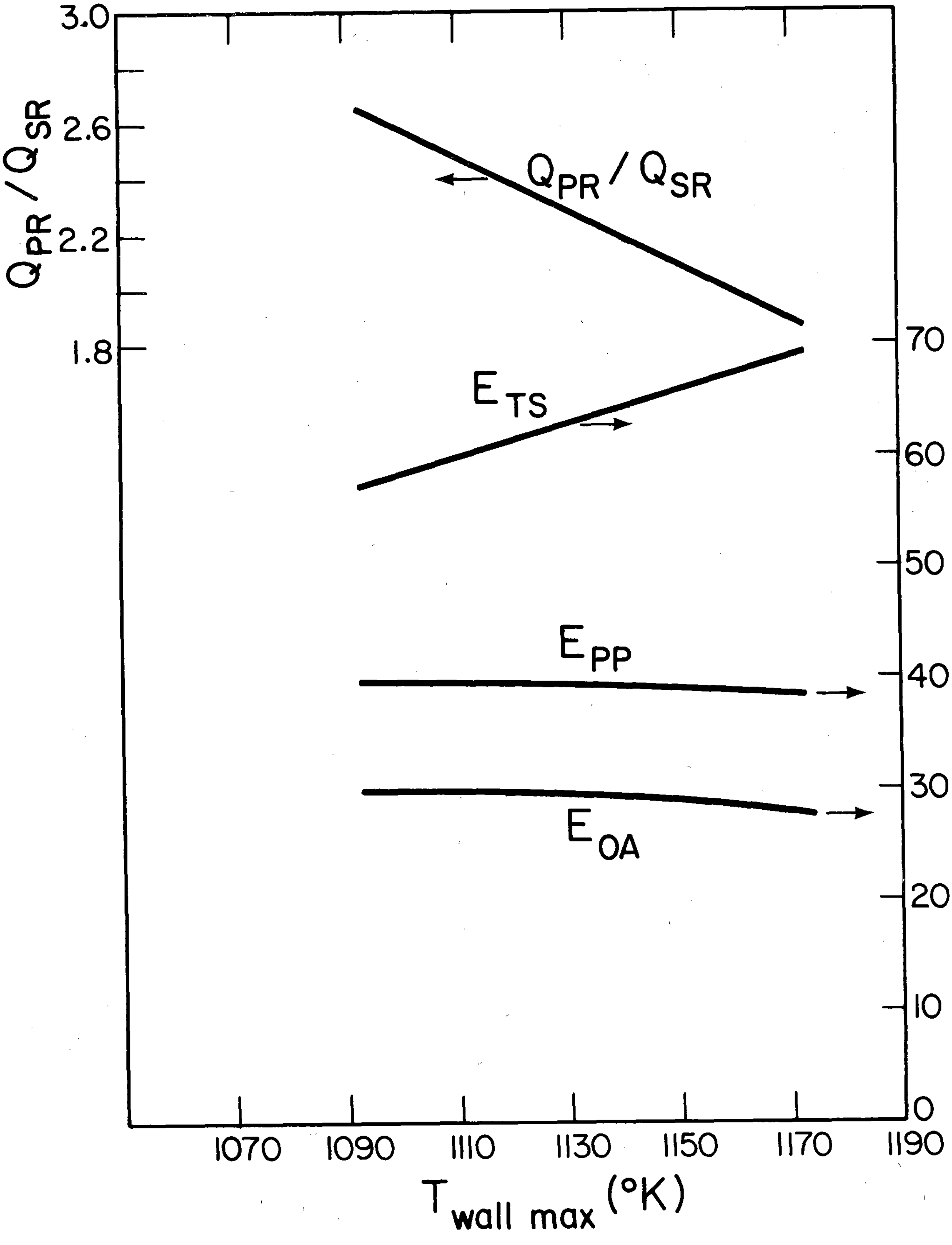


FIGURE 3 - EFFECT OF MAXIMUM ALLOWABLE TUBE WALL TEMPERATURE ON SYSTEM PERFORMANCE

PROJECT SUMMARY

Project Title: Duplex Steam Reformer Development

Principal Investigator: G. R. Pflasterer, D. C. Allen

Organization: General Electric Company
Advanced Reactor Systems Department
310 DeGuigne Drive
Sunnyvale, California 94086

Project Goals: Design, develop fabrication techniques, fabricate, test, and evaluate a duplex steam reformer tube for potential application as a high temperature nuclear heat source with applications to production of synthetic fuel gas.

Project Status: The project has four phases:

Study and Planning - evaluate high temperature nucleate process heat applications and develop duplex reformer tube design. The study and planning phase was completed in May 1976 with the establishment of the tube design.

Duplex Tube Procurement - evaluate and select fabrication methods and manufacture a duplex tube assembly. The fabrication method selection and demonstration was completed in August 1977, procurement is in progress with tube delivery in first quarter of CY79.

Test Performance - conduct test at Kernforschungsanlage (KFA) in Federal Republic of Germany. The test performance is scheduled at KFA in the second quarter CY79.

Post Test Evaluation - evaluate the performance and metallurgical test data and assess future applications. The post test evaluation is scheduled for completion in CY80.

Contract Number: EY-76-C-02-2841

Contract Period: FY79 continuing into FY80

Funding Level: $1,126,000

Funding Source: Jointly funded by Department of Energy Divisions of Energy Storage Systems and Nuclear Power Development

I. PURPOSE

The duplex tube program, which is funded jointly by the DOE Divisions of Nuclear Power Development and Energy Storage Systems, is part of a United States and Federal Republic of Germany international program to study high temperature nuclear process heat applications. The successful development of a duplex reformer tube has the potential to eliminate the need for a costly and complicated intermediate heat exchanger (IHX). The two walls of the duplex tube potentially provide the required double isolation between the reformer process gas and the radioactive reactor coolant gas. Replacing the IHX with a duplex tube unit potentially reduces the cost of construction of a 3,000 MW plant by an estimated 10%, increases overall efficiency by an estimated 1.5%, and reduces the required maximum coolant temperature of the reactor by 30°C.

II. INTRODUCTION

The steam reforming process, which is an established technology, when combined with a high temperature gas-cooled reactor provides the opportunity to apply nuclear heat to industrial processes. The heat from the nuclear reactor can be transmitted chemically by the chemical heat pipe system under study at General Electric (Reference 1). Industrial processes that follow from the development of this concept are:

- Hydrogasification
- Reduction of Iron Ore
- Ammonia Synthesis
- Methanol Synthesis
- Hydrocracking
- Chemical Heat Pipe
- Hydrogeneration of Coal
- Fischer-Tropach Synthesis
- Oxosynthesis

Recognizing the potential advantages of the duplex tube, General Electric proposed a program for its development and in 1975 ERDA awarded this contract to General Electric Company to begin work. The duplex steam reformer (DSR) program is divided into four sequential phases:

Phase 1 - Study and Planning

Phase 2 - Duplex Tube Procurement

Phase 3 - Test Performance

Phase 4 - Post Test Evaluation

II. INTRODUCTION (continued)

Phase 1 of this contract was completed in May 1976 and the results are described in Reference 2. In this reference the performance characteristics of a Duplex Steam Reformer-High Temperature Gas Reactor application are reported and a recommendation is made that Incoloy 800H be the material used in the fabrication of the duplex tubes. The recommendation is based on mechanical and chemical properties, resistance to hydrogen and tritium permeation, cost and availability.

Concern over the ability to fabricate tubes of the required size (90 mm inside diameter, 130 mm outside diameter and 12 meters long) led to the separation of Phase 2 into two parts. Phase 2A has been completed and had the objective to demonstrate the feasibility of kinetically forming duplex tubes of the required size. This procedure was successfully demonstrated by Foster Wheeler Development Corporation (FWDC) under subcontract to General Electric and a report describing the work was submitted in July 1977 (Reference 3). The fabrication procedure consists of explosively expanding the inner tube into the outer tube. This expansion is done in two steps with an intermediate anneal. The second part of Phase 2 provides for kinetic fabrication of production tubes and is presently in progress.

III. DESCRIPTION

Figure 1 compares helium heated and conventional reformers and Figure 2 shows the design of the DSR tube assembly being fabricated for testing in Germany. Characteristics of this tube include a 0 to 3 mil radial gap, a 90 mm inside diameter, and axial grooves between the tubes to insure flow of gas for leak detection. The tube is constructed of Alloy 800H. The normal operating conditions for the tube are shown in Figure 3. With these conditions approximately 250 KW of heat are removed with each tube. The licensability of such a duplex tube operating as an integral part of a reformer under these conditions has been studied and a report has been released for possible consideration by appropriate federal agencies.

IV. ACCOMPLISHMENTS

Thus far in the program, the following activities have been completed:

1. Duplex Tube assembly designed
2. Kinetic expansion fabrication process demonstration completed
3. Tube material ordered and received
4. Fabrication subcontract negotiated and fabrication started

IV. ACCOMPLISHMENTS (continued)

5. Reached agreement with cognizant West German organizations and project Work Statement has been prepared and approved
6. Prepared and issued Metallurgical Evaluation Plan
7. Licensability study completed and report released
8. Performance computer code developed
9. Test Plan has been prepared
10. Fabrication plans prepared to support the start of manufacture
11. Cold Work and Annealing Studies for Alloy 800H prepared
12. First trial fit-up of full size mock-up tubes successfully completed

V. FUTURE ACTIVITIES

In CY79 and early CY80 the following activities are planned:

1. Complete tube fabrication and ship to Germany for testing
2. Conduct test at KFA, Federal Republic of Germany
3. Issue Manufacturing Report
4. Conduct performance and metallurgical evaluations and issue Program Report
5. Complete application studies

VI. REFERENCES

1. "Closed Loop Chemical Systems for Energy Storage and Transmission," (Chemical Heat Pipe) H. V. Vakil and J. W. Flock, General Electric Company (Contract EY-76-C-02-2676) February 1978, COO-2676-1.

2. "Design of a Helium Heated Duplex-Tube Steam-Methane Reformer," J. A. Bond et al June 1976, ESTD 76-06.

3. "Duplex Tube Fabrication Feasibility Demonstration Program," O. F. Kimball and J. W. Schroeder, General Electric Company (Contract E(11-1)-2481), May 1977, AES 2841-(1).

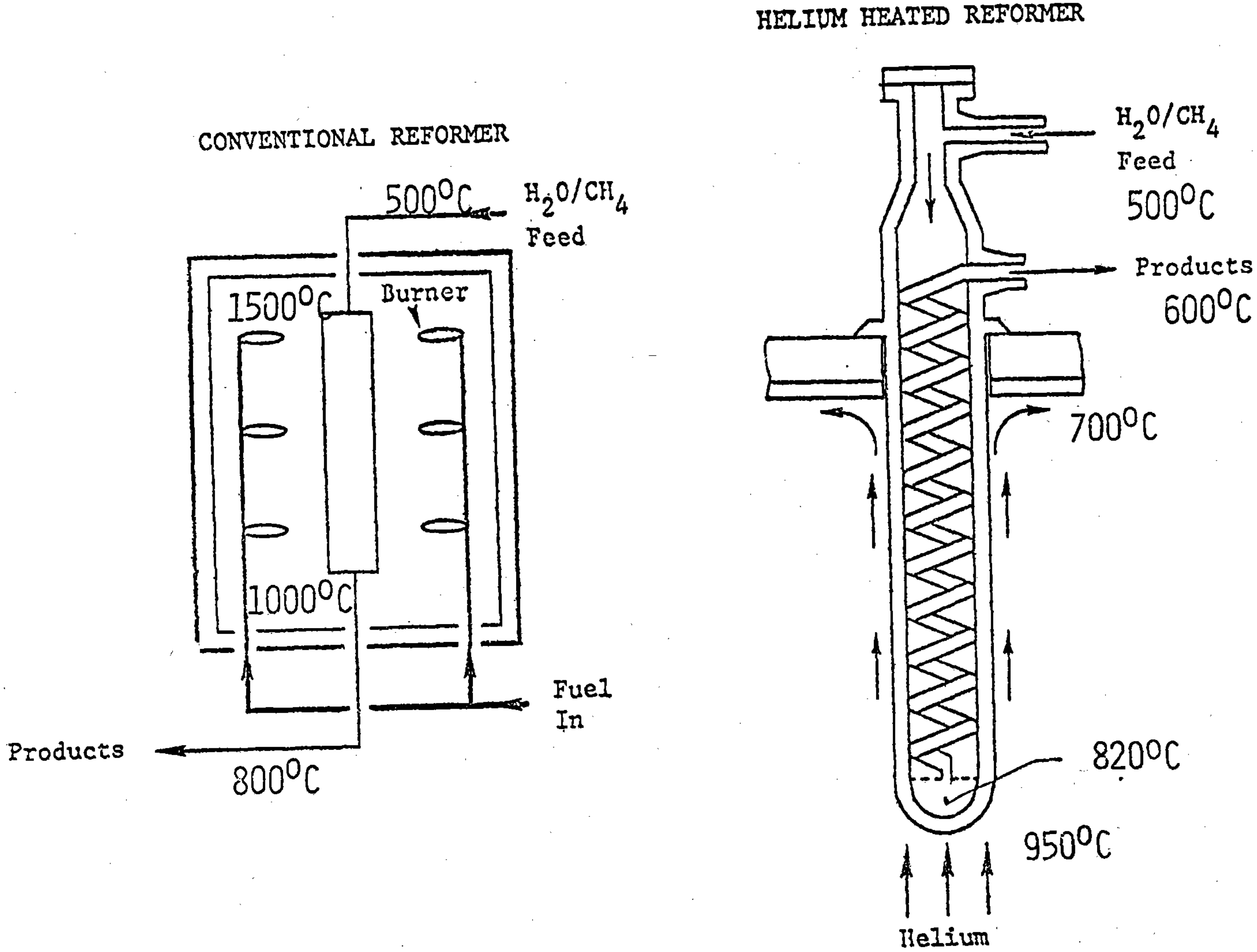
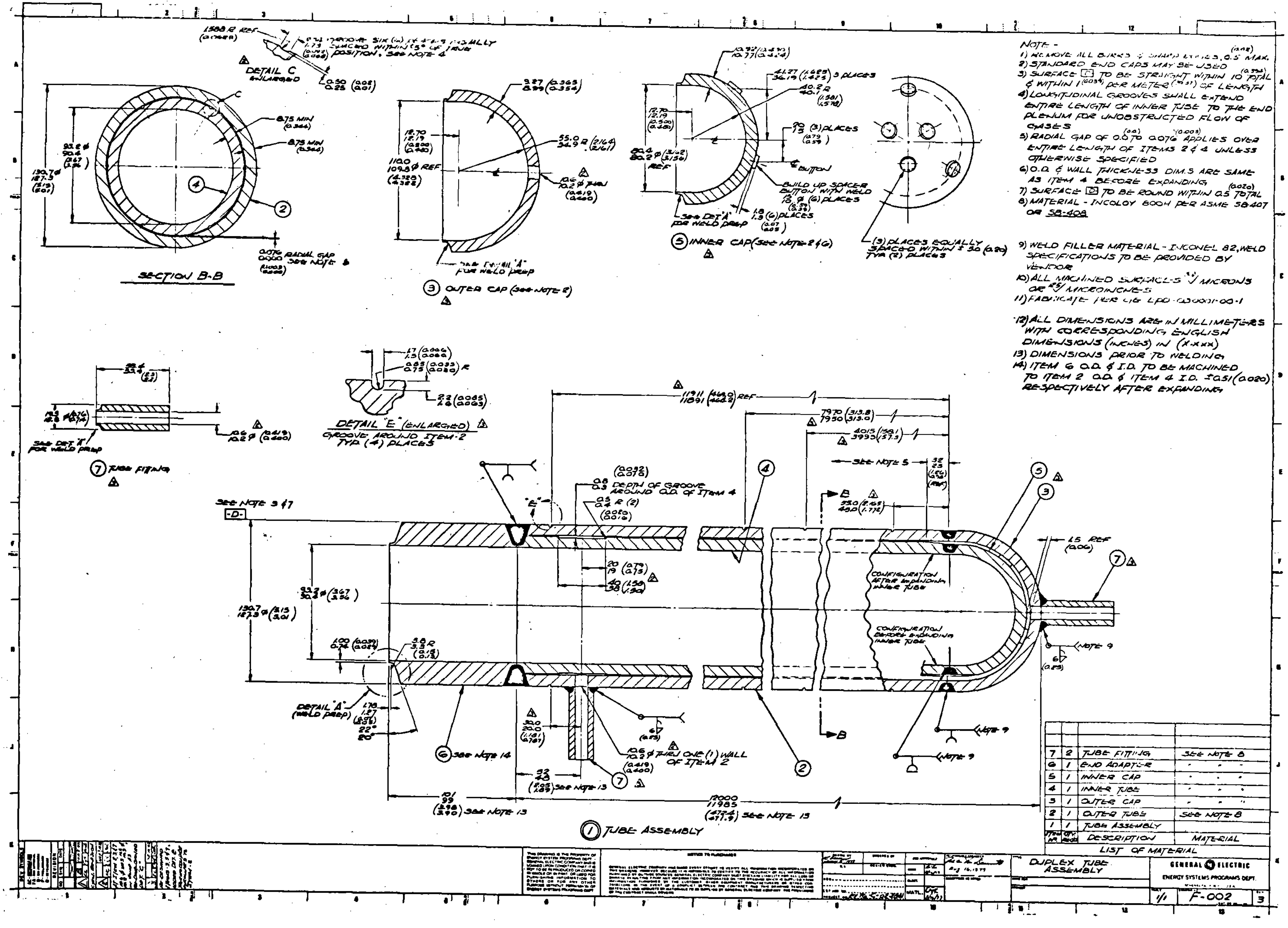


FIGURE 1.
CONVENTIONAL AND HELIUM HEATED REFORMER COMPARISON


NOTE -
1) REMOVE ALL BURRS & SHARP EDGES, 0.5 (0.02) MAX.
2) STANDARD END CAPS MAY BE USED
3) SURFACE C TO BE STRAIGHT WITHIN 10 (0.394) TOTAL & WITHIN 1 (0.039) PER METER (39.37) OF LENGTH
4) LONGITUDINAL GROOVES SHALL EXTEND ENTIRE LENGTH OF INNER TUBE TO THE END PLENUM FOR UNOBSTRUCTED FLOW OF GASES
5) RADIAL GAP OF 0.0 (0.0) TO 0.076 (0.003) APPLIES OVER ENTIRE LENGTH OF ITEMS 2 & 4 UNLESS OTHERWISE SPECIFIED
6) O.D. & WALL THICKNESS DIM.S ARE SAME AS ITEM 4 BEFORE EXPANDING
7) SURFACE D TO BE ROUND WITHIN 0.5 (0.020) TOTAL
8) MATERIAL - INCOLOY 800H PER ASME SB-407 OR SB-408
9) WELD FILLER MATERIAL - INCONEL 82, WELD SPECIFICATIONS TO BE PROVIDED BY VENDOR
10) ALL MACHINED SURFACES 0.6 MICRONS OR 25 MICROINCHES
11) FABRICATE PER GE LPD-03000I-00-1
12) ALL DIMENSIONS ARE IN MILLIMETERS WITH CORRESPONDING ENGLISH DIMENSIONS (INCHES) IN (X.XXX)
13) DIMENSIONS PRIOR TO WELDING
14) ITEM 6 O.D. & I.D. TO BE MACHINED TO ITEM 2 O.D. & ITEM 4 I.D. ±0.51 (0.020) RESPECTIVELY AFTER EXPANDING
DETAIL C ENLARGED
SECTION B-B
③ OUTER CAP (SEE NOTE 2)
⑤ INNER CAP (SEE NOTE 2 & 6)
(3) PLACES EQUALLY SPACED WITHIN ± 5.0 (0.20) TYP (2) PLACES
BUILD UP SPACER BUTTON WITH WELD
⑦ TUBE FITTING
DETAIL 'E' (ENLARGED)
GROOVE AROUND ITEM 2 TYP (4) PLACES
DEPTH OF GROOVE AROUND O.D. OF ITEM 4
CONFIGURATION AFTER EXPANDING INNER TUBE
CONFIGURATION BEFORE EXPANDING INNER TUBE
DETAIL 'A' (WELD PREP)
⑥ SEE NOTE 14
10.6 ⌀ THRU ONE (1) WALL OF ITEM 2
① TUBE ASSEMBLY
7 | 2 | TUBE FITTING | SEE NOTE 8
6 | 1 | END ADAPTER | " " "
5 | 1 | INNER CAP | " " "
4 | 1 | INNER TUBE | " " "
3 | 1 | OUTER CAP | " " "
2 | 1 | OUTER TUBE | SEE NOTE 8
1 | 1 | TUBE ASSEMBLY
ITEM NO. | QTY. REQD. | DESCRIPTION | MATERIAL
LIST OF MATERIAL
DUPLEX TUBE ASSEMBLY
GENERAL ELECTRIC
ENERGY SYSTEMS PROGRAMS DEPT.
F-002

Helium Side

Inlet Temperature	950C
Outlet Temperature	varies: ∼700C
Inlet Pressure	40 bar
Max. Pressure Drop	0.2 bar
Mass Flow Rate	varies: 0.1 to 0.4 kg/s

Process Side

Inlet Temperature	500C
Reforming Temperature	810 - 825C
Outlet Temperature	varies: ∼600C
Inlet Pressure	35 bar
Max. Pressure Drop	∼6 bar
Methane Inlet Flow Rate	varies: 75 to 150 Nm^3/h
Steam Inlet Flow Rate	varies: ∼100 to ∼400 kg/h
H_2O/CH_4 Inlet Mole Ratio	varies: 2/1 to 4/1

Figure 3. PROPOSED TEST CONDITIONS FOR DSR TUBE

PROJECT SUMMARY

Project Title: Sulfuric Acid and Water Chemical Heat Pump/Thermal Energy Storage

Principal Investigator: E. C. Clark

Organization:
Rocket Reserach Company
York Center
Redmond, Washington 98052
(206) 885-5000

Project Goals: The objective of this program is to study the development of a sulfuric acid heat pump for thermal energy storage.

Project Status: This project is divided into three tasks as follows:

Conduct an economic analysis to study the major system variables affecting the total integrated system design and cost. An integrated simplified computer model is being developed to compute collected solar energy, building loads, and storage size on an hourly basis using weather tape data. (Complete by February 1979) Commercial component costs including collectors are being generated to compute the system costs. (Complete by February 1979)

Using an engineering model test system, conduct component optimization testing for cost effectiveness. The engineering model heat pump has been updated to utilize commercial grade valves and plumbing. Testing for component size optimization is in progress.

Assess the ability to commercialize the sulfuric acid system considering such things as institutional barriers, building codes, and public acceptance. The assessment of commercialization is underway and is scheduled to be completed by January 1979.

Contract Number: 18-495B

Contract Period: FY78, complete by February 10, 1979

Funding Level: $250,000

Funding Source:
Sandia Laboratories
Livermore, California

SULFURIC ACID AND WATER CHEMICAL HEAT PUMP/THERMAL ENERGY STORAGE

ABSTRACT

A chemical heat pump/thermal energy storage system has been designed, fabricated, and successfully tested under U.S. Department of Energy (DOE)/Sandia funding. This first operational chemical heat pump is a key milestone in DOE's long-term thermal energy storage goals.

The sulfuric acid/water chemical heat pump is suitable for both heating and cooling with COP's > 1 possible and has an inherent energy storage capacity up to 600 Btu/lbm. Long-term storage appears promising for this system because the chemicals are stored at ambient temperature and are inexpensive. Moreover, temperatures required for charging (150F to 400F or 66C to 200C) are suitable for low-cost solar collectors; and both the mass and volumetric energy storage densities are considerably higher than alternatives such as ice or hot water storage.

This paper covers the work conducted to date since the previous contractors meeting in September 1977, plus the anticipated activities for the future.

APPROACH

The initial Phase I effort with the H_2SO_4/H_2O program was a 9-month conceptual design and laboratory demonstration of the primary components, which proved the feasibility of the thermal storage concept and demonstrated the separation and recombination of the chemicals (1). During the Phase II program, the chemical heat pump concept was identified; and an engineering model was designed, constructed, and tested (2).

Phase II-A, now in progress, involves continued testing, component optimization, and assessment of cost-effective system designs. Future plans include full-scale component development, solar interface studies, and ultimately full-scale demonstration projects.

ENGINEERING MODEL TEST SYSTEM

The engineering model system built during the Phase II program is shown without insulation in Figure 1, and a system diagram is given in Figure 2. The primary components consist of two glass acid tanks, one 316 stainless steel water tank, and two glass shell and tube heat exchangers. All components are supported by a steel tube framework. A control panel is mounted on the structure containing system rotometers and pertinent valve controls.

Each acid tank is a composite assembly of 18-inch diameter glass column components. Both tanks are identical in configuration. At the top of the tank assembly is a Teflon plate to support 1/2-inch ceramic Raschig rings. This column packing is used to limit acid carryover during the charging process and provide a liquid/gas interface during the discharge process. Two acid tanks have been incorporated because of component availability; the system should operate equally well using a single larger tank. However, the additional tank provides the added benefit of backup hardware and system flexibility for design optimization testing. The system contains 400 pounds of dilute sulfuric acid with a total energy capacity in excess of 300,000 Btu's.

The stainless steel water tank contains 1/2 inch diameter copper tubing used for the condenser (19.5 ft^2) and water boiler heat exchangers (96.7 ft^2). Two 5-inch diameter view ports and a sightglass are provided for liquid level measurements. The two acid tanks and water tank are connected using 4-inch diameter glass pipe. A shutoff valve is provided between the acid tanks and the water tank.

Thermal energy is input to the system using two glass shell and tube heat exchangers. Each heat exchanger contains 13.5 ft^2, and the two in series provide a nominal heat transfer rate of 25,000 Btu/hr. Acid is pumped from the bottom of the tanks through the internal tube passages using a commercial silicon iron centrifugal acid pump. The acid is then returned to the tanks through two separate channels, depending on the mode of operation (charge/discharge). All plumbing containing the sulfuric acid is fabricated from Teflon schedule 40 pipe.

The heat transfer fluid employed for this test series is Dowtherm G. The thermal input for charging is provided by electric heaters. The thermal output (simulation of a building demand) used for discharging is simulated using a fabricated copper shell and tube heat exchanger with city water used as the heat sink. City water is also being used for test purposes as the low-temperature source in the water tank during discharging and as the heat sink for condensation during charging.

TEST RESULTS

To date, the engineering model test system has been subjected to a series of initial demonstration tests followed by component optimization testing. The system has been disassembled and all components inspected for wear. Most recently, the system was reassembled with commercial grade plumbing. Continued component testing is now in progress.

A total of 58 closed-loop charge/discharge cycles have been completed with an accumulated operational time of 338 hours. Maximum thermal sources temperatures of 170°F to 400°F have been tested. Nineteen closed-loop cycles were conducted at 400°F with peak acid concentrations repeatably reaching 97% H_2SO_4 (by weight). During these tests, the amount of acid carryover in the vapor phase which becomes condensed in the water tank was measured at 0.02 grams per cycle. This measured value represents unlimited cycle capability since assuming 1 gram per cycle is carried over, a total of 10,000 cycles can be accumulated before the design storage capacity is reduced 5 percent. This represents 27 years with a diurnal duty cycle and unlimited seasonal storage. A special test was conducted to measure the quantity of noncondensible vapors produced by dissociation of H_2SO_4 (SO_2 and O_2). A liquid nitrogen cold trap was used to take a gas sample. No noncondensibles were found.

A typical temperature/time function for the sulfuric acid test system is presented in Figure 3. Both the thermal source temperature and out of the acid heat exchanger is shown. For this test, the starting acid concentration was 60% H_2SO_4 (by weight) and reached a peak value of 98% H_2SO_4 (by weight). Analysis of the test results indicate that of the 310,900 Btu's were input to the acid heat exchanger during the charge cycle, the net heat input available to store thermal energy as a chemical heat pump was 231,147 Btu's yielding a stored energy density of 570 Btu/lbm of dilute sulfuric acid. This compares favorably to a predicted value of 557 Btu/lbm.

A total COP of 0.75 was calculated for the test including the measured parasitic work of 80,000 Btu's necessary to drive the acid pump (with the three to one thermal electric conversion factor). The parasitic work is much higher than needed for an optimum design because an "off the shelf" acid pump, which was larger than needed, was procurred to meet program schedule constraints. An estimated COP of 0.9 is possible using an optimized pump. Figure 4 presents accumulated energy content as a function of time for the total heat pump system, the acid, the various system components, and system heat losses.

Condenser and evaporation optimization tests were conducted to determine the effects of reduced surface area. The results verified theoretical predictions and assumption of the analytical computer model (2). As the condenser/evaporator surface areas are reduced, the total working concentration range between a fully charged and fully discharged system is reduced which therefore reduces the storage capacity. These tests further verified that the process followed a normal condensing/evaporating process with no interaction with acid vapor generated in the acid tank.

Tests were conducted with sulfuric acid added to the water storage tank to demonstrate the antifreeze potential for system use with air driven low-temperature sinks. Concentrations of 0.5%, 2% and 5% $H2SO4$ (by weight) were tested and the results showed no reduction in charge/discharge rates. The water tank temperature was allowed to reach the corresponding freezing point temperature to determine if ice formation would block the water evapoaration during discharge. A slurry formed rather than solid ice with no blockage of heat transfer surfaces.

PROBLEMS AND SOLUTIONS

Several equipment problems occurred with the engineering model test system. During the first demonstration test, the initial magnetic drive, all teflon centrifugal acid pump failed. A failure analysis was conducted and revealed an improper thrust bearing design and undersized magnetic drive unit. The pump was replaced with a larger commercial grade cast silicon iron pump running in a derated mode. Troublefree operation occurred during the remainder of the test program.

Another problem occurring frequently was vacuum leaks. The leaks were caused by yielding of the schedule 40 teflon pipe threaded joints. Sealant was applied where-ever leaks were found. However, the complexity in the plumbing system due to instrumentation ports made total elimination of the leaks impossible. Also, stem leakage around the system acid valves made by Dow Corning was observed. A larger capacity vacuum pump was installed to eliminate buildup of inert gases from the vacuum leaks. The solution to this problem has been demonstrated in recent testing conducted with the upgraded commercial plumbing system. All acid plumbing lines were replaced with teflon lined steel pipes using flanged joints.

The Dow Corning teflon lined plug valves were replaced with a Resistoflex clamp valve and Durco plug valves with a different stem seal design. A complete charge/discharge cycle was conducted with the system vacuum pump turned off.

During initial discharge testing, ice and snow formation occurred in the water tank. System operational discharge rates were reduced somewhat. However, the process was not stopped due to sublimation of the ice. This problem was eliminated with the addition of a small 1/20 horsepower water circulation pump. Further testing with the circulation pump resulted in improved discharge rates and no further ice formation.

ECONOMIC ANALYSIS

The system economic analysis is currently under progress. A simplified computer model is being constructed to compute both collected solar energy and building load demand on an hourly basis using annual weather tapes. The model takes into account collector efficiency and will optimize storage volume as a function of collector size. To determine the most cost effective integrated system design, cost models for individual system components will be generated. Where appropriate, projected cost ranges for technology development will be utilized. The total system integrated costs will be compared with projected energy costs using fossil fuels.

ASSESSMENT FOR COMMERCIALIZATION

Sulfuric acid has been used for many years in thousands of industrial applications such as petroleum refining, car batteries, pharmaceuticals, and food processing, to name a few, and is produced in greater quantities than any other chemical by a considerable margin. The result is that much is known about handling, use, and storage of the acid; and a wealth of materials compatibility data is available. Numerous plastics are known to withstand exposure to sulfuric acid for long periods of time, which raises expectations of low tankage costs for seasonal storage systems. Portions of the system which are exposed to hot acid will require more expensive materials, but numerous moderate cost materials are available, and clever system design is expected to keep such costs to a minimum. The high volumes of production of sulfuric acid and the almost limitless supply of its constituent chemicals are responsible for its extremely low cost of around $.02/lbm (3), and significant cost increases are not expected in the future. Moreover, increased sulfuric acid demand would complement air quality control programs by providing a market for by-products of stack gas scrubbing and other processes.

It is believed that the primary obstacle to commercial acceptance of the sulfuric acid chemical heat pump/storage device will be overcoming resistance to having large amounts of acid on-site. Potential installers and users of the system must be educated on safe handling practices and safety precautions. Designs are underway which will limit the potential dangers of the system to an absolute minimum. For example, intermediate working fluids will be used between the acid and the solar collectors or the heated space. Numerous containment schemes are being studied which will provide inexpensive fail-safe containment in the event of an acid leak. Below grade storage, use of absorptive catch liners, and leak sensors are among the many schemes being considered. Moreover, it should be pointed out that the sulfuric acid system when used for heating or cooling applications operate at or below atmospheric pressure, so that the potential for rupture and acid splatter is limited.

To obtain an early indication of potential problems in commercializing the sulfuric acid system, research work is being conducted on applicable code and safety regulations including NFPA, OSHA, WISHA, ASHRAE, UBR, ANBS and Military Regulations. System requirements imposed by these regulations such as location, size, limitation, backup systems, safety requirements will be studied. Suggested amendments for codes and regulations will be addressed where necessary. Institutional barriers will be studied in the following areas: building design, system installation, maintenance and instrumentation and removal and replacement. The sulfuric acid system will be compared to other conventional systems for residential and commercial buildings.

FUTURE PLANS

The present Phase II-A program will be completed in February, 1979. During Phase III, a larger H_2SO_4 chemical heat pump will be constructed for heating and cooling. This system will represent as closely as possible a commercial design sized approximately for 10^6 Btu storage capacity and 150,000 Btu/lbm charge/discharge rate. The unit will be designed to couple with solar collectors for an integrated system demonstration with simulated building loads. This effort is anticipated to start in FY 79.

REFERENCES

1. Rocket Research Company, "Phase I Final Report, Sulfuric Acid-Water Chemical Energy Storage System, ERDA Contract No. E(04-3)-1185," Rocket Report No. RRC-76-R-530, August, 1976.
2. Clark, E. C., "Final Report - Phase II Sulfuric Acid-Water Chemical Heat Pump and Storage System, DOE Contract No. EY-76-C-03-1185" to be published.
3. "Chemical Marketing Reporter," June 5, 1978, pg. 85.

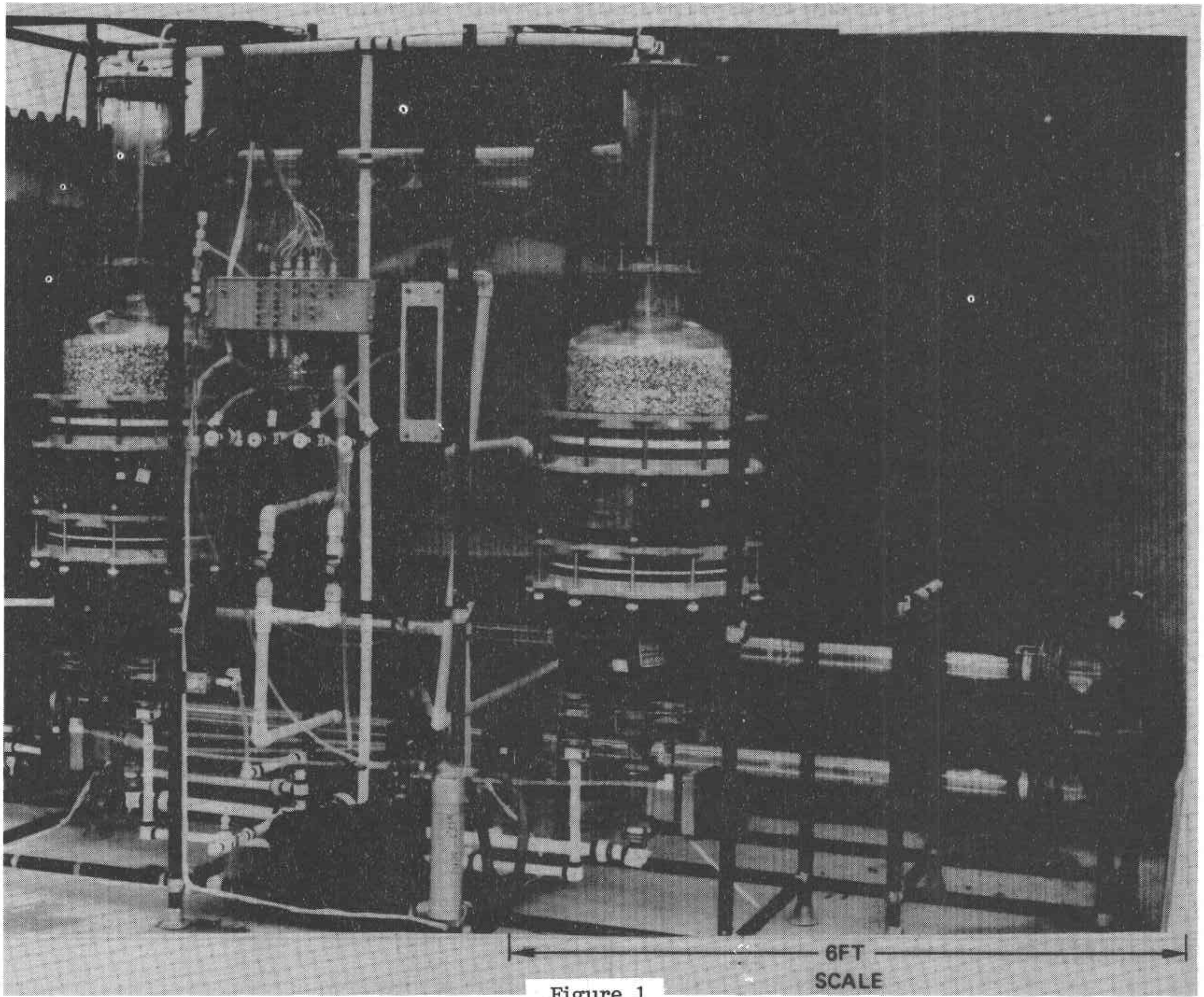
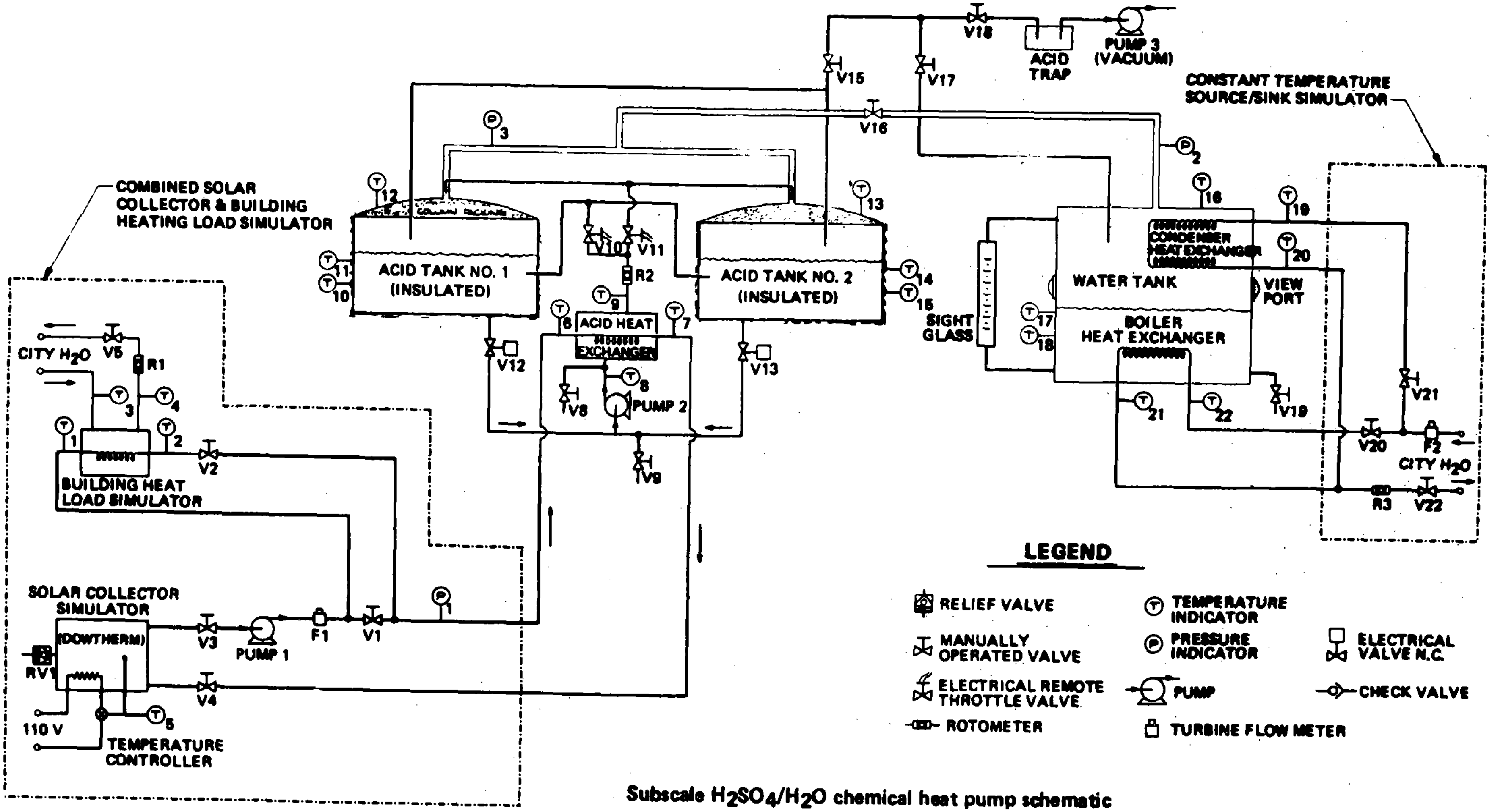
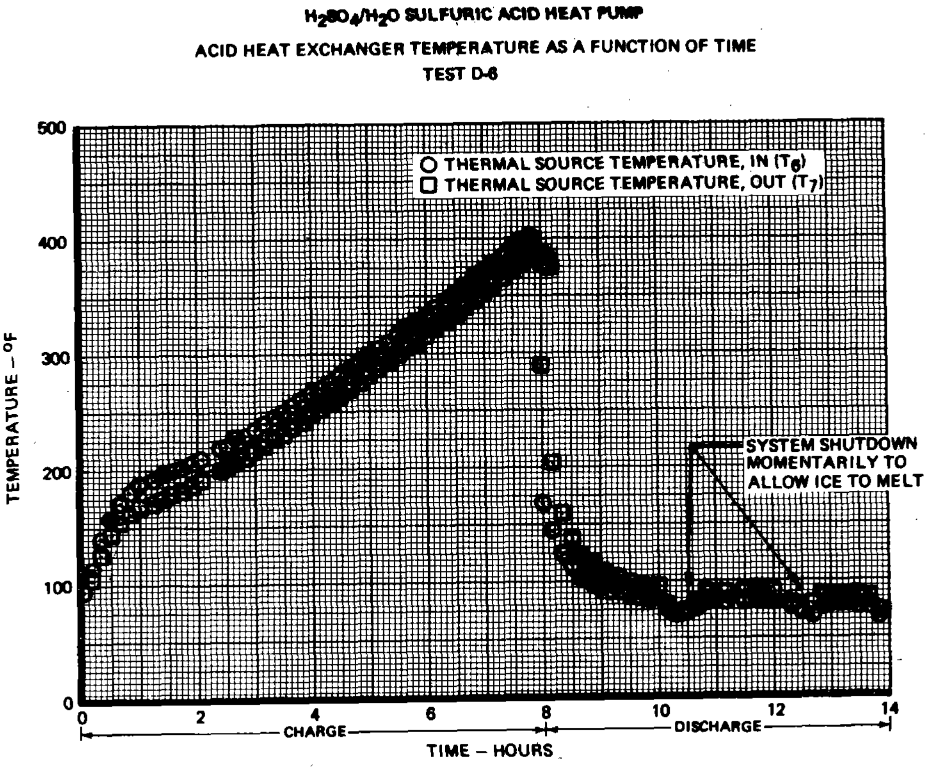


Figure 1



Subscale H_2SO_4/H_2O chemical heat pump schematic

Figure 2

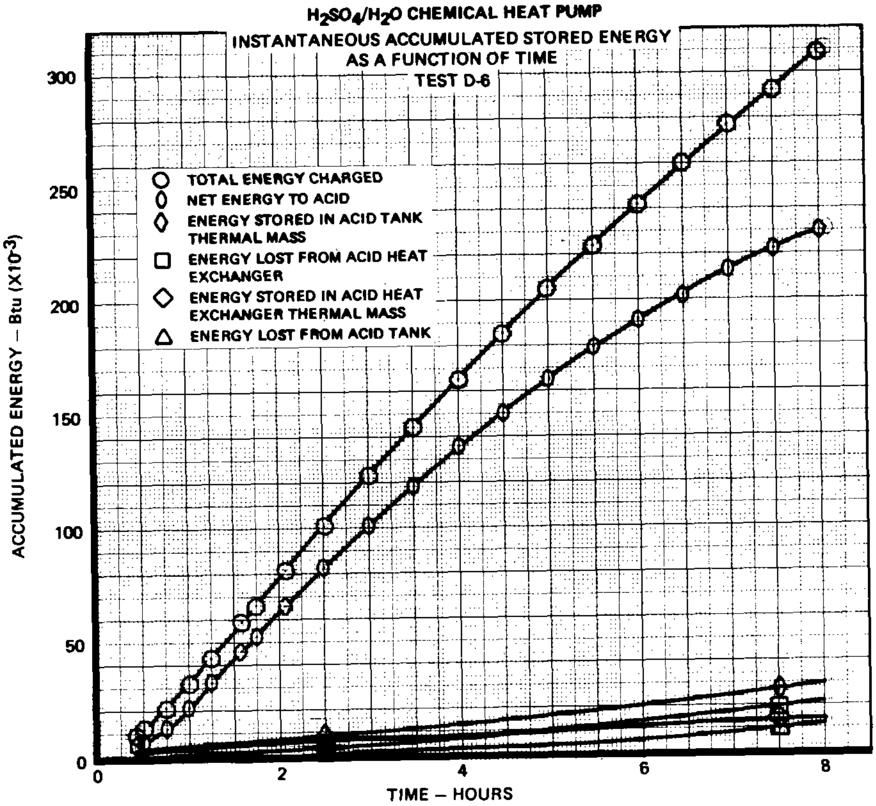


H_2SO_4/H_2O SULFURIC ACID HEAT PUMP

ACID HEAT EXCHANGER TEMPERATURE AS A FUNCTION OF TIME

TEST D-6

Figure 3



H_2SO_4/H_2O CHEMICAL HEAT PUMP

INSTANTANEOUS ACCUMULATED STORED ENERGY AS A FUNCTION OF TIME

TEST D-6

Figure 4

PROJECT SUMMARY

Project Title: Methanol-Based Heat Pumps for Storage of Solar Thermal Energy

Principal Investigator: Peter O'D. Offenhartz

Organization:
EIC Corporation
55 Chapel Street
Newton, Massachusetts 02158
(617) 965-2710

Project Goals: Design and construct a heat pump storage system based on the reaction of CH_3OH with one or more solid-state inorganic salt substrates, suitable for use in residential heating and cooling.

Project Status: This project consists of four major tasks:

Carry out screening experiments with a variety of inorganic substrates, and select the optimum salt(s). Obtain thermodynamic, kinetic, and heat transfer data on the optimum salt(s). In addition, obtain data on side reactions, corrosion, and cycle life. Roughly two dozen salts were screened. The reaction of anhydrous $CaCl_2$ to form solid $CaCl_2 \cdot 2CH_3OH$ has been selected for further work. Thermodynamic, kinetic, and heat transfer data on this reaction have been obtained. No side reactions or corrosion of Al or Cu have been observed. Over 300 methanolation/demethanolation cycles have been carried out without apparent degradation of performance.

Design appropriate heat exchanger(s) for solid-gas reactions. A low cost heat exchanger has been designed, based on the use of pelletized $CaCl_2$ loaded on externally finned tubes.

Design, construct, and test both a small scale and a large scale prototype system. The small scale prototype has been constructed and tests are now being carried out. Preliminary data indicate the unit performs as expected. Design of the large scale prototype is largely complete. Construction will be complete by July 1979 and testing will be carried out in late FY79 and early FY80.

Contract Number: (1) 87-9118; (2) 18-8423

Contract Period: April 25, 1977 continuing

Funding Level: (1) \$120,000; (2) \$276,000

Funding Source:
Sandia Laboratories
Livermore, California

I. INTRODUCTION

The basis of the heat pump storage system is a chemical reaction that proceeds in one direction at high temperature and in the opposite direction at low temperatures. A gas-solid reaction maximizes storage energy density and provides ready separation of the chemical products. Methanol is particularly suited as the vapor due to its low freezing point, high entropy of vaporization, and relative freedom from hazards.

The reaction scheme is

$$\text{Salt}\cdot n\text{CH}_3\text{OH (solid)} \xrightarrow{T_2} \text{Salt (solid)} + n\text{CH}_3\text{OH (vapor)}$$

$$\text{CH}_3\text{OH (vapor)} \xrightarrow{T_1} \text{CH}_3\text{OH (liquid)}$$

In the storage mode, T_2 is the solar collection temperature, ca. 150°C, and T_1 is a temperature suitable for heat exchange to the space to be heated, ca. 45°C. The reaction proceeds in the forward direction, as written. In the heat pump mode, T_2 is a temperature suitable for heat exchange to the space to be heated, ca. 50°C, and T_1 is the outdoor ambient, ca. -10°C. The reaction proceeds in the reverse direction. The projected coefficient of performance as a heat pump, including energy delivered to the space to be heated during solar collection, is approximately 1.6. The same system should work well as an air conditioner; the projected coefficient of performance is 0.6, comparable to a LiBr system. However, unlike the LiBr air conditioner, energy storage is inherent in the demethanolated salt, and a separate storage subsystem is not required.

II. PROJECT DESCRIPTION - PHASE I

Phase I of this project, which was aimed at selecting substrates suitable for heat pump use, is now complete. Twenty inorganic salts (1) were screened in a specially designed thermogravimetric analyzer (TGA) employing fixed CH_3OH vapor pressure and slowly varying temperatures. Appreciable reaction was found for a dozen salts, and four salts were found to have thermodynamic and kinetic behavior approximately suitable for use in a heat pump: $MgCl_2$, $FeBr_2$, $CoBr_2$, and $CaCl_2$. Later experiments showed evidence that $MgCl_2$ undergoes side reactions with CH_3OH, and $FeBr_2$ and $CoBr_2$ were rejected on the basis of cost. Calcium chloride was hence selected for further investigation.

Thermodynamic studies on the reaction of $CaCl_2$ with CH_3OH vapor were carried out in the TGA apparatus at a variety of temperatures and pressures. Rates of methanolation and demethanolation appear to be nucleation-limited at temperatures close to equilibrium, which complicates the determination of equilibrium data. However, it was possible to show that $CaCl_2$ absorbs two moles of CH_3OH, either in a single step, or in two steps separated by a few degrees. The heat of reaction is approximately 20 kcal/mole CH_3OH. The temperature-pressure behavior can be summarized by the statement

$$T_2/T_1 = 1.25 \quad (2)$$

where T_2 is the equilibrium absolute temperature of a mixture of $CaCl_2$ and $CaCl_2 \cdot 2CH_3OH$ at a fixed pressure P, and T_1 is the absolute temperature of liquid CH_3OH in equilibrium with vapor at the same pressure. (This is a form of the Ramsey-Young Rule.) Thus, with a liquid pool of CH_3OH at -15°C (258K), the vapor is also in equilibrium with the salt at 50°C (323K = 258 x 1.25). Further work on the salt-vapor equilibrium is being carried out by Sandia.

As noted above, the kinetics are complicated close to equilibrium. However, when the reaction is more than about 10°C away from equilibrium, rates are approximately first-order and reaction is over 80% complete in less than an hour.

Heat transfer data were obtained by carrying out reaction rate measurements under conditions where the rate was limited by heat transfer rather than intrinsic reaction kinetics. A computer model of the reaction process was developed, and experimental data were fit to the model. Russel's equation (2) relating salt-bed thermal conductivity k_b to the thermal conductivity of the continuous medium (CH_3OH vapor) k_v and the bed void fraction E was confirmed:

$$k_b = \frac{k_v}{1-(1-E)^{1/3}} \quad (3)$$

The implication of this equation for design purposes is that cycle times of the order of 8 hours can be obtained with salt bed depths of the order 0.5-1.0 cm.

During the initial reaction of $CaCl_2$ with CH_3OH, the salt expands to accommodate the vapor. However, the salt particles maintain a constant size upon further cycling. This is important for several reasons: (1) the salt does not exert any pressure on the container during cycling; (2) there is no tendency for the salt to contract during demethanolation, and good contact with the heat exchanger surfaces is maintained. (Deleterious effects of this type have been observed in the reaction of NH_3 with a variety of inorganic salts.) In addition, methanolation of $CaCl_2$ tends to fill the pore volume in the salt, which reduces E and results in increased bed thermal conductivity. Thus, as the reaction interface grows away from the heat transfer surface, the rate of heat transfer tends to remain constant despite the increased heat transfer distance.

Cycle life and corrosion tests have been carried out in small sealed Y-tubes over a three month period. No corrosion of Al or Cu has been observed.

No side reactions or degradation of the reactants was found. In tests on pelletized $CaCl_2$ without a binder, some minor tendency for the salt to agglomerate or break down into fines was observed. Furthermore, in some tests, cycling ceased quite early, while in others cycling continued without change for over 300 cycles. An uncontrolled experimental artifact is suspected, and additional cycling tests, including tests with $CaCl_2$ pellets held together with a binder and coated with various anti-agglomerating agents, are in progress.

A variety of heat exchanger designs were considered. At present, the most cost-effective design is one based on the use of a relatively thick (ca. 15 cm) bed of $CaCl_2$ pellets contained within the fins of an externally finned tube through which the heat transfer fluid flows. Use of pellets permits essentially unhindered vapor transport through the bed. A series of beds through which the heat treansfer medium circulates may be contained within a single hermetically sealed container, thereby simplifying the methanol and heat transfer medium piping requirements, and reducing the number of points at which hermetic sealing is required. Schematic diagrams of the salt bed, container, and manifold arrangement are shown in Figures 1-3.

The major potential obstacle to the use of thick pellet beds is the possibility that the pellets will break down into fines upon cycling. This would tend to cause an excessive CH_3OH pressure drop within the bed, which in turn would limit the ability of the system to pump heat. In effect, the heat exchanger design that has been selected substitutes a potential mass transport problem for the original heat transport problem. Fortunately, even $CaCl_2$ pellets without binders maintain their integrity upon cycling and, to date, production of fines has not been a problem. Nevertheless, the system must be designed for thousands of reversible cycles, and pellet stability must be maintained for many years. For this reason we are examining the use of a variety of pellet binders, as well as alternative heat exchange methods. Preliminary work indicates that intrinsic reaction kinetics remain rapid when pellet binders are used.

III. PROJECT DESCRIPTION - PHASE II

A small scale prototype, containing a liter of CH_3OH and 1.5 kg $CaCl_2$, has been constructed. Evaluation tests are now in progress. Preliminary results indicate that the unit performs as anticipated. Measurement of the rate of mass transfer will be made for a variety of pressures, temperatures, and fin spacings to determine the optimum heat exchange configuration, to obtain design data for the larger scale prototype, and to identify potential design problems.

Design work on a larger scale prototype, with approximately 100,000 BTU storage capacity, is largely complete. Work to date has focused on specification of auxiliary hardware, heat exchangers, piping, valves and controls. Design of the actual salt-bed heat exchanger will not begin for several months, until a substantial body of design data has been obtained from the small-scale unit. Operation of a larger scale prototype, which will begin in mid-1979, will permit a detailed heat balance on the system, and will be useful in identifying potential control and cycling problems. Data from the larger scale prototype will be used in the design and construction of a residential-scale unit, which will be capable of storage, space and hot water heating, and air conditioning.

Fundamental engineering chemistry on the cycling behavior of the $CaCl_2$-CH_3OH reaction, including pellet stability, the use of binders and anti-agglomerating agents, and corrosion testing, is continuing in Phase II.

IV. SUMMARY

The use of the reaction between $CaCl_2$ and CH_3OH vapor in a thermally activated heat pump for solar storage, heating and cooling appears highly promising for residential use. The physical and chemical properties of the reaction are exceptionally well suited to the application, and the heat and mass transfer problems associated with solid-phase absorption can be solved within the framework of a low-cost reactor design.

V. REFERENCES

1. P. O'D. Offenhartz, "Methanol-Based Single-Substrate Heat Pump for Solar Thermal Storage," Proc. Second Annual Thermal Energy Storage Contractors' Information Exchange Meeting, September 29-30, 1977, Gatlinburg, Tenn. (CONF-770955).

2. C. Russel, J. Am. Ceram. Soc., 18, 1 (1935).

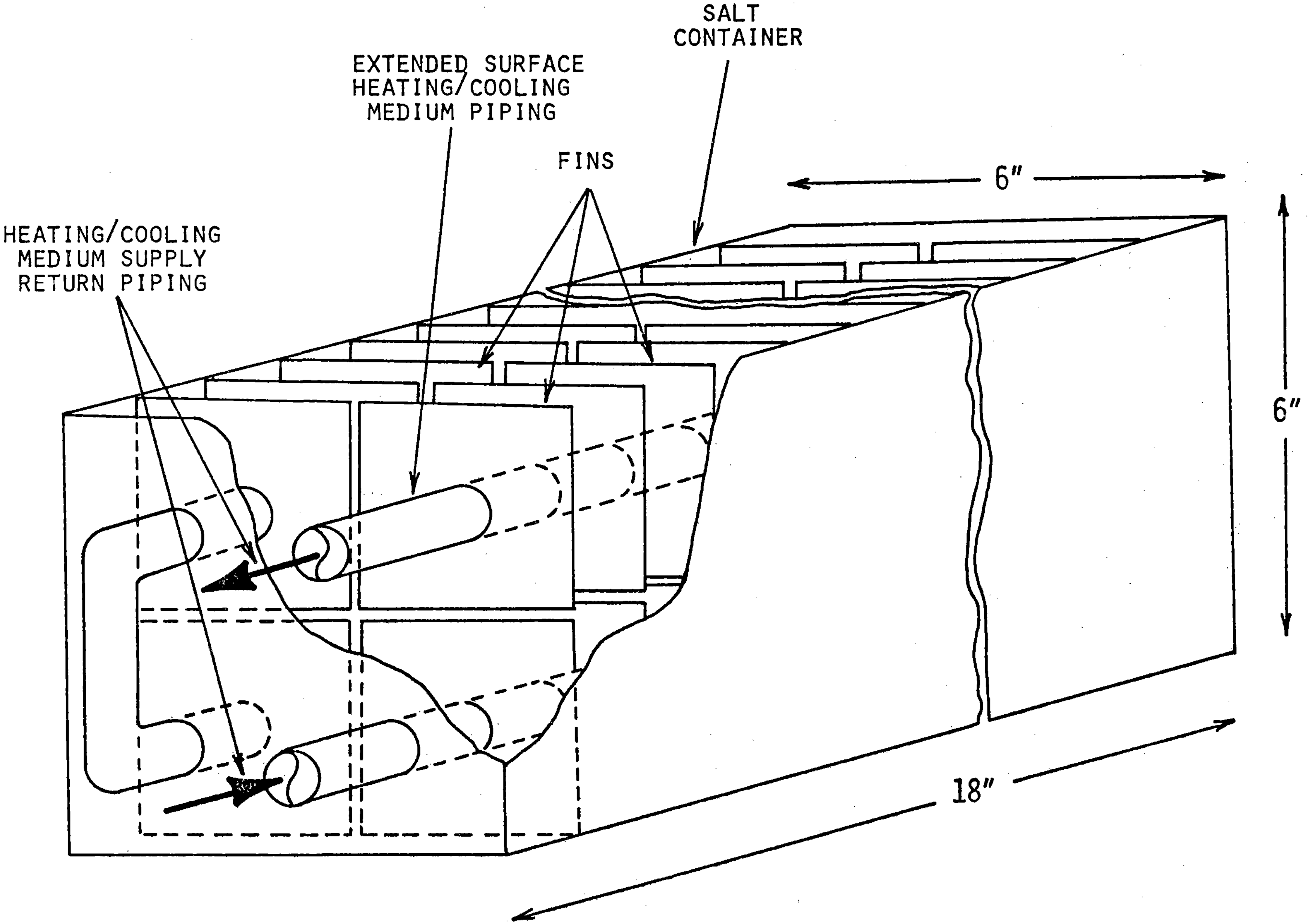


Fig. 1. Preliminary design of small scale prototype.

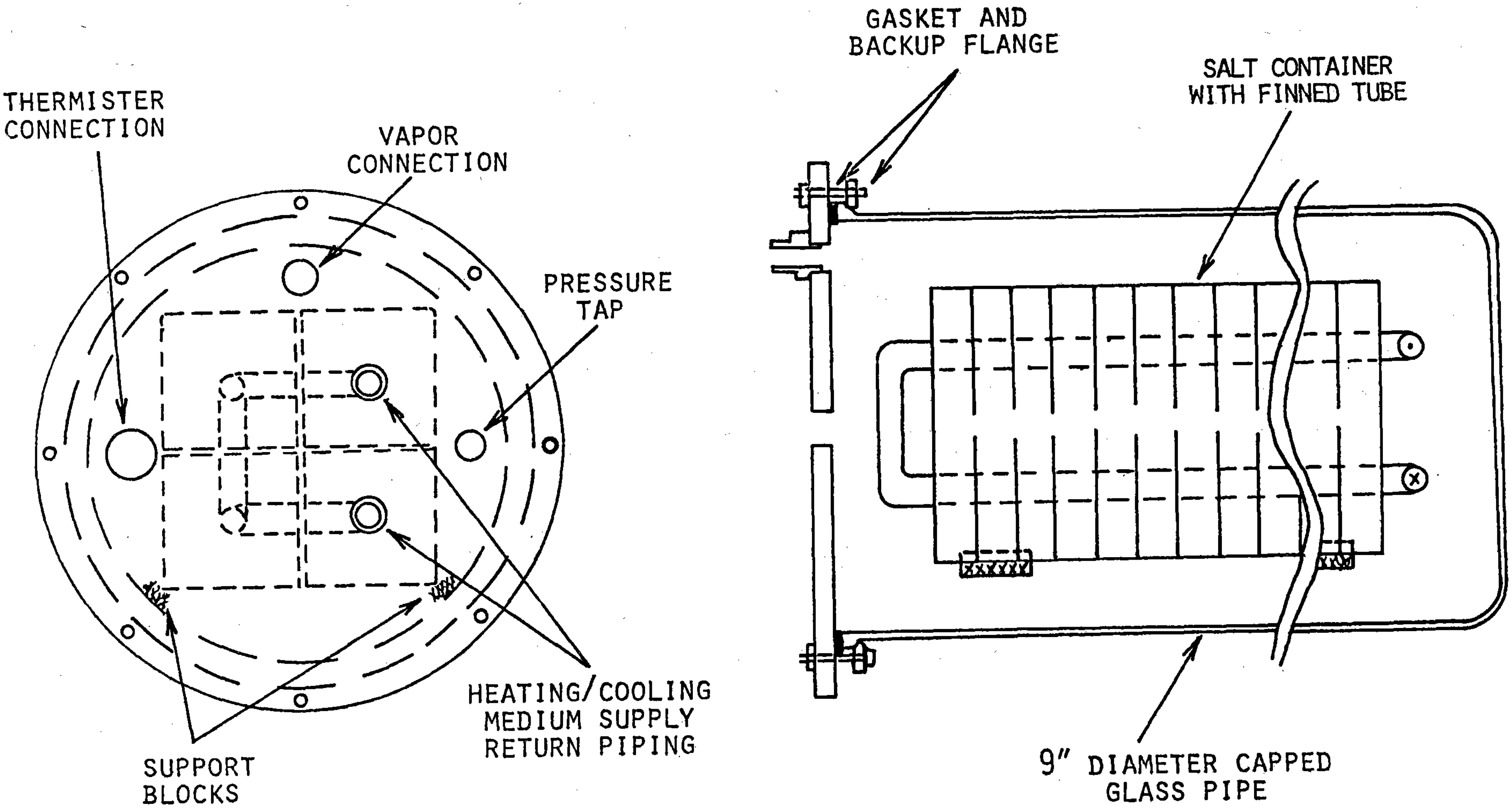


Fig. 2. Small scale prototype unit assembly.

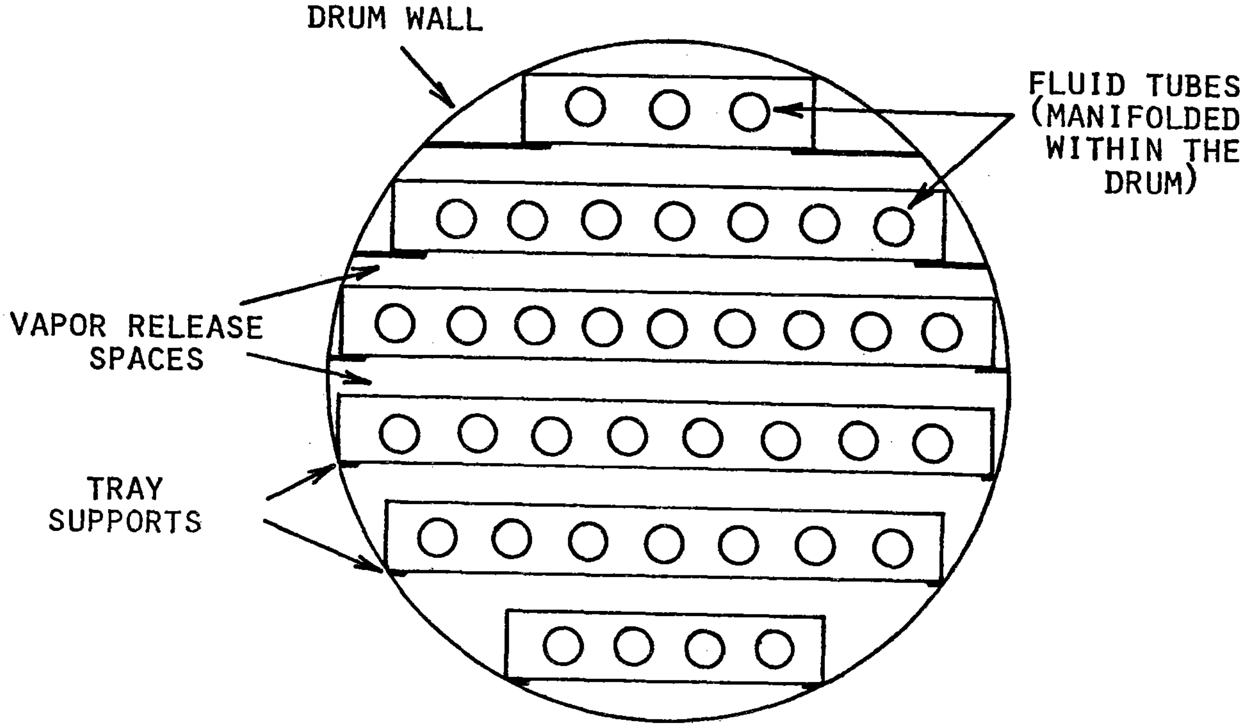


Fig. 3: Schematic arrangement of finned-tube salt-bed heat exchangers within a vapor containment drum.

PROJECT SUMMARY

Project Title: Development of Ammoniated Salts, Thermochemical Energy Storage System - Phase II

Principal Investigators: F. A. Jaeger and W. R. Haas

Organization:
Martin Marietta Aerospace
Denver Division
Post Office Box 179
Denver, Colorado 80201
(303) 979-7000

Project Goals: To demonstrate the operational feasibility of an ammoniated salt heat pump/thermal storage system.

Project Status: The project is divided into three tasks:

Chemical Tests: Determine the reaction rates for the $MgCl_2 \cdot 6NH_3$, $CaCl_2 \cdot 8NH_3$, and $MnCl_2 \cdot 6NH_3$ ammoniates at 0.25 and 0.5 atmospheres. Measure the heats of reaction for $NH_4Cl \cdot 3NH_3$ and $MnCl_2 \cdot 6NH_3$. Measure the density and viscosity of $NH_4Cl \cdot 3NH_3$. The reaction rate and heat of reaction for $NH_4Cl \cdot 3NH_3$ and $MnCl_2$ $6NH_3$ have been determined. Measurements of the reaction rate and heat of reaction fo $CaCl_2 \cdot 8NH_3$ and $MgCl_2 \cdot 6NH_3$ are in progress and will be completed this year. The density of $NH_4Cl \cdot 3NH_3$ was measured. Viscosity of $NH_4Cl \cdot 3NH_3$ will be measured in December.

Subscale System Testing: Design, fabricate and test a small scale reactor system using the following ammoniated salt pairs:

$MgCl_2 \cdot 6NH_3$ with $NH_4Cl \cdot 3NH_3$

$MNCl_2 \cdot 6NH_3$ with $NH_4Cl \cdot 3NH_3$

The design of the test system has been completed. Fabrication is in progress and testing will begin in December.

Computer Modeling: Develop a computer program to simulate a typical home heating and cooling system. The computer program has been written and checked out. Revisions will be made as a result of the subscale testing. The model will then be used to predict performance of a residential system.

Contract Number: Sandia 18-6825

Contract Period: July 1978 - June 1979

Funding Level: $112,000

Funding Source:
Sandia Laboratories
Livermore, California

I. INTRODUCTION

This program is a follow-on to a contract with the Division of Energy Storage in which ammoniated salt systems were studied as potential storage systems for electric power generation plants. The results of that program indicated that the ammoniated salt systems might be better used in lower temperature applications (i.e., residential heating and cooling). Therefore, this phase is concerned with systems that can be used as heat pump/storage systems with either solar or low temperature waste heat as the energy source.

The major objective of the program is to determine the feasibility of using systems with ammonium chloride in the low temperature reactor and either manganese or magnesium chloride in the high temperature reactor as a residential heat pump/thermal storage system.

II. PROJECT DESCRIPTION AND RESULTS TO DATE

A. Chemical and Physical Property Tests - Reaction Rate

Reaction rate data over a range of temperatures above and below the equilibrium temperature at one atmosphere is available for the $CaCl_2$, $MnCl_2$ and $MgCl_2$ reactions (Ref. 1) and preliminary correlations have been made. Application of this system to space cooling requires additional data at lower temperatures and pressures. Therefore, reaction rate measurements are necessary for absolute pressures of 0.25 atmospheres and 0.50 atmospheres. In the case of NH_4Cl, no data were available on the reaction rate.

Rate constant data at subatmospheric pressures will be obtained with the Mettler TA-1 Thermoanalyzer. Ammoniates are prepared in-situ by first preparing the anhydrous salt with an appropriate thermal-vacuum bake. After a stable weight is obtained, the salt is cooled to ambient temperature and the system is backfilled with the desired pressure of NH_3. When the weight gain indicates a fully ammoniated salt, the sample temperature is slowly raised until a weight loss is indicated. The sample temperature is held constant until the ammoniate is completely dissociated. The procedure is reversed, and the sample temperature is slowly decreased until a sample weight gain is indicated. The sample temperature is held constant until the recombination reaction is complete. The dissociation/recombination kinetics are systematically obtained in this manner for several temperatures above and below the equilibrium temperature.

Results have been obtained for the $MnCl_2 \cdot 6NH_3 \rightleftarrows MnCl_2 \cdot 2NH_3 + 4NH_3$ reaction indicating that the rate constants are essentially the same for 0.25, 0.5 and 1.0 atmosphere pressure conditions.

Ammonium chloride triammoniate vapor pressure versus temperature was determined experimentally and is shown in Figure 1. The heat of reaction calculated from these data using the Clausius-Clapeyron equation is 29 Kj/mole NH_3 or 728 Btu/lb NH_3. This agreed with the heat of reaction obtained from the DTA data.

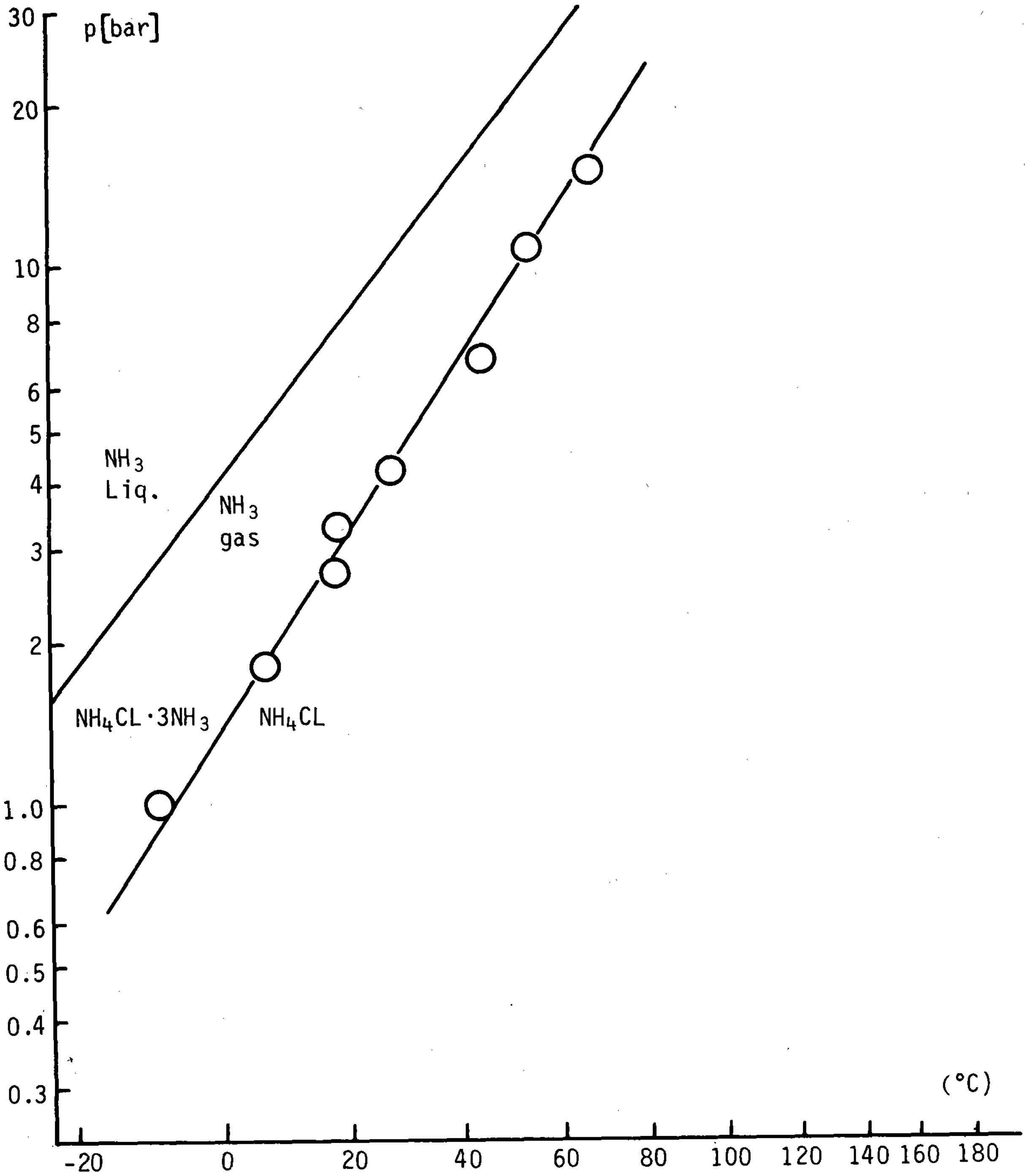


Figure 1 Equilibrium Curves: Reaction $NH_4Cl + 3\ NH_3 \leftrightarrows NH_4Cl \cdot 3\ NH_3$

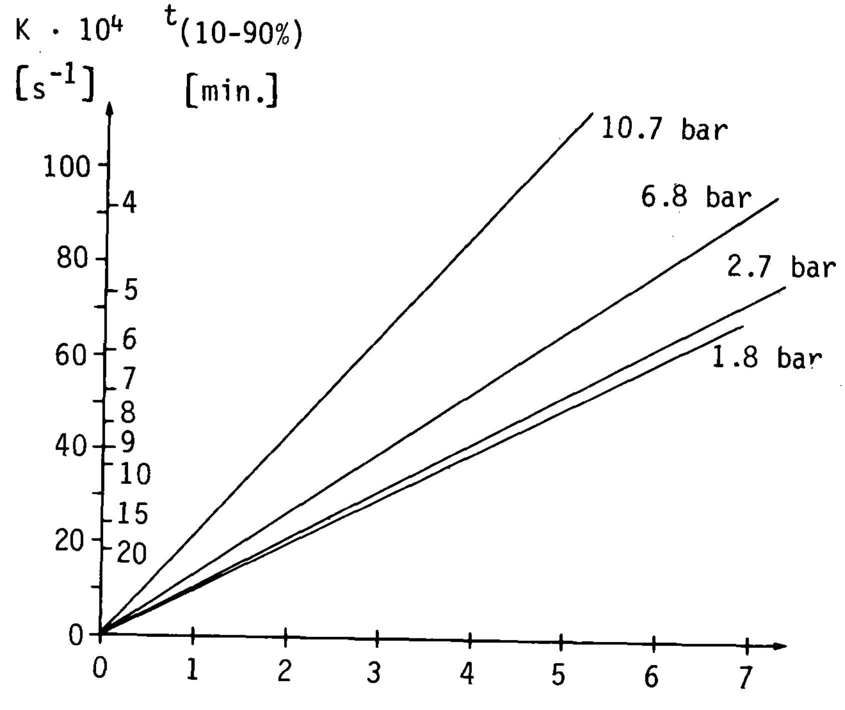


Figure 2 Absorption

ΔT[°C]

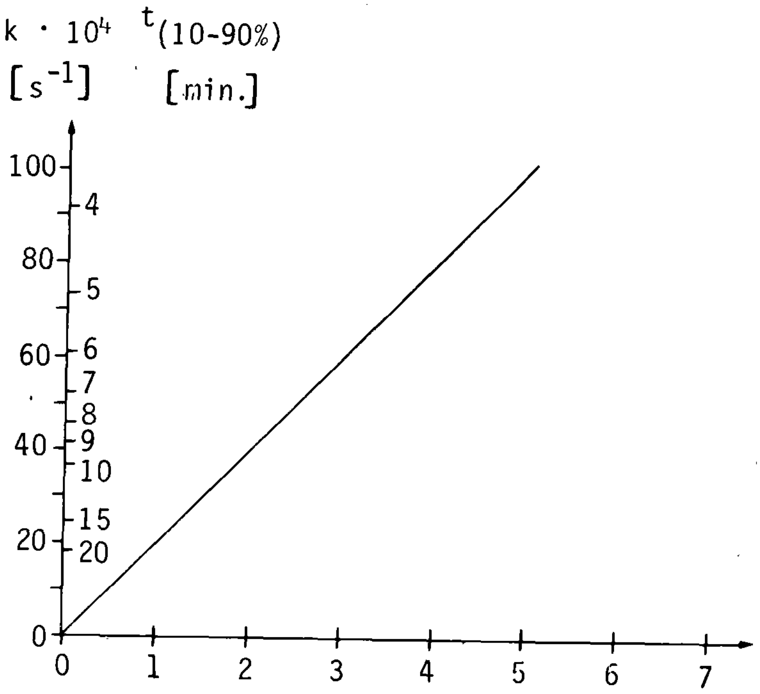


Figure 3 Desorption (1-15 bar)

ΔT[°C]

The ammonium chloride triammoniate is a liquid with a freezing point of approximately 40°F. Since it would be impractical to operate a system in the solid state, reaction rate data were measured at temperatures above 40°F and thus above one atmosphere. Reaction rates were measured using a modified Mettler 2000 DTA that would allow pressurization of the sample with ammonia gas. The rate constant (K) was determined for various delta-Ts (deviation from the equilibrium temperature). The absorption and desorption rate constants are plotted in Figures 2 and 3. No significant pressure dependence could be shown for the desorption reaction.

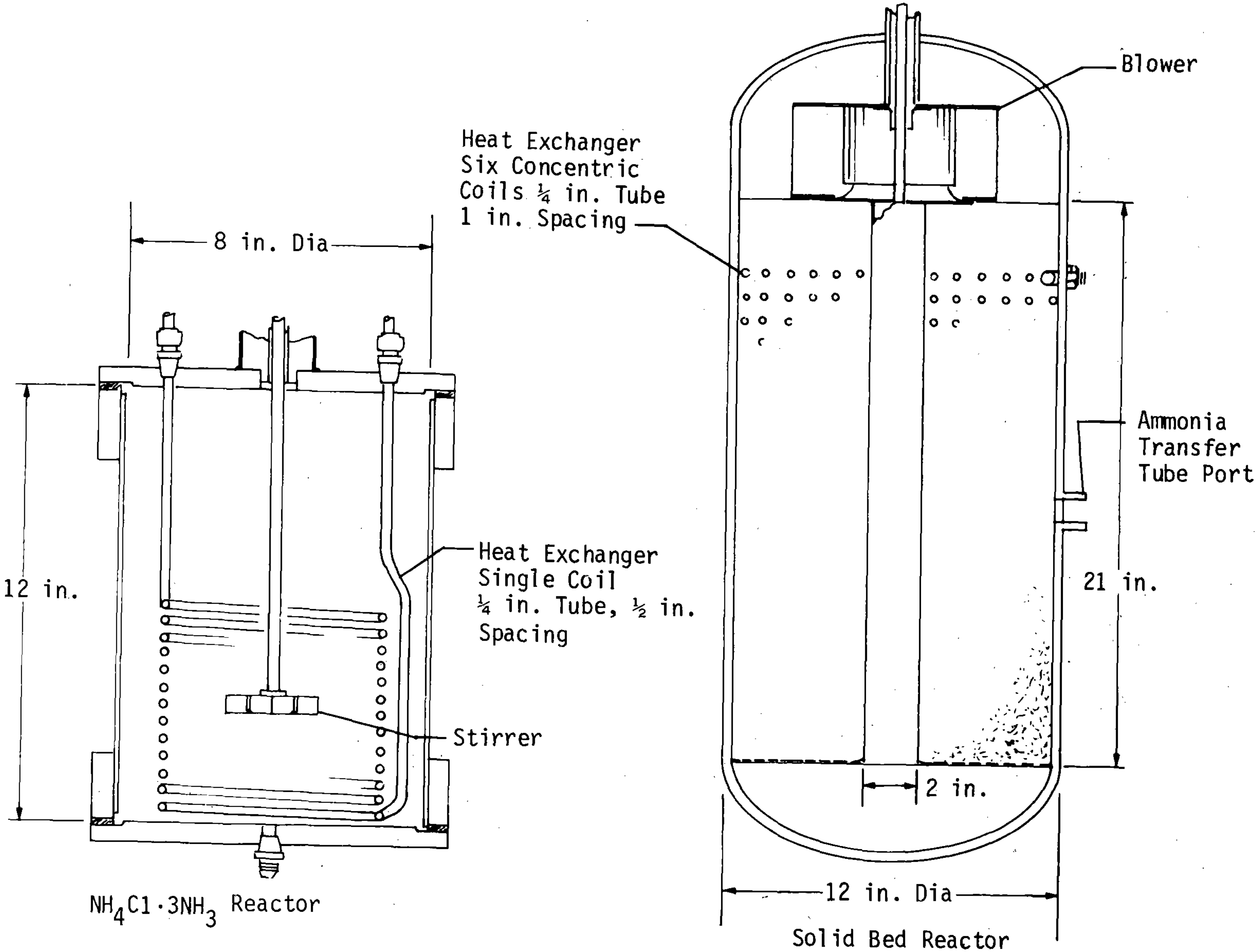
The reaction rates are unusually high (one order of magnitude) compared to systems such as $CaCl_2/NH_3$ for comparable pressure and temperature ranges.

The density of ammonium chloride triammoniate was determined to be 50 lb/ft^3 at 72°F. The viscosity has not been measured at this time, but the fluid is colorless and appears to have the same viscosity as water.

B. Subscale System Testing

In these tests, two small reactors (15 to 30 liters) will be coupled together to form a heat pump/storage system. Ammonium chloride will be used in the low temperature reactor and calcium, manganese or magnesium chloride will be used in the high temperature reactor. These tests will be used to demonstrate the feasibility of the paired reactions to evaluate the use of forced ammonia circulation on the heat transfer rate in the solid ammoniate reactors and to obtain design data for the design of a home heating and cooling system.

The reactor designs have been complete and sketches of the designs are shown in Figure 4. Each reactor was designed to provide the same amount of transferable ammonia in order that the two ammoniate reactions would go to completion simultaneously. The reactor size provides a total storage capacity of about 5000 Btu. The heat exchangers are designed to give a heat transfer rate of about 1000 Btu/hr. The significant difference in heat exchanger size between the two reactors is due to the higher heat transfer coefficient of the liquid ammonium chloride system. The volume of the ammonium chloride reactor is about 1/4 that of the solid salt reactor due to the higher density of the liquid and due to the volume of the heat exchanger in the solid reactor. The degree of dissociation of the $NH_4Cl \cdot 3NH_3$ is limited to 60% in order that the resulting slurry of NH_4Cl and $NH_4Cl \cdot 3NH_3$ retains sufficient fluidity to maintain a high heat transfer coefficient. The $NH_4Cl \cdot 3NH_3$ inhibits adsorption of ammonia by the crystals of NH_4Cl. Therefore, a stirring device is used to promote absorption. The reactor for the solid salts has a small, variable speed blower to circulate ammonia through the salt bed. The fine particles of salt are enclosed in top and bottom by 100 mesh stainless steel screen. Several tests will be run at varying flowrates to establish the effect of forced circulation on heat and mass transfer.



$NH_4Cl \cdot 3NH_3$ Reactor

Solid Bed Reactor

Figure 4 Subscale Test Reactors

Fabrication of the reactors and test system is almost complete. Checkout and testing will begin in December with completion scheduled for March 1979.

Computer Model

This computer program models an ammoniated salt reactor system composed of two separate ammoniated salt reactors linked together by an ammonia flow channel. Each reactor is modelled by a single node. The program simulates operation of the reactor system in the following manner. Heat is added through a heat exchanger model to a reactor (Reactor A) containing an ammoniated salt generating or releasing ammonia from the salt. The ammonia gas is transported to the second reactor (Reactor B) through the flow channel. In Reactor B, an unsaturated or partially saturated salt absorbs the ammonia generating heat that is removed by a second heat exchanger model. A basic assumption employed in this program is that all the ammonia released from Reactor A is absorbed in Reactor B.

The reactor kinetic equations employed for release or absorption of ammonia in each reactor were developed during Phase IB of Contract EY-76-C-03-1229-1. These equations together with the basic assumption stated above, define the required system operating pressure.

Heat and mass balances are conducted on each reactor and heat exchanger combination in order to define reactor and heat exchanger operating temperatures, salt mass histories, and ammonia transfer rates. The heat balances include sensible heating of the salt as well as the heat absorbed or generated due to ammonia release or absorption. Thus, preheating of Reactor A without ammonia generation up·to the system operating conditions may be simulated.

Variable heat loads may be applied to the reactor system through Reactor A. This may be accomplished by varying the heat exchanger coolant fluid inlet temperature.

Typical outputs from the computer program are presented in Figure 5 for a reactor system with the following initial characteristics:

	Reactor A	Reactor B
Salt	$CaCl_2 \cdot 8NH_3$	$NH_4Cl \cdot 3NH_3$
Salt Weight, lbm	26.0	12.0
Temperature, °F	70	70
Pressure, psia	44	44
Heat of Reaction, Btu/lbm NH_3	1040	733.5
Coolant Inlet Temperature, °F	175	70

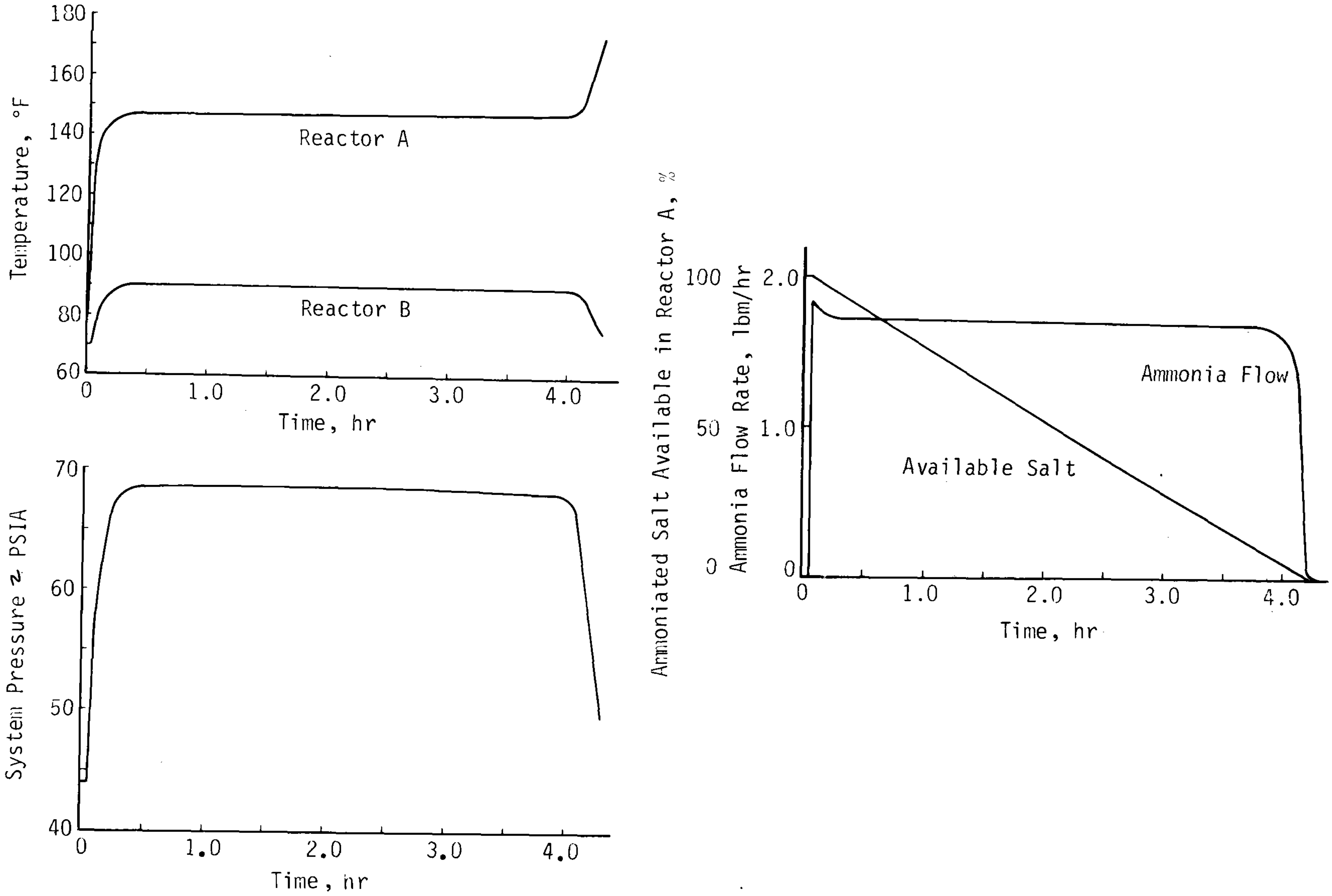


Figure 5 Computer Simulation Results

Figure 5 presents the system pressure and the two reactor temperature histories. Sensible heating of Reactor A begins initially and continues to 0.05 hour when the vapor pressure of Reactor A reaches the initial system pressure (44 psia). At this time, ammonia transfer from Reactor A to Reactor B begins as shown in Figure 5. Ammonia transfer continues for 4.0 hours until ammonia availability in Reactor A decreases resulting in a decreasing ammonia flow, also shown in Figure 5.

D. Future Effort

This contract is being performed in conjunction with a contract funded by DOE Division of Solar Energy R&D entitled "Thermal Energy Storage for Solar Cooling Using Paired Ammoniated Salts." If the results of the subscale tests and preliminary economic analyses to be performed in the solar contract show that the ammoniated systems show promise, then a full-scale residential prototype system will be built and tested.

References:

1. Final Report, "Development of Ammoniated Salts Thermochemical Energy Storage Systems - Phase 1B," SAN/1229-1, May 1978.

PROJECT SUMMARY

Project Title: Development of a Long-Life High-Temperature Catalyst for the SO_2/SO_3 Energy Storage System

Principal Investigator: Dr. E. W. Schmidt

Organization:
Rocket Research Company
York Center
Redmond, Washington 98052
(206) 885-5000

Project Goals: Develop a catalyst which catalyzes the exothermic oxidation of sulfur dioxide and the endothermic dissociation of sulfur trioxide at temperatures up to 1144°K (1600°F). The material should not be volatile and should retain its activity after exposure to 1144°K for up to ten years.

Project Status: This project is divided into four phases as follows:

Current Catalyst Evaluation - (completed). It has been concluded that none of the commercially available vanadium catalysts currently used in the production of sulfuric acid meets the high-temperature stability and nonvolatility requirements of reversible chemical reactions for thermal energy storage.

Catalyst Development - Constitutes the major portion of the overall effort and is currently still in progress. To date, 28 supported and co-precipitated catalysts have been prepared and tested in a pulsed micro reactor and in a differential isothermal reactor at 1100°K. Typical test duration was of the order of 300 hours. Conversions were measured as a function of space velocity both in the endothermic and exothermic mode.

Economic Evaluation - Will be initiated shortly.

Life Test - Two 25mm diameter quartz reactors have been built to be used in the 6 month life test and are currently being checked out.

Contract Number: Sandia Laboratories 87-9119

Contract Period: April 25, 1977 through November 30, 1979

Funding Level: $320,274

Funding Source:
Sandia Laboratories
Livermore, California

DEVELOPMENT OF A LONG-LIFE HIGH-TEMPERATURE CATALYST FOR THE SO_2/SO_3 ENERGY STORAGE SYSTEM

INTRODUCTION

The reversible dissociation of sulfur trioxide has been identified as a means for transmission as well as storage of thermal energy by reversible chemical reactions (RCR). The source of energy is irrelevant at this time, but the most likely application would be in the collection and storage of solar energy in distributed (Reference 1) or central receiver (References 2 and 3) solar thermal conversion power plants. The realization of these concepts hinges on the availability of a catalyst which sustains the reaction in both directions at high rates.

Most concepts discussed so far anticipate to use the same catalyst in both the endothermic and exothermic mode possibly using one and the same reactor in both modes. However, if the loss in Carnot efficiency can be tolerated, it is feasible that the exothermic reactor might operate at lower temperature and use a different catalyst than the endothermic reactor. In the case of distributed systems and chemical heat pipes, the two reactors would of course be geographically separated.

TECHNICAL APPROACH

Based on experience in high-temperature exothermic reactor design/catalyst development for rocket engines and gas generators, Rocket Research Company (RRC) has outlined a program plan for developing and testing a catalyst for the reversible dissociation of sulfur trioxide.

In the following discussion, we frequently refer to SO_x catalysts or SO_x reaction where x stands for x=2 or x=3 for sulfur dioxide and sulfur trioxide, respectively.

The major differences between current technology sulfuric acid production catalysts and SO_x catalysts required for RCR energy applications are outlined in Table 1.

During Task 1, seven catalyst suppliers were contacted and 13 fresh catalyst samples and 5 used catalyst samples were obtained for evaluation and analysis. All catalysts supplied were of the vanadium pentoxide/potassium pyrosulfate on kieselguhr type. None of the suppliers provide commercial iron or platinum catalysts for SO_2 oxidation, although such catalysts are being made for other applications. Along with the vanadium catalysts, other catalysts were obtained which were not specifically advertised as sulfur dioxide oxidation catalysts. These catalysts contained platinum, iron, chromium and other transition elements and were tested for their activity as well. From the supplier survey, no information could be obtained on catalysts for SO_3 dissociation. Obviously, the objective of the sulfuric acid industry is to make SO_3 and not to dissociate SO_3. To them, the dissociation of product SO_3 is an undesirable, yield-limiting back reaction which has to be suppressed if possible. Generally, catalysts will accelerate both the forward and the reverse reaction, but the individual rates may vary depending on the diffusion and catalytic rates involved. It may be assumed that catalysts which are good for SO_2 oxidation will also be good for SO_3 dissociation and vice versa.

TABLE 1

CURRENT VERSUS REQUIRED SO_x CATALYST OPERATING CHARACTERISTICS

	CURRENT TECHNOLOGY	REQUIRED FOR RCR TES
TEMPERATURE	770°K (950°F)	1,144°K (1,600°F)
PRESSURE	1.01 BAR (14.7 PSIA)	15 BAR (220 PSIA)
FEED GAS COMPOSITION	AIR/SO_2	O_2/SO_2
FEED GAS PURITY	IMPURE	PURE
MODE OF OPERATION	OPEN LOOP	CLOSED LOOP
SPACE VELOCITY	2,000 h^{-1}	10,000 h^{-1}
CATALYST LIFE	2 TO 10 YEARS	30 YEARS (DESIRABLE)

The used catalyst samples obtained during the survey were very poorly documented with regard to usage time, tons of acid produced per pound of catalyst and makeup of the feedgas. The used catalysts were analyzed and compared to fresh catalysts of the same source. It was concluded that catalyst poisoning by arsenic, lead, calcium and copper constitute the main degradation mechanism in commercial plants. This mechanism will not occur in closed loop RCR energy transmission/storage systems because the system will be loaded with pure chemicals to start with. The main degradation mechanism expected in RCR reactors is linked to the high operating temperature. Exposing commercial vanadium catalyst to temperatures beyond recommended operating temperatures resulted in rapid loss of vanadium. In an RCR energy transmission/storage system, volatility of catalyst ingredients would be very deleterious to conversion efficiency because the catalyst would precipitate in downstream, colder components (heat exchangers) of the system. The product gas composition of e.g., a dissociating reactor would then no longer be frozen at the high temperature, but would continue to react during cooldown and revert some of the dissociation work performed at high temperature. A low-vapor pressure, non-migrating active metal is therefore a prerequisite in catalyst selection.

Prior to catalyst development, the type of catalyst had to be selected from supported catalysts for packed bed reactors, supported catalyst for fluidized bed reactors, homogeneous molten catalysts and monolithic catalysts. Supported catalysts in packed bed reactors were chosen for this initial development effort because more background existed on laboratory test methods for this than for any other type of catalyst. The other types of catalysts may show advantages for specific applications, but are not suitable for laboratory development testing.

The task of developing supported catalysts consists of selecting a catalyst carrier and an active metal and mating the two in optimum proportions. If the active metal loading is too high, the metal may block the pores in the carrier and the net metal surface area exposed is less than at lower active metal loadings. Catalyst carriers have to be compatible with the SO_x environment and have to maintain their active surface area at high temperatures for long times. Unfortunately, all catalyst supports will lose active surface area by sintering. The task then is to identify a candidate carrier with the slowest loss rate. Carriers used during the current program are alumina and silica/alumina based. The materials come as granules, pellets or extrudates.

The criteria for selecting active metals are: high activity in SO_x conversion reactions and low volatility of the metal or its oxides. In reviewing the periodic table of elements, 14 elements have been identified which could possibly possess catalytic activity. To date, 28 catalysts have been prepared with these metals on a variety of catalyst carriers and at different metal loadings. The rationale in selecting active metals is based on past experience and reports by other investigators. It is attempted to support the selection process by more scientific argumentation, e.g., electron configuration or crystal lattice structure, but so far no correlation between atomic/molecular properties and SO_x activity has been detected.

DESCRIPTION OF TEST APPARATUS

Catalyst test reactors for SO_x catalysts reported in the literature were exclusively designed for SO_2 oxidation in air and operating at very low space velocities. Limited work on SO_3 dissociation reactors was conducted with argon dilution at low SO_3 partial pressures (Reference 4). Thus, in addition to developing new catalysts, new test techniques had to be developed capable of operating in oxygen/SO_2 instead of air/SO_2, and capable of operating at high space velocities in both the oxidizing and dissociating mode. Two types of reactors were used during the current program: a pulsed micro reactor and an isothermal differential reactor, both of a packed bed configuration with granular catalyst.

The pulsed micro reactor was used as a screening tool to eliminate catalysts which had no or only very little catalytic activity. It was operated in the exothermic mode only. The catalyst was heated to the test temperature (usually 1100°K) in flowing helium and pulsed with a small volume (1 ml) of a stoichiometric SO_2/O_2 mixture at constant flow velocity. The composition of the feed and product gas was analyzed by absorbing all SO_x and passing the oxygen peak through the thermoconductivity cell of an attached dedicated gas chromatograph. The conversion was calculated from the change of oxygen counts. Space velocity could be varied by changing the catalyst bed length. The apparatus is useful to measure conversion as a function of space velocity at constant temperature or conversion as a function of temperature at constant space velocity. Measurement of one set of data requires only a fraction of the time required by any other method.

More detailed data were obtained using an isothermal differential reactor consisting of a very short catalyst bed in a 25-mm diameter quartz tube resting on a porous quartz disc. The entire assembly including inert quartz shards as a preheat zone is kept at isothermal conditions by a surrounding tube furnace. In order to maintain catalyst temperature as constant as possible, the system operates at very small (= differential) conversions, minimizing energy release or uptake by the catalyst which otherwise might change the catalyst temperature. The differential changes in gas composition places high demands on the accuracy of the analysis method. Unfortunately, no reliable and rapid gas analysis methods were available at the onset of the program. A method with a direct on-line continuous readout of concentrations of one or more of the reactants would have been preferred. Unfortunately, wet titration or gas chromatography give only point sample analyses and are very time consuming. In addition, it is very difficult to prevent sulfur trioxide (boiling point 318°K = 112.6°F) from condensing at ambient temperature prior to taking the sample. As a compromise, all sulfur oxides were adsorbed on a molecular sieve cartridge prior to entering the gas chromatograph and the oxygen count alone was taken as an indication of oxygen concentration in the sample. A paramagnetic oxygen analyzer was used initially but was found to be incompatible with SO_3. It has since been used for dry SO_2/O_2 feed gas mixtures only. In the meantime, information has been obtained indicating that a commercial photometric analyzer can be converted to read high SO_2 concentrations without interference by SO_3. It is planned to evaluate the use of a photometric analyzer during the remainder of the program.

The lack of analytical instrumentation capable of operating in the corrosive environment of hot sulfur oxides has been the only major problem encountered so far in the course of the research program and has caused a slight schedule delay.

For the exothermic mode, the reactor was fed with a mixture of 66.6% by volume SO_2 and 33.3% O_2. For endothermic tests, the same mixture was first passed through an overdesigned pre-reactor filled with platinum catalyst and held at 750°K, where the gas was almost quantitatively converted to SO_3. Some unconverted SO_2 and O_2 was carried along, but only at the higher space velocities. This mode of generating SO_3 in-situ was more convenient than drawing liquid SO_3 from a supply tank and vaporizing it. In particular, for a limited duration until failure of a diaphragem recirulation pump, it was possible to operate the test reactors in a closed loop, thus minimizing the amount of sulfur oxides which had to be scrubbed or vented. In the current mode of testing, gases leaving the reactor after a single pass are passed through a packed column trickle flow absorber where SO_3 is absorbed into concentrated sulfuric acid and the remaining gases are vented.

DISCUSSION OF RESULTS

A comparison of catalyst activity is shown in Figure 1. This graph shows the conversion as a function of space velocity for a given reactor temperature (1100°K) and bed length (5 mm). Most reproducible results were obtained in the endothermic mode, but a similar graph exists for tests in the exothermic mode. The dropoff of conversion with increasing space velocity is typical for (deliberately) undersized packed bed reactors. The ability of the catalyst to achieve high conversions in spite of high space velocities is an indication of activity of the catalyst. Thus, the catalysts represented by the top curves are the most active ones tested in the current program. SOX-014 and SOX-017 are platinum catalysts while SOX-001, SOX-006, and SOX-019 are iron catalysts. As can be seen from Figure 1, the activity of catalyts under evaluation is superior to or at least comparable to that of commercial vanadium catalysts. Vanadium catalysts, of course, cannot be used in RCR applications.

Similar plots were obtained for activity as a function of time at temperature (typically to 300 hours) with space velocity as an auxiliary parameter. During the first 300 hours, catalyst activity changes only by 10 to 20% and then levels off or decreases at a slower rate. The initial activity dropoff has been linked to changes in the support surface area. Additional catalysts will, therefore, be prepared on stabilized pre-calcined carrier. This should result in a more constant activity profile.

RELATED ACTIVITIES

Besides providing a granular catalyst for packed bed reactors, the knowledge gained during this program is useful to prepare other catalyst shapes for special applications. Thus, a catalytic coating can be developed to be used as a liner for the ceramic converter/heat exchanger of the SOLCHEM distributed system being developed by NRL. Monolithic catalyst inserts can be prepared for the same application to increase conversion and increase turbulence in the converter passages. Another potential application of the catalysts developed herein is in thermochemical water splitting cycles involving the dissociation of sulfuric acid into sulfur dioxide, water and oxygen. This reaction proceeds most likely via dissociation of sulfur trioxide. Thus, catalysts developed during the current program should be equally useful for thermochemical water splitting/hydrogen production cycles under development at Westinghouse, General Atomic and LASL.

In the production of sulfuric acid, much of the energy released is wasted because it is not of sufficient quality to produce power. If catalytic converters were operated with oxygen/SO_2 or at higher pressures, high quality steam could be obtained which would be hot enough to feed to a multistage turbine. Of course, this requires catalysts different from those currently used in the production of sulfuric acid. Both schemes (oxygen or high pressure or both) would also facilitate tailgas cleanup and reduce environmental pollution.

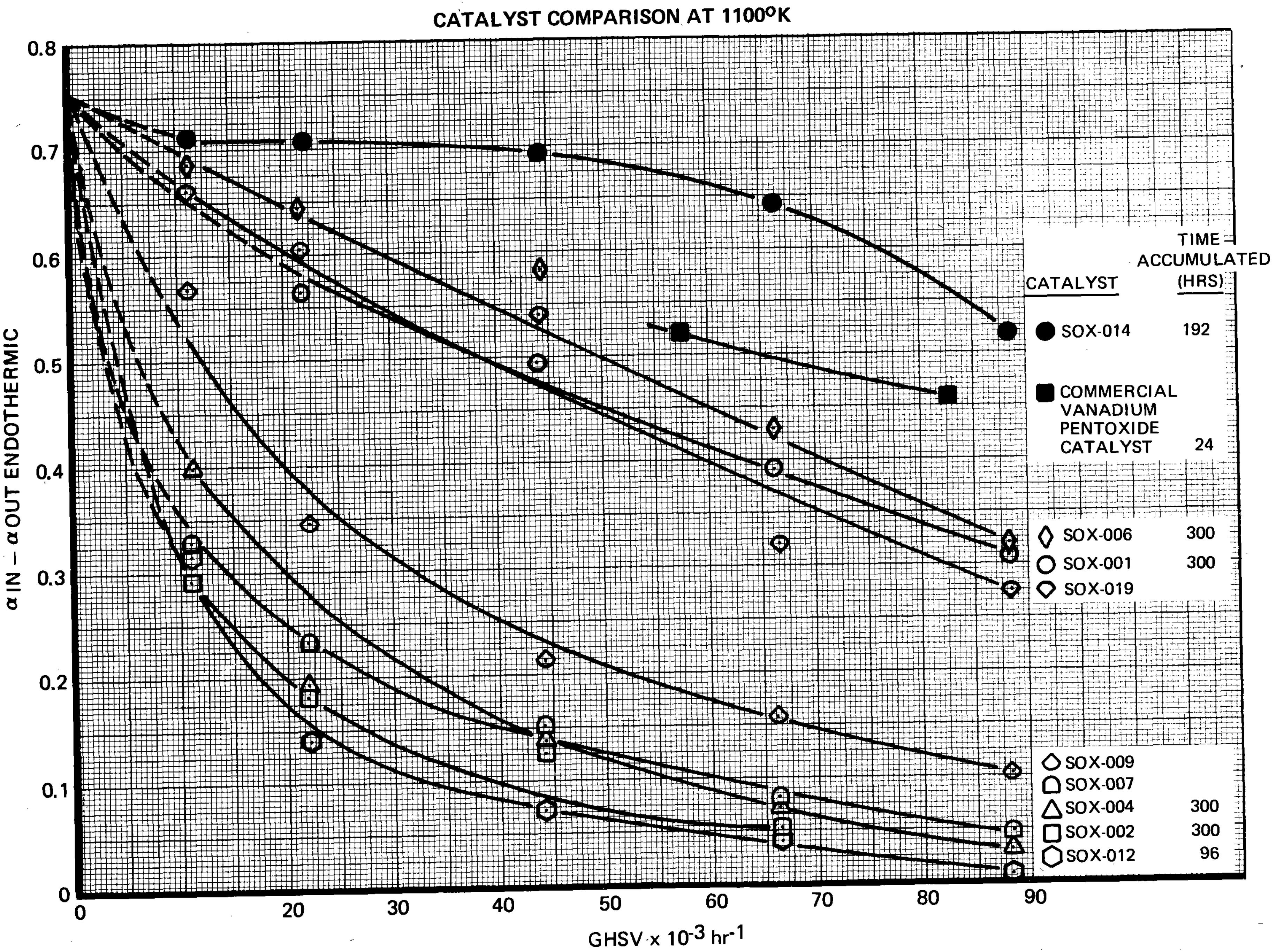

CATALYST COMPARISON AT 1100°K
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
α IN – α OUT ENDOTHERMIC
0
20
30
40
50
60
70
80
90
GHSV x 10⁻³ hr⁻¹
CATALYST
TIME ACCUMULATED (HRS)
● SOX-014 192
■ COMMERCIAL VANADIUM PENTOXIDE CATALYST 24
◊ SOX-006 300
○ SOX-001 300
◇ SOX-019
◇ SOX-009
⌂ SOX-007
△ SOX-004 300
□ SOX-002 300
⬡ SOX-012 96

FIGURE 1

FUTURE PLANS

Within the next two months, one or two catalysts will be selected from the group of 40 plus catalysts prepared. During the 6-month life test, the reactor will be operated both in the endothermic as well as in the exothermic mode. At two-month intervals during the life test, catalyst samples will be withdrawn for analysis and diagnostic tests. The life test will be conducted either with two different catalysts at a constant temperature or with one and the same catalyst, keeping one sample at constant temperature while allowing the other sample to go through numerous heatup/cooldown cycles. There is concern that temperature cycling which is typical for solar input may cause chemical changes in the carrier resulting in rapid catalyst degradation. In almost all industrial catalyst applications, reactors are carefully kept at constant temperature and temperature cycling is avoided if possible.

A preliminary economic analysis will be performed to conduct a trade-off between a more expensive and more durable catalyst compared to a less durable, but cheap catalyst. Investment cost and replacement cost will determine the outcome of this evaluation.

A test plan will be prepared for a proposed follow-on effort involving a closed-loop bench scale energy storage system based on the reversible dissociation of sulfur trioxide. This effort is dependent on the availability of SO_x compressors and distillation columns, components which need further development.

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PROJECT SUMMARY

Project Title: Sandia Laboratories In-House Research for the Thermochemical Energy Storage and Transport Program

Principal Investigator: R. W. Mar

Organization: Sandia Laboratories
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Project Goals: The Sandia in-house research is intended to augment and complement the contracted portions of the program. Research topics are selected to maintain technical expertise, study problems generic to several projects and to perform confirming investigations where the results are controversial.

Project Status: Research has been performed in the following areas: thermochemical/thermophysical characterization, coordination chemistry, corrosion research and catalyst research. An apparatus for making static vapor pressure measurements from room temperature to 573°K has been assembled. The dissociation pressures of several reactions have been experimentally determined with this equipment to complement the sparse data in the literature.

A corrosion research program has been initiated. Immersion tests are underway in which candidate alloys are being heated for extended periods of time in a chemical environment; they will be examined by metallographic techniques.

Catalyst reaction mechanisms are being studied by infrared techniques. Apparatus have been designed and fabricated which allow in situ catalyst preparation, degassing and purification of the catalyst under vacuum, and independent monitoring of gas phase and surface species by infrared techniques.

Contract Number: AD-03-01

Contract Period: October 1977 - October 1978

Funding Level: $100,000

Funding Source: Department of Energy, Division of Energy Storage Systems

SANDIA LABORATORIES IN-HOUSE RESEARCH ON THE THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT PROGRAM*

Raymond W. Mar
Sandia Laboratories
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Introduction

Sandia Laboratories Livermore is responsible for planning and implementing the Thermochemical Energy Storage and Transport (T.E.S.T.) Program as part of the Department of Energy National Thermal Energy Storage Program[1]. An essential part of the T.E.S.T. Program is the conduct of in-house research, the objectives being:

- to develop and maintain the level of technical expertise required to provide effective management and direction of the T.E.S.T. Program
- to support subcontracted development efforts by performing research which 1) uses established in-house technical expertise or 2) is outside of subcontractor interest and capabilities
- to identify and/or investigate the feasibility of high risk concepts
- to study problems generic to several subcontracted efforts
- to perform the in-depth studies required for confidence in long term performance and reliability

Research has been performed in the following areas: thermochemical/thermophysical characterization, coordination chemistry, corrosion research, catalyst research, and miscellaneous problems; results obtained in FY78 are summarized below. The investigators responsible for these studies are: R. W. Bradshaw, R. W. Carling, D. M. Haaland, R. W. Mar, and D. A. Nissen.

Thermochemical/Thermophysical Characterization

An apparatus for making static vapor pressure measurements from room temperature to 573K has been assembled. Temperatures are controlled by a constant temperature oil bath, and pressure measurements made with a capacitance manometer. A displacement balance has been incorporated into the apparatus, thereby enabling the simultaneous measurement of sample weight (and therefore, sample composition) and pressure.

The dissociation pressures for the reaction

$$MgCl_2 \cdot 4H_2O = MgCl_2 \cdot 2H_2O + 2H_2O \qquad (1)$$

have been determined because previously reported pressures for this reaction are in discord[2,3]. Hydrated salts are of interest for use in chemical heat

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*Work supported by U. S. Dept. of Energy, DOE, under Contract AT(29-1)-789.

pump storage systems, and Chemical Energy Specialists[4] is basing its system on this reaction. Pressures were measured over the temperature range 292K to 405K, and a least squares fit of the data gave

$$\ell nP(atm) = -(7767/T) + 23.42 . \qquad (2)$$

The derived second law enthalpy of hydration is calculated to be 15.4 kcal.

The pressure/temperature curves were determined for the following reactions:

$$CaCl_2{\cdot}8NH_3 = CaCl_2{\cdot}4NH_3 + 4NH_3 \qquad (3)$$

$$CaCl_2{\cdot}4NH_3 = CaCl_2{\cdot}2NH_3 + 2NH_3 \qquad (4)$$

$$CaCl_2{\cdot}2NH_3 = CaCl_2{\cdot}NH_3 + NH_3 . \qquad (5)$$

The impetus for this study was the desire to resolve the discrepancy between Martin Marietta's results[5] and those reported in the International Critical Tables (ICT)[6]; of particular concern was the 25% difference in the enthalpy of the reaction (5).

Results from our study are given in Table I where it is seen that the ICT values are substantiated.

TABLE I. SUMMARY OF RESULTS FOR THE REACTION $CaCl_2{\cdot}yNH_3 = CaCl_2{\cdot}xNH_3 + (y-x)NH_3$

	$\ell nP(atm) = A+B/T(K)$		$\Delta H_{Reaction}$ (kcal/mole NH_3)		
Reaction	A	B	RWC[1]	MMC[2]	ICT[3]
$CaCl_2{\cdot}8NH_3 = CaCl_2{\cdot}4NH_3+4NH_3$	22.89	-4951	9.8	9.8	9.8
$CaCl_2{\cdot}4NH_3 = CaCl_2{\cdot}2NH_3+2NH_3$	22.98	-4747	10.2	10.6	10.1
$CaCl_2{\cdot}2NH_3 = CaCl_2{\cdot}NH_3+NH_3$	24.85	-7995	15.9	12.8	15.1

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1. R. W. Carling, Sandia Livermore
2. Martin Marietta Corporation (Ref. 5)
3. International Critical Tables (Ref. 6)

A capability for measuring the viscosity, surface tension, and density of fluids at high temperatures (up to 1550K) and high pressures (up to 10 atm) exists at Sandia. The characteristics of $NH_4Cl \cdot 3NH_3$ are being determined.

Coordination Chemistry

Coordination compounds formed by salts (e.g., $CaCl_2$, $MgCl_2$) and ligands (e.g., H_2O, NH_3, CH_3OH) have been proposed for use in heat pump storage systems. The thermochemical behavior of hydrated salts has been studied in an attempt to identify useful correlations. Such a study will aid in the identification of hydrated salt candidates, identifying erroneous data in the literature, and estimating the behavior of analogous compounds such as ammoniates, methanolates and mixed salts. A simple electrostatic model (salt cation-ligand dipole interaction) is satisfactory for explaining the thermodynamic behavior of hydrated salts. The ionic potential of the salt cation has the greatest influence on hydration energies. Of secondary importance are the effects of coordination number, nature of the anion and type of ligand. These effects have been empirically correlated with hydration energies to result in a means for estimating enthalpies of formation of hydrated salts:

$$H_f = H_a - N(H_h + 57.8) \qquad (6)$$

$$H_h = (.91 - .02\ pK)\ (11.8 + 1.9\phi + .5N) \qquad (7)$$

where H_f is the enthalpy of formation of the crystalline hydrate, H_h is the enthalpy of hydration, ϕ is the ionic potential (charge/radius (Å)), N is the coordination number, H_a is the enthalpy of formation of anhydrous salt, and pK is the acid constant of the anion acid. It has been shown that enthalpies of formation can generally be calculated to within 1% or better using equations 6 and 7.

A serious concern with using coordination compounds in thermochemical systems is the poor heat transfer in porous solid beds. One approach to circumventing this problem is to suspend the solid in an inert liquid solvent[7,8]. Another alternative is to find a chemical system in which a liquid phase is formed and maintained. Such a system is the $CaCl_2/H_2O$ system as seen on Figure 1. A liquid/solid mixture is maintained at the charge and discharge temperatures shown on Figure 1. The presence of a liquid phase serves two functions: 1) enhance heat transfer and 2) lubricate the solid particles thereby mitigating the effects of volume expansion on material migration and stress generation. Such a reaction can be approximated by

$$CaCl_2 \cdot 4H_2O\ (liq) \rightarrow CaCl_2 \cdot 2H_2O\ (sol) + 2H_2O\ (gas) \quad . \qquad (8)$$

Of prime concern is the close proximity of the pressure/temperature curve for reaction (8) to that of water; the driving force for the discharge reaction may be negligible at low water bath temperatures. The rates of hydration in the $CaCl_2/H_2O$ system were measured at a salt temperature of 313K and at three different water vapor pressures (.023 atm, .017 atm, and .012 atm corresponding to water bath temperatures of 293K, 288K, and 283K respectively). The rates of hydration are high enough for use in chemical heat pump systems for almost all $CaCl_2/H_2O$ composition ratios as long as the water bath was maintained at 293K (see Figure 2). However, once the temperature of the water bath was reduced to practical heat pump application temperatures (<288K), the rate of hydration at compositions where a liquid phase existed were too low to be of practical interest.

Corrosion Research

A corrosion research program has been initiated. Immersion tests are underway in which candidate alloys are being heated for extended periods of time in a chemical environment; they will be examined by metallographic techniques. To date, the objective has been to assess the suitability of commercially available alloys in T.E.S.T. systems of interest. Candidate alloys for use in thermochemical schemes which contain SO_3 and SO_2 species are under test. We are also studying the interaction of water vapor with alloys; this effort supports the development of systems based on the decomposition of hydroxides and hydrated salts.

Catalyst Research

Since a major class of reactions of interest for T.E.S.T. applications are catalyzed reactions, an in-house catalyst research effort was initiated. The initial emphasis will be on hydrogenation/dehydrogenation reactions, which are attractive for use in chemical heat pipe applications. The key concerns are associated with catalyst specificity and lifetime, and a mechanistic understanding of the catalytic processes should prove valuable in predicting performance and identifying directions for improvement. Catalyst reaction mechanisms will be studied by infrared techniques. Apparatus have been designed and fabricated which allow in situ catalyst preparation, degassing and purification of the catalyst under vacuum, and independent monitoring of gas phase and surface species by infrared techniques. A Fourier transform infrared spectrophotometer will be used to provide the sensitivity needed to detect small quantities of chemical species on catalyst surfaces.

Miscellaneous Problems

Methanolated salt heat pump storage systems are currently being developed by the EIC Corporation[9]. It is generally unrecognized that methanol, $CH_3OH(g)$, is thermodynamically unstable. Complex gas equilibrium calculations have been performed, and the results are shown on Figure 3. It is seen that $CH_3OH(g)$ tends to dissociate to $CH_4(g)$ and $CO_2(g)$, with minor amounts of $H_2(g)$, $CO(g)$ and $H_2O(g)$. However, the kinetics of methanol dissociation are expected to be very slow, and methanol may indeed be a viable chemical heat pump transport species. Preliminary experiments have been performed to show that temperatures and times of 573K and 14 days are sufficient to completely dissociate $CH_3OH(g)$, primarily into $CH_4(g)$, $CO_2(g)$ and $CO(g)$. However, it has been found that a more realistic heat pump temperature of 473K was not high enough to cause any decomposition over a seven day period. Experiments are continuing in an effort to assess the dissociation problem.

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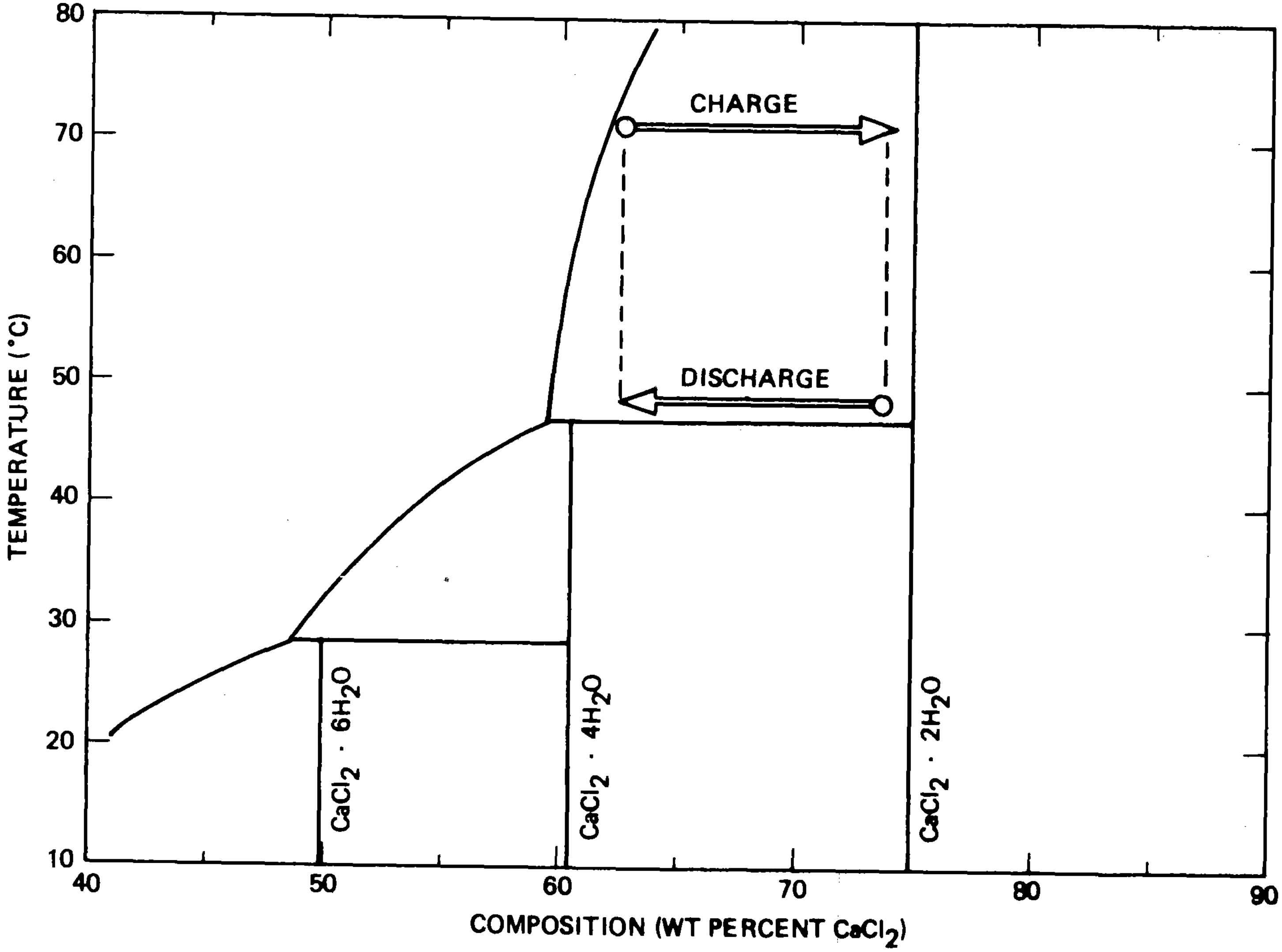

Figure 1. A liquid phase will be present in the reactor if the charge and discharge conditions shown in this figure are maintained.

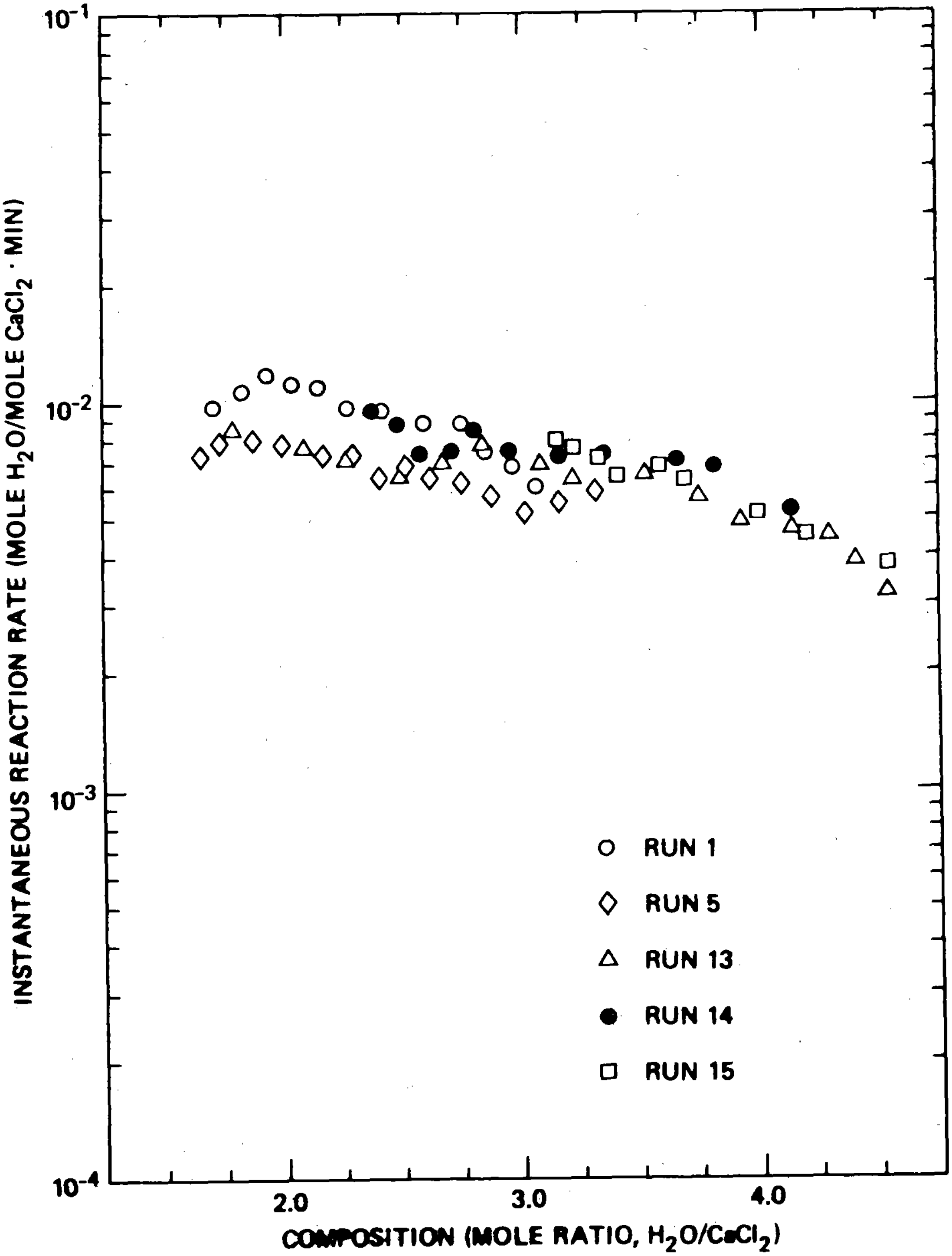

Figure 2. Measured hydration rates of $CaCl_2 \cdot xH_2O$ with the water source at 293K.

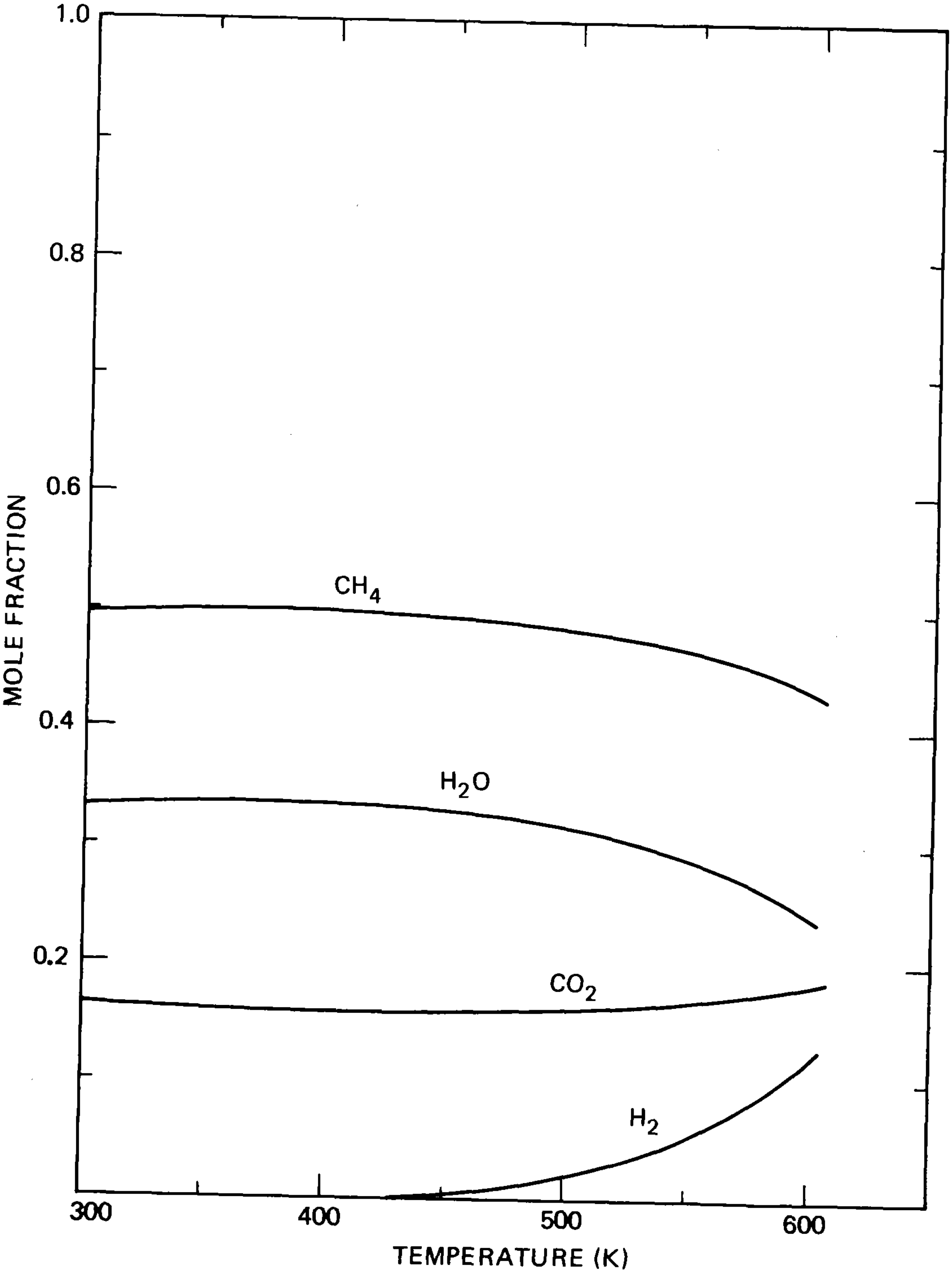

Figure 3. Calculated equilibrium decomposition products of $CH_3OH(g)$ at 1 atm.

PROJECT SUMMARY

Project Title: Transmission of Energy by Open Loop Chemical Energy Pipelines

Principal Investigator: N. R. Baker

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Project Goals: Evaluate the technical and economic feasibility of transmitting and storing energy by an open loop modification of a methane-based, reversible chemical reaction energy transport and storage system known as EVA/ADAM.

Project Status: The final report for this project was published in June 1978. In the open loop pipeline concept, hydrocarbons are supplied at a heat source with both heat and substitute natural gas being the products at an end-use site. The study looked at an HTGR supplying heat for steam reforming, a coal gasification plant producing carbon monoxide and hydrogen and an HTGR supplied with hydrocarbons by an LNG terminal.

The major conclusions drawn are that the open loop chemical energy pipeline is technically feasible, existing natural gas transmission systems could be used, transmission of coal synthesis gases over long distances is more economically attractive than shipment of coal by rail and ample markets exist for the process steam electricity and SNG produced from the system.

Product prices calculated for the goal gasification case may be competitive currently and would almost certainly be attractive in the near future. The HTGR design did not produce product prices competitive in the near future but the coupling of the HTGR with LNG could be viable in the 1980 to 1990 time frame.

Contract Number: 87-9181

Contract Period: May 1977 - June 1978

Funding Level: $96,400

Funding Source: Sandia Laboratories
Livermore, California

This report presents the results of a study conducted by the Institute of Gas Technology (IGT) for the U.S. Department of Energy (DOE) and administered through Sandia Laboratories under Contract No. 87-9181. It is intended to provide DOE with a technical feasibility and economic viability analysis of the transmission of energy by open-loop chemical energy pipelines.

The chemical energy pipeline is a method of converting thermal energy from centralized heat sources, such as nuclear, solar, or coal, to a gaseous chemical form that allows this energy to be transmitted by pipeline, stored, and released for use at some distant location. It is based on the EVA/ADAM concept, first developed by Kernforschunganlange (KFA) in Jülich, West Germany, of a closed loop that conducts an equilibrium mixture of endothermic reaction products in one direction and returns exothermic reaction products in the reverse direction. In this manner, thermal energy from a heat source is transmitted by means of a chemical carrier to one or more distant sites where this heat is required.

Most work to date on the closed-loop concept has centered on the use of methane. The heat source is usually a high-temperature gas-cooled nuclear reactor (HTGR) that supplies thermal energy to a steam reformer operating at approximately 1100 K. In the catalytic reformer, a methane-rich gas and water mixture combine in an endothermic reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (1)$$

At the other end of the pipeline, the reverse exothermic reaction occurs, producing heat and methane; i.e., the reformed gas is methanated over a suitable catalyst at approximately 700 K.

$$3H_2 + CO \rightarrow CH_4 + H_2O \qquad (2)$$

Simultaneously with these reactions, both the forward and reverse shift reactions take place:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (3)$$

It is the objective of this program to assess the possibilities of opening the loop, that is, to supply hydrocarbons at the heat source and produce both heat and substitute natural gas (SNG) for end-use at the methanator site. Three open-loop systems have been evaluated. The first, which forms a "base" case, consists of 1) an HTGR supplying heat for the steam reforming of methane, and 2) a 161-km (100-mile) pipeline transmitting the reformed gas to a methanator producing heat (as steam) and SNG that is available for use in the existing natural gas distribution system. In what is known as the near-term case, the HTGR/reformer is replaced by a coal gasification plant producing carbon monoxide and hydrogen, while the rest of the system (pipeline, methanator, end-use) remains conceptually the same as in the base case.

In the mid-term version of the open-loop chemical energy pipeline, the HTGR/reformer is supplied with hydrocarbons by a liquified natural gas (LNG) receiving terminal, with the whole complex situated on a floating platform 4.8 km (3 miles) or less off the United States coastline. An undersea pipeline connects the complex to the shore and to the remaining system components.

It is important to note that both the near- and mid-term versions of the open-loop chemical energy pipeline may be transitional energy concepts because their implementation will provide the experience and component development necessary <u>before</u> full implementation of a closed-loop system, based on non-fossil fuels, is required.

In view of the preliminary economic evaluation discussed in this report, the coal-based chemical energy pipeline concept can also be considered a competitor to high-Btu coal gasification concepts: The projected SNG costs from both processes are similar.

Since the base case design was assembled using components from the work of others, the selection of the heat source was based upon design and cost information availability. As a result, the base case heat source was selected to be a design published by General Atomic, and consists of a HTGR, reformer module, and steam generator. The heat source for the near-term case is a coal gasification plant, and after a review of potential candidate designs, the Ash Agglomerator Gasifier (AAG) process was selected because of its product composition and efficiency. A scaled-up version of the KFA-developed 500 MW_t Pebble Bed Reactor was chosen as the mid-term heat source, primarily because of the compactness of the design and high availability. Reformer operating conditions were selected based upon chemical equilibrium calculations and thermal considerations. Process water is produced by a modified freeze desalination process resulting from the coupling of the plant to the LNG vaporization complex.

Existing natural gas transmission systems were assessed with regard to potential conversion to reformed or coal synthesis gas operation. In particular, problems associated with materials compatibility, compressor adaptability, and compressor driver conversion were analyzed. In general, no problems of a serious nature were identified, but a detailed analysis of each existing natural gas pipeline system is required before specific conclusions may be reached. In the three variations of the open-loop chemical energy pipeline, transmission systems were designed as a function of pipeline length, gas properties, and cost of transmission. For the near-term case, the cost of shipping coal by rail was compared with the transmission of the coal synthesis gas and was found to be less attractive because of the tonnage and distance involved.

Storage of the reformed or synthesis gas was evaluated for three different methods: linepack, high-pressure pipe-bottle, and underground storage. Because both the reformed and synthesis gases are mostly hydrogen, work by IGT and others with underground and pipe-bottle storage of hydrogen was reviewed with reference to the current study. Linepack storage in the transmission systems was evaluated under both static and dynamic flow conditions with regard to cost and contained volume. All three methods of storage were found possible and could provide increased system versatility.

The principal methanation processes were reviewed and selection of the process used in the current study, the cold gas recycle scheme, was based upon its stage of development, temperature control, operating flexibility, and costs. Alternative designs for the exported energy from the plant resulted in a selection of product forms and quantities. An evaluation of supplementing two of these products, process steam and electricity, with additional energy produced by combusting SNG, showed, in general, that such modifications are economically unjustified.

Markets were identified for the thermal, gaseous, and electric products. District heating, as a load for the low-temperature products, was considered marginal at best and alternative loads were examined from a location and time product is sold at \$3.32/GJ (\$3.50/10^6 Btu), and electricity at 27 mills/kWhr, the selling price of the SNG would be \$3.13/GJ (\$3.30/10^6 Btu). This value, however, is not considered competitive with that which a simple LNG off-loading and vaporization facility would produce for its gas product.

Because it was found that the SNG price and LNG purchase price were related on a one-to-one basis, further analysis revealed that the mid-term chemical energy pipeline will be competitive with the simple LNG facility when process steam prices rise to \$4.79/GJ (\$5.05/10^6 Btu). In turn, this steam price will be reached when the cost of steam generator fuel (either natural gas, LNG, oil, or SNG) rises to \$3.73/GJ (\$3.93/10^6 Btu). While this price is above current fuel costs, future prices expected in the 1980-to-1990 time frame would make the system economically viable. Thus, though not competitive at today's energy prices, the mid-term system may be competitive when viewed within the time frame of its implementation.

The major conclusions reached in this study may be summarized as follows:

1. The open-loop chemical energy pipeline is technically feasible. No major problems were found in mating the various components of the systems designed.
2. Existing natural gas transmission systems could potentially be converted for use as part of a chemical energy pipeline. Identification of a specific pipeline for conversion will require a detailed study, based upon current capacity, compressor and/or driver type, and materials used in its construction.
3. Transmission of coal synthesis gases over long distances is more economically attractive than the shipment of coal by rail, for the tonnages involved in the near-term coal-gasification-based chemical energy pipeline.
4. No significant problems are envisioned in converting or building storage capacity for the gases produced by or formed in the chemical energy pipeline.
5. Design of the methanation plant and heat exchanger train is inherently a function of the thermal products desired. Supplementation of these products by SNG combustion is not suggested by the economics involved.
6. Ample markets exist for the process steam, electricity, and SNG products from the system. Several potential markets have been identified for the lower temperature thermal energy. In general, however, loads for this energy are difficult to quantify, and in particular, difficult to justify economically when used for residential district heating.
7. No major problems should exist for domestic gas equipment when the product SNG's are substituted for typical natural gases.

of energy use viewpoint. Use of the product SNG in current domestic gas equipment was evaluated and showed that few problems should exist with the interchange of these SNG's with typical natural gases.

Capital and annual operating costs from previously published studies were used, as in the base case analysis, where possible; in general, however, costs could only be assessed after the particular component or process was designed in sufficient detail to allow cost estimation.

The installed plant costs for the base case system (one HTGR-reformer, pipeline, and methanation complex) totaled approximately \$1.03 billion and annual operating and maintenance costs, including fuels, were estimated at \$596 million/year. As was the case for the near- and mid-term designs, the base case economics were analyzed using the Discounted Cash Flow - Net Present Value method. This produced an annual revenue requirement of \$835.5 million, which must be raised by the sale of the two system products: process steam and SNG. If the SNG is sold at the same assumed purchased natural gas price (\$/unit energy), the steam would have to be sold at \$8.60/GJ (\$9.07/10^6 Btu). This value is not competitive at current prices, even if converted to electricity.

For the near-term case, the system was designed such that the coal gasification plant feeds two separate methanation complexes. Only one end-use site was specified: that in Escanaba, Michigan, some 1790 km (1110 mi) from the coal plant in Montana. However, if the other methanation complex had identical costs and distance from the coal plant as the Montana to Michigan system, the installed operating costs totaled \$118 million/yr including the coal (at \$8.68/tonne or \$7.87/ton) costs. The prices charged for the steam product were set at \$3.32/GJ (\$3.50/10^6 Btu) and 27 mills/kWhr for electricity; this produced a SNG selling price of \$3.66/GJ (\$3.86/10^6 Btu), delivered. These values are considered competitive with other conventional processes and merit further study.

The mid-term design was set to have one VHTR-reformer-LNG terminal supplying six separate methanation complexes. The one end-use site specified is Perth Amboy, New Jersey, and the floating complex 145 km (90 miles) southeast and just off the coastline north of Atlantic City. If all six methanation complexes contribute identical costs as the one specified, the installed system cost would total approximately \$1280 million. Annual operating costs, including LNG at \$1.98/GJ (\$2.20/1000 SCF) and nuclear fuel, total \$534 million/yr. If the steam

8. The base case design did not produce product prices that were competitive, either now or in the near future.

9. Product prices calculated for the near-term case may be competitive currently and would almost certainly be attractive in the immediate future.

10. The mid-term design, while not producing product prices competitive now, could be economically viable in the 1980 to 1990 time frame.

11. No serious or unique institutional or safety problems have been identified to prevent the implementation of an open-loop chemical energy pipeline.

12. It is felt that these systems are environmentally benign. In particular, locating the methanation plant at the load site should contribute minimum air pollution and would replace existing boilers with a heat source with little waste heat.

13. The chemical energy pipeline is very versatile with respect to site locations for both the heat sources and methanation plants. Remote siting of heat sources, far from the end-use sites, is a major advantage of this system.

14. The open-loop chemical energy pipeline may not be an energy concept whose sole purpose is to provide experience and component development necessary for the transition to a closed-loop mode. In view of the results of the near-term (coal-based) design economic analysis, the open-loop concept has merit in itself, independent of the implementation of a closed-loop system.

15. Future work in this area should be directed at decreasing system costs, optimizing methanation plant operation and quality of products, and experimentally providing a data base from which further work could be identified.

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