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Proceedings of Second Annual

THERMAL ENERGY STORAGE CONTRACTORS' INFORMATION EXCHANGE MEETING

September 29–30, 1977
Gatlinburg, Tennessee

OAK RIDGE NATIONAL LABORATORY
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PROCEEDINGS OF SECOND ANNUAL THERMAL ENERGY STORAGE CONTRACTORS' INFORMATION EXCHANGE MEETING

September 29–30, 1977
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Sponsored by:

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Hosted by:

Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37830

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*Operated by Union Carbide Corporation for the Department of Energy.

CONTENTS

PREFACE

The Department of Energy (DOE), which incorporates the former Energy Research and Development Administration through the Chemical and Thermal Storage Branch of its Division of Energy Storage Systems (STOR), is engaged in developing and disseminating thermal and thermochemical energy storage technology as a means for achieving use of such energy source alternatives as solar, waste heat, and off-peak electricity. The overall national program has been subdivided into three logical subprograms:

1. Low-Temperature Thermal Energy Storage (LTTES) — by sensible and latent heat storage modes at temperatures up to $\sim$250°C.
2. High-Temperature Thermal Energy Storage (HTTES) — by sensible and latent heat storage modes at temperatures above $\sim$250°C.
3. Thermochemical Energy Storage and Transport (TEST) — using reversible chemical reactions at all temperature levels.

DOE-STOR is assisted in the management of these three subprograms by the Oak Ridge National Laboratory, NASA-Lewis Research Center, and Sandia Laboratories-Livermore, respectively.

Because of the dispersed management and the size of the effort, it was felt that an annual gathering to review the individual studies and provide perspective was in order. It was agreed that attendance at these meetings would be limited to program participants (subcontractors), government sponsors and users, and representatives of some coordinate activities in order to maximize the impact on the planning and implementation functions of the national Thermal Energy Storage Program. At the same time, it was also agreed that the information presented at these meetings should be more widely disseminated through publication of the proceedings.

The proceedings of the first meeting, which held at the NASA-Lewis Research Center in September 1976, were not published; since the program was felt to be still in its formative stage and the results too limited to provide a representative picture of thermal energy storage technology development. The proceedings of the second meeting are presented in this document. It is organized in terms of each of the subprogram areas, with a program overview by the responsible program area manager leading off each section. While not all studies were presented from the podium, essentially all program participants are represented in this volume.

The Oak Ridge National Laboratory is pleased to have had the opportunity to serve as host for this important meeting. We are particularly appreciative of the enthusiastic involvement of all Thermal Energy Storage Program participants, whose dedication not only made the meeting worthwhile, but also assures the success of this major component of national energy development and conservation.

It should be noted that the program reports which make up these proceedings were prepared by the responsible subcontractors, and the function of the Oak Ridge National Laboratory in preparing this document was only that of assembling and printing — no technical editing or evaluation was performed.

Herbert W. Hoffman, General Chairman
Second Annual Thermal Energy Storage
Contractors' Information Exchange
Meeting

I. LOW-TEMPERATURE THERMAL ENERGY STORAGE

LOW-TEMPERATURE THERMAL ENERGY STORAGE PROGRAM[a]

H. W. Hoffman, Program Area Manager
Oak Ridge National Laboratory

1. INTRODUCTION

The Low-Temperature Thermal Energy Storage Program (LTTES) at the Oak Ridge National Laboratory (ORNL) is one of three elements in the national TES technology development effort. LTTES is addressed to advancing the application of such alternative energy sources as solar, waste heat, and off-peak electricity in the residential, commercial, industrial, and agricultural use sectors through sensible and/or latent heat storage at temperatures generally below 250°C. This is illustrated in Fig. 1, wherein storage is shown graphically to be the element wedding source and application. LTTES finds its principal application in building heating and cooling, hot water supply, and such industrial/agricultural processes as drying.

ORNL has responsibility (in consultation with and with the concurrence of ERDA-STOR[b]) for planning the low-temperature storage effort, awarding contracts to implement this plan, maintaining technical and fiscal control of subcontracts, appropriately disseminating the results obtained, and assisting in the transfer of developed technologies to demonstration and eventual commercialization. While the bulk of the program is being carried out through subcontracts with industry, universities, research institutes, and other national laboratories, a small amount of supporting research has been reserved to ORNL. All of this work is considered in the succeeding sections of this paper.

2. PROGRAM OBJECTIVES AND GOALS

The twofold objectives of the LTTES Program are (1) to develop sensible and latent heat storage technologies capable of effectively accepting, storing, and discharging thermal energy supplied at temperatures up to 250°C and (2) to define the potential of these technologies in the utilization of alternative, plentiful energy sources and the conservation of natural, nonrenewable energy resources. Alternately expressed, we will develop attractive TES concepts and identify attractive TES applications.

Technologies will be proven in the LTTES Program up through the prototype-system development stage. Both the technical and economic feasibilities of the concepts being developed will be established sufficiently to recommend their viability for subsequent demonstration and ultimate commercialization. All of these technologies will be considered in the context of both new and retrofit applications for centralized or decentralized systems.

Development of sensible heat storage technologies under the LTTES Program is restricted to advanced concepts. Thus, the uses of fluids

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[a] Work performed by the Oak Ridge National Laboratory under contract to the Department of Energy.

[b] Energy Research and Development Administration (now Department of Energy) — Division of Energy Storage Systems.

such as water and oils in atmospheric or pressurized tanks and in rock, sand, or gravel beds with energy transport by gases or liquids are considered existing practices requiring only optimization in respect to specific designs, containment materials, and costs. In contrast, the LTTES Program will consider technologies where feasibility has not yet been demonstrated and ability to predict performance is limited. Included in this category are water (aquifers and surface ponds), earth, and fluidized beds.

On the other hand, storage through latent heat — while offering such advantages over sensible heat storage as reduced volume requirements and essentially constant temperatures — is still in the research and development stage. Thus, utilization of phase-change materials (PCM's) for storage is still beset by problems relating to costs, stability, corrosion, heat transfer, volumetric changes, supercooling, toxicity, and containment. While emphasis has generally been on heat of fusion systems, technologies based on heats of transition (solid state) and heats of solution also warrant examination. Categorization within this area is in terms of macroencapsulated, bulk, and dispersed storage.

The heat sources of interest to the LTTES Program are the following:

1. Waste Heat. This category encompasses energy discharged to the environment from utility or industrial operations, principally cooling water and exhaust stack gases.

2. Energy Management. This category encompasses energy held within a system for subsequent use — e.g., off-peak electricity or heat transferred (via storage) from one step in a manufacturing process to a later step.

3. Solar Thermal. This category encompasses energy deriving from the solar heat source through various collection devices.

4. Environmental. This category encompasses energy originating naturally in consequence of atmospheric (climatic) or geographic conditions.

Applications relevant to the LTTES Program fall within the Household and Commercial (H/C) and the Industrial and Agricultural (I/A) use sectors. In the H/C sector, the focus is on space heating and cooling and hot-water supply both for single and multi-unit buildings in individual or district arrangements. Among the storage systems being considered for this purpose, several have been designated for near-term (primary) emphasis: (1) acquifers for annual storage cycles with warm waste waters and natural cold waters and (2) building materials containing PCM's (macroencapsulated or dispersed) for diurnal storage cycles with solar energy, off-peak electricity, or day/night temperature differences. Secondary emphasis is being given to the use of the earth itself for annual storage of solar energy and to bulk or macroencapsulated PCM's for intermediate-term storage of solar or off-peak electrical energy. In the I/A sector, emphasis will be given to improving process efficiency through waste heat utilization, accelerating the utilization of solar-generated process heat, and implemented TES in energy management. Priorities in this area lie with aquifer utilization in respect to environmental or waste heat sources, fluidized beds for heat recovery from waste water or gas streams, and bulk latent heat storage of solar thermal energy.

3. PROGRAM IMPLEMENTATION

The LTTES Program is organized to achieve both near-term (by 1985) and mid-term (1985 to 2000) goals with emphasis directed to concepts displaying current technical and economic viability. Thus, principal attention will be given to certain key project areas ("thrusts") that correspond generally to those described above, namely, (1) seasonal storage of waste hot water in geo-structures (aquifers, ponds, etc.), (2) diurnal storage of solar heat in PCM's contained in building materials, and (3) short-term storage of solar or off-peak electricity in PCM's (bulk or encapsulated) arranged to form compact heat exchange units. At the same time, a sufficient corollary effort will be maintained to accommodate studies generic to low-temperature TES and to assure a reasonable "hearing" for novel storage concepts as such may be proposed.

The program is structured such that, in general, national laboratories, universities, and research institutes will carry out feasibility evaluations and perform fundamental laboratory studies; while industrial concerns will establish engineering and economic feasibility and conduct technology (system) validations. This arrangement provides for application of individual talents and organizational strengths in contexts appropriate to the problems and, hence, should expedite the progression from concept to utilization. Finally, industry in concert with DOE end-use divisions will carry the burden of commercialization of the most attractive technologies; in some instances, the LTTES Program may support a technical monitoring aspect for purposes of predictive model validation.

Implementation will be principally by means of Program Research and Development Announcements (PRDA's) and Requests for Proposals (RFP's), so that technology development directions can be responsive to conservation needs; however, unsolicited proposals will also be evaluated and are expected to be useful in providing new and novel ideas.

The specific projects being carried out under the LTTES Program banner in FY 1977 are identified and discussed briefly in the following paragraphs; each of these is considered in greater detail in the papers following this program overview.

Aquifer Storage. This storage mode is being developed as a means for energy conservation through use of "energies of opportunity." These "energies of opportunity" include both waste heat and cold from industrial and utility sources and, importantly, environmental sources. The latter are such as winter-chilled water or summer-heated ponds. As already indicated, this is a primary thrust effort.

Systems in this area are generally characterized by large capacity in storage and application (e.g., district heating) and by their seasonal nature. Studies currently funded are indicated in Fig. 2. Under concept development, Auburn University is carrying out field studies on heat storage in a confined aquifer; and Texas A&M University, cold storage in an unconfined (alluvial) aquifer. The work being done by these institutions is supported by analysis at the Lawrence Berkeley Laboratory using existing and/or modified aquifer performance models. The U.S. Geological Survey serves in a general advisory capacity to this portion of the LTTES Program. In addition, we are planning activities to (1) identify appropriate energy sources, locate nearby useable aquifers, and define significant neighboring uses, (2) establish aquifer storage economics, and (3) determine the environmental effects of aquifer storage.

Earth Storage. Another seasonal technology being considered is the use of the earth contiguous to the source for storage; this is currently primarily identified with solar heat, though other sources (such as off-peak electricity) can also be accommodated. These systems are generally of small capacity with application to single residences or, at most, small groups of residences.

George Washington University is at present the only institution funded in this area (Fig. 3); this organization is examining a heat pipe system for injection and recovery of heat from a water-saturated subsurface sand bed.

PCM's in Building Materials. Short-term (diurnal) storage in building materials (concrete blocks, wall panels, ceiling tiles) is an exciting prospect for "comfort zone" heating and cooling. In this concept, room surfaces maintained at appropriate constant temperatures provide for the physiological perception of comfort despite reduced air temperatures. Further, building-material storage permits incorporation of energy storage devices within buildings without consuming "living space." The energy source is seen to be solar, thermal, or off-peak electricity.

This area has also been designated a principal thrust. Current efforts (Fig. 4) are confined to a study by Suntek Research Associates on infusion of PCM's into light-weight, surface-sealed concrete blocks and a parallel investigation by the Brookhaven National Laboratory on incorporation of PCM's into the concrete mix before casting. Continued pursuit of these efforts will depend on preliminary demonstration of economic potential; future efforts — given technical feasibility — will concentrate on proving the concept in respect to costs, energy savings, and industry acceptance.

PCM Bulk Storage. An alternative way of utilizing PCM's for thermal energy storage is to contain large quantities in tanks, providing economy of size. However, there are some significant problems associated with use of PCM's in this geometry; e.g., limitations on rate of energy input/discharge associated with freezing of the PCM on the heat exchange surfaces and incongruent melting and phase separation occasioning performance degradation with freeze/melt cycling. Responses to these problems have been varied, with some clever mechanical and chemical solutions being proposed.

The LTTES Program is currently supporting three studies in this category (Fig. 5): (1) Clemson University is examining a concept involving a salt hydrate PCM with heat transfer by direct contact with an immiscible fluid circulating through the pool, (2) Franklin Institute Research Laboratory is determining the feasibility of a concept utilizing the latent heat of crystallization of solutes from saturated aqueous solutions, and (3) Monsanto Research Corporation is investigating the technical and economic parameters affecting the use of a form-stable, crystalline polyethylene for use in a packed bed geometry.

PCM Macroencapsulation. Some of the problems associated with the use of bulk PCM's can be circumvented by packaging the PCM into smaller units. This is being considered by Dow Chemical Company (Fig. 6) in a study involving PCM/container compatibility, encapsulation techniques (shape, size, etc.), and encapsulated material performance (thermal cycling tests). The University of Delaware study constitutes the low-temperature portion of a subcontract funded by NASA-LeRC through the High-Temperature TES Program; this effort will document the work at Delaware on Glauber's salt ($Na_2SO_4 \cdot 10H_2O$), including both procedures for preparing the particular mixture developed and cyclic performance results.

Supporting Studies. In addition to the technical elements described above, the LTTES Program is engaged in a number of studies assessing TES impact on energy conservation and potential market penetration, identifying new storage materials and new applications, and determining basic heat transfer and (for PCM's) nucleation characteristics. Work in this category is listed (by subcontractor) in Fig. 7; thus:

•Argonne National Laboratory has been examining the commercial feasibility of thermal energy storage;

•Desert Research Institute has been addressing the problems of crystal nucleation;

•Oak Ridge National Laboratory has been developing a computational model describing heat transfer with the moving phase boundary associated with PCM freeze/melt, identifying and characterizing PCM's with potential for application to absorption air conditioning, and determining the crystal structures of hydrates and their nucleators;

•Pennsylvania State University has been studying the transient behavior of heat exchange systems with significant heat storage in the walls;

•TRW Energy Systems Group has been considering a method for improving the efficiency of home heating furnaces through incorporation of a TES element; and

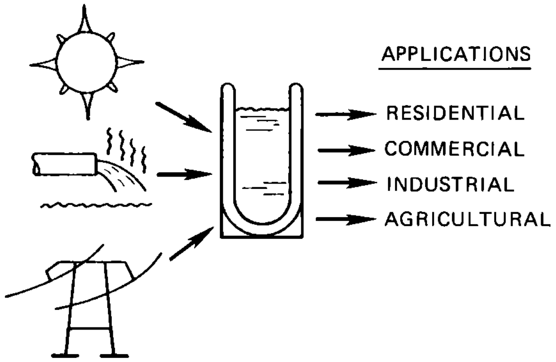
•Villanova University has been surveying materials exhibiting solid-state transitions of sufficient magnitude to be useful for TES.

Applications. The final line in the development of TES technology is the demonstration of uses that result in significant conservation of fossil fuel (oil and natural gas) through source substitution or consumption reduction. To this end, ERDA has awarded a number of contracts to determine the feasibility for recovery, storage, and reuse of waste heat from industrial sources. In the LTTES Program area, the two awards (Fig. 8) were to (1) Rocket Research Corporation with the Intalco Corporation to investigate heat recovery from a primary aluminum plant and heat use for district heating of several small communities in the neighborhood of the Intalco plant and (2) Westinghouse Electric Company with the Heinz Company to determine the potential for recovery and onsite reuse of thermal energy at a major Heinz food-processing facility.

Two other application areas being supported by the LTTES Program are also listed in Fig. 8; namely, a regenerated desiccant system being developed by Lockheed-Huntsville Research and Engineering Center for agricultural drying (crops and grains) and the aquifer storage of winter-chilled water being developed by Desert Reclamation Industries (with technical support from Dames & Moore) for the summer air conditioning of J. F. Kennedy Airport (New York).

4. CONCLUSION

The papers following in this Section consider in further detail the projects identified above as currently part of the LTTES Program. These projects of necessity reflect only some of the ideas advanced over recent years for thermal energy storage to effect energy conservation and alternate source utilization. In succeeding years, as some of these presently promising concepts succumb to technical or economic failings and the survivors move to demonstration, the LTTES Program will shift even more strongly to emphasizing and advancing the key thrusts. In the process, we will act principally through advertised bids and will be less responsive to unsolicited proposals. However, hopefully, there will still be room for funding the truly novel and the long-shot.



LTTES PROGRAM CONSERVES PRIME
ENERGY SOURCES

Fig. 1. The LTTES Program develops interface between alternate energy sources and end uses.

SYSTEM STUDIES	LAWRENCE BERKELEY LAB U. S. GEOLOGICAL SURVEY
CONCEPT DEVELOPMENT	AUBURN UNIVERSITY TEXAS A&M UNIVERSITY
TECHNOLOGY VALIDATION	

AQUIFER STORAGE PERMITS EFFECTIVE USE OF "ENERGIES OF OPPORTUNITY"

Fig. 2. LTTES Program activities relative to aquifer thermal energy storage.

SYSTEM STUDIES	GEO. WASHINGTON UNIV.
CONCEPT DEVELOPMENT	GEO. WASHINGTON UNIV.
TECHNOLOGY VALIDATION	

EARTH STORAGE HAS POTENTIAL IN SOLAR HEAT UTILIZATION

Fig. 3. LTTES Program activities relative to earth thermal energy storage.

SYSTEM STUDIES	
CONCEPT DEVELOPMENT	SUNTEK RESEARCH BROOKHAVEN NAT'L LAB
TECHNOLOGY VALIDATION	

PCM'S IN BUILDING MATERIALS ARE AN EXCITING PROSPECT FOR DIURNAL STORAGE

Fig. 4. LTTES Program activities relative to thermal energy storage through PCM's incorporated in building materials.

SYSTEM STUDIES	
CONCEPT DEVELOPMENT	CLEMSON UNIVERSITY FRANKLIN RESEARCH INST. MONSANTO RESEARCH CORP.
TECHNOLOGY VALIDATION	

PCM BULK STORAGE EFFORTS CURRENTLY CONSIDER DIVERSE CONCEPTS

Fig. 5. LTTES Program activities relative to thermal energy storage in bulk phase change materials.

SYSTEM STUDIES	
CONCEPT DEVELOPMENT	DOW CHEMICAL CO. UNIV. OF DELAWARE
TECHNOLOGY VALIDATION	

MACROENCAPSULATION PROVIDES FOR CONTROL OF HEAT EXCHANGE GEOMETRY

Fig. 6. LTTES Program activities relative to thermal energy storage with macroencapsulated phase change materials.

ARGONNE NATIONAL LAB
DESERT RESEARCH INSTITUTE
OAK RIDGE NATIONAL LAB (3)
PENN. STATE UNIVERSITY
TRW ENERGY SYSTEMS GROUP
VILLANOVA UNIVERSITY

LTTES TECHNOLOGY DEVELOPMENT IS SUPPORTED BY GENERIC SYSTEM STUDIES

Fig. 7. Basic studies in support of LTTES Program thermal energy storage technology development.

INVESTIGATOR	APPLICATION
LOCKHEED-HREC	CROP DRYING
DESERT RECLAMATION/ DAMES & MOORE	JFK AIRPORT COOLING
ROCKET RESEARCH/ INTALCO	DISTRICT HEATING
WESTINGHOUSE/HEINZ	FOOD PROCESSING

DETERMINING TES VIABILITY FOR SPECIFIC APPLICATIONS IS AN LTTES PROGRAM FUNCTION

Fig. 8. Thermal energy storage applications being studied under the LTTES Program.

PROJECT SUMMARY

ORGANIZATION: Energy and Environmental Systems Division
Argonne National Laboratory

ADDRESS: 9700 South Cass Avenue
Argonne, Illinois 60439

PROJECT TITLE: Commercial Feasibility of Thermal Energy Storage

PRINCIPAL INVESTIGATOR: J.G. Asbury
Telephone No. 312-379-7711 X5724

CONTRACT NO.: W-31-109-Eng-38

CONTRACT PERIOD: October 1975 - July 1978

CONTRACT AMOUNT: ERDA FY77: $375,000[a,b]
OTHER

PROJECT GOALS: The objectives of the Commercial Feasibility of Thermal Energy Storage Project are:

1. Identification of cost-effective, near commercial thermal energy storage technologies and systems,
2. Specification of cost/performance goals for advanced storage technologies and systems,
3. Specification of strategies for commercializing cost-effective storage technologies,
4. Recommendations for storage technology R&D.

PROJECT STATUS: By October 1, 1977 the Project will have accomplished:

1. Evaluation of baseline (near-commercial) storage technologies in the following applications:
    - Electric resistance heating
    - Electric heat pumps
    - Electric air conditioning
    - Electric water heating
    - Solar space heating
    - Solar water heating
2. A preliminary comparison of after-the-meter thermal storage with utility central station (pumped hydro, thermal, and compressed air) and dispersed (electric battery storage).

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[a] Covers a $200K subcontract with TRW Energy Systems Group for technology characterization work.

[b] Work supported by Chemical and Thermal Energy Storage Branch and Applications Analysis Branch, Division of Energy Storage Systems.

I. PURPOSE

The Project is assessing the commercial feasiblity of TES and TES-augmented devices for the heating and cooling of buildings. Major objectives of the Project are:

- determination of the economic competitiveness of TES devices relative to other heating and cooling systems,
- estimation of the market capture potential of TES devices and an estimation of the associated capital and energy savings,
- development of strategies for commercializing cost-effective TES systems,
- recommendations for TES technology RD&D.

II. BACKGROUND

The heating and cooling of buildings represents one of the most important applications of TES technology.

Under Phase I of this Project, we evaluated individual TES technologies for electric utility load leveling. The general procedure was to estimate the utility savings associated with each TES system and then to compare these savings with the additional capital cost of the TES system over the conventional system. For space heating applications, the utility savings were estimated by calculating the difference between the utility cost (capital, fuel, and operating) of meeting the conventional direct resistance load and the cost of meeting the storage electric heating load. If the calculated utility savings exceeded the difference between the capital cost of the storage heating system and the conventional heating system, the system was deemed "cost-effective." A similar procedure was employed to evaluate storage air conditioning and storage hot water systems.

The commercialization of TES depends upon transferring enough of the utility's storage-related benefits to customers to justify the customers' use of the storage devices. Table 1, summarizes the Phase I commercial feasibility findings for the two winter-peaking (A and B) and the two summer-peaking (C and D) service areas analyzed in the study. In the table, utility savings, expressed in cents per kilowatt-hour of device energy use, are compared with the energy price discounts required for simple paybacks of three and five years. The utility savings, computed under the utility accounting method, represent the maximum revenues per kilowatt-hour that the utility can transfer to purchasers of TES devices without having to increase the price of energy to other customers. As shown in the table, paybacks as short as three years

Table 1. Utility Savings Versus Customer Payback Requirements

Service Area	TES System	Discharge Period[a] (hrs)	Annual Consumption (kWh)	Utility Savings[b] (¢/kWh)	TES Incremental Cost ($)	Payback Required to Commercialize[c]			
						3-Year		5-Year	
						($/yr)	(¢/kWh)	($/yr)	(¢/kWh)
A	Water Htg.	4	5,840	1.0	105	35	0.6	21	0.4
A	Water Htg.	16	5,840	2.3	320	107	1.8	64	1.1
A	Space Htg.	8	28,000	5.1	2,840	946	3.4	568	2.0
B	Water Htg.	4	5,840	2.0	105	35	0.6	21	0.4
B	Water Htg.	16	5,840	3.3	320	107	1.8	64	1.1
B	Space Htg.	8	27,600	2.9	2,760	945	3.4	552	2.0
C	Water Htg.	4	5,840	0.8	105	35	0.6	21	0.4
C	Water Htg.	16	5,840	2.2	320	107	1.8	64	1.1
C	Air Cond.	8	2,500	14.6	1,095	365	14.6	219	8.8
D	Water Htg.	4	5,840	1.9	105	35	0.6	21	0.4
D	Water Htg.	16	5,840	3.1	320	107	1.8	64	1.1
D	Air Cond.	8	6,500	14.6	1,325	442	6.9	265	4.1

[a] Discharge periods for air conditioning and space heating systems correspond to devices in Table 1.1, ANL/ES-54 (August 1976). For storage hot water heaters, the 16-hour system offers the greatest net benefits; the 4-hour system is included because it is the easiest to commercialize.

[b] Utility savings per kWh calculated from annual consumption column and from annual utility savings in Table 1.1, ANL/ES-54 (August 1976).

[c] Simple payback; does not include cost of money.

can be offered for all the TES systems, with the exception of storage space heating in Service Area B. In addition to examining simple off-peak rate discounts, the Phase I study analyzed the feasibility of several other mechanisms for commercializing TES systems.

Since completion of Phase I, several additional storage and non-storage heating and cooling technologies have been evaluated. Because of the multiplicity of competing systems and the difficulty of defining a conventional, or reference technology, a total cost-of-service framework has been devised for evaluating and ranking the competing systems. Under the study method, both the utility's cost of service and those device investment and maintenance costs borne directly by the customer are evaluated and separately displayed. Notable additions to the list of competing systems are conventional and storage-augmented heat pumps, and several solar space heating systems. Here we present the method and findings for electric and electric-assisted heating and cooling systems. Work currently underway is covering oil- and gas-fired heating technologies.

III. PROJECT DESCRIPTION

Study Method. A case study approach, involving the evaluation of TES and competing-system technologies in each of a number of electric utility service areas, was adopted. The two service areas for which results are presented here were selected to illustrate the important factors affecting the overall cost of service for the different heating and cooling technologies. One service area is located in the Northeast and is supplied by a winter-peaking utility; the other service area, located in the Middle Atlantic Region, is served by a summer-peaking utility.

In each service area the individual heating and cooling systems were matched to the load requirements of a 1500 ft^2, well-insulated, detached single family dwelling unit. The heating load amounted to approximately 4 kWh_t/degree-day.

The Argonne cost allocation model, SIMSTOR, was used to calculate the utility costs of meeting the individual heating and cooling device loads. The model uses hourly synoptic load and weather data and device performance characteristics to generate load profiles over a full annual (8760 hour) cycle. It then calculates the incremental utility capital and fuel costs to meet changes in the utility's load. SIMSTOR incorporates a load dispatch model and observes operating constraints such as scheduled and forced outages and the cycle time of each type of generating unit. It calculates transmission and distribution costs as well as generating costs. Because SIMSTOR uses an equilibrium method to solve for optimum plant capacity and mix, the long-run marginal cost estimates pertain to planning horizons beyond the construction times of projects to which utilities are already firmly committed.

The building-load submodels used to simulate the performance of the heating and cooling devices are based on ASHRAE-recommended response factor methods and take into account such effects as solar radiation incident on exterior walls and windows, internal heat generation, and wind surface film phenomena. All the major energy inputs and outputs for the devices were simulated, except water pump and fan electrical requirements. (The latter loads are small and, because they are roughly equal for all the technologies, do not significantly affect relative costs.) Device-specific load profiles were generated on an hourly basis over the full annual cycle.

In order to value units of capital consistently on both sides of the electric meter, one set of system cost comparisons was made with heating/cooling device capital costs calculated on the basis of the utility capital recovery rate. This accounting procedure is conceptually equivalent to assuming utility ownership of the heating/cooling device. Another set of comparisons was made with the customer cost of money equal to present mortgage rates less an effective income tax credit.

The annual utility capital costs were calculated with a 17% capital recovery rate for plant of 30-year lifetime. This rate, which is representative of recent utility experience, incorporates a large (≃6%) inflation component in the cost of both bond and equity money. For consistency, fuel costs, which were assumed to have a 0% real rate of escalation, were inflated at the same 6% rate and were discounted by the same (11%) discount rate. The resulting annual fuel levelization factor was equal to 1.77. Because intitial-year fuel was valued at full marginal cost, this procedure is not expected to understate fuel costs relative to capital costs.

Utility energy supply costs for space heating technologies were calculated for an incremental load corresponding to the addition of 1000 space heating customers; for air conditioning technologies, the addition of 2000 customers. These load increments represent approximately 10 MWe of diversified peak electrical demand if met with conventional heating and cooling technologies. Although utility supply costs change as the number of installations increase - for example, the marginal cost of supplying storage heating customers increases as the nighttime valleys are filled - the dependence of supply costs on market penetrations is not discussed here.

Because load curves and weather data for a specific year, 1975, were used, the estimated utility supply costs do not constitute a forecast of the costs of meeting device-specific loads. Rather, the calculated costs may be interpreted as representative for utilities expecting to face load curves having shapes similar to the ones used here.

Heating and Cooling Technologies

Electric Storage Heating. Both central furnace and dispersed room electric storage heating units are available from European manufacturers. For applications in new residential buildings, the central furnace systems are generally less expensive than the dispersed room units. Incorporating either refractory brick or cast iron as the storage medium, imported central furnace units can be installed at a cost of $8-10 per kWh over the cost of a standard electric furnace. Eventually, domestic production will reduce the costs of both dispersed and central storage systems.

Electric storage heaters can also be used with heat pumps, providing an alternative to direct resistance heaters that conventionally augment output below the heat pump balance point. Because in most climates the heat pump operates in a nearly fully resistance mode on the design-day, capacity requirements for the storage unit in such a hybrid system will be approximately the same as for the simple electric storage heating system described above.

Storage air conditioning systems are currently under development and testing by several domestic manufacturers. The most economical and practical systems for residential applications incorporate ice storage tanks which are connected to the central air conditioning system. As water in the tanks is chilled, it forms ice on evaporator coils. A water-level sensor turns off the compressor before the ice rings merge, allowing water to circulate freely for efficient heat exchange during system discharge. Compressor size, due to the reduced hours of operation and lower evaporator temperature, is greater than for a conventional air conditioner. Depending upon the house size and the local climate, 150 to 300 gallons of storage capacity are required. Larger tanks can be used in commercial buildings. In residential applications, the incremental cost of storage air-conditioning ranges from \$30-45 per kWh_e (\$14-20 per kWh_t) of storage capacity.

Bivalent Systems. An alternative to the use of storage for reducing the electric peak loads associated with space heating systems is the incorporation of a gas- or oil-fired backup unit in the central heating system. The backup unit, ideally under the direct control of the electric utility, is switched on during peak load hours, thereby reducing utility peak capacity and fuel requirements. Bivalent heat pump and bivalent resistance heating systems are available from European and domestic manufacturers.

In simulations of the performance of the bivalent heat pumps, the auxiliary fuel unit operated in either of two modes. Under the first mode, the auxiliary unit is operated so as to simulate and exactly substitute for the heat pump's electric resistance backup. Under the second mode of operation, the auxiliary unit is switched on during those periods when normally either resistance backup or utility peakers would be used.

When substituting for the operation of peaker plant, the bivalent system not only reduces peak capacity requirements but also saves fuel, because the oil furnace has a higher conversion efficiency than utility peaker plant.

In our simulations of the performance of bivalent direct resistance heating systems, we assumed the backup unit was turned on during periods when utility peaking plant otherwise would have been used.

Solar Systems. Two types of solar heating systems were evaluated - direct solar heating systems with electric resistance backup and solar-assisted heat pumps. Residential space heating represents one of the most promising applications of solar energy; however, as described in an earlier paper, active solar energy systems and conventional electric utilities are a poor technological match. In particular, because of the high fixed costs of electric generation, transmission, and distribution facilities, these facilities cannot be economically justified as a "standby" energy system to cover periods of solar insolation outage. Nevertheless, because of widespread interest in electric-solar heating systems, we have included them in the present analysis.

For solar augmented by resistance heating, either of two operating strategies can be adopted. Under the first strategy, or operating mode, the backup furnace switches on as required to augment the heat flow from the solar collector or the storage reservoir to the load. This is the mode of operation of most conventional solar systems.

The second mode, as conceived and advanced by several solar system designers, would take advantage of low cost off-peak electricity to augment solar energy supplies. Under this strategy, which requires predictive information about the following day's insolation and heating load, auxiliary energy requirements are input to the storage unit during the previous nighttime period. In practice to prevent degradation of solar collection efficiency, this mode of operation requires either the addition of a separate storage reservoir or maintenance of perfect stratification within the existing reservoir. For purposes of our analysis, we assumed perfect stratification with no increase in storage system cost.

Parametric studies were performed to analyze the tradeoffs between utility and customer costs as a function of collector area and storage capacity. Systems sized to meet 25, 50 and 75% of the annual space heating load were evaluated. For Mode 1, the optimum storage capacity was found to be approximately equal to the average daily output of the collector system. For Mode 2, because of the possible unavailability of solar input on the peak winter day, the storage capacity was set equal to the full design-day building load, independent of the collector size.

A number of different solar/heat pump systems were also analyzed. The results presented here refer to the solar-assisted heat pump configuration in which solar energy is input to a storage reservoir on the cold side of the heat pump before delivery to the building load. Second phase heating is provided by the heat pump drawing from ambient air; and final phase heating, by resistance heaters. The solar/heat pump system in which storage is on the hot side of the heat pump and both the heat pump and solar collector supply energy directly to the storage reservoir was also examined. Our analysis indicated that this design concept is inferior to the one incorporating a solar-supplied storage unit on the cold side of the heat pump.

The costs assumed for the solar system components represent somewhat optimistic projections of near-term installed system costs. Relative to direct resistance heating systems, solar heating systems were assumed to have an incremental cost of $1,000 for plumbing and controls, $15 per square foot of collector area, and $1.00 per gallon of storage capacity. For the solar-assisted heat pump system, where lower performance collectors are acceptable, collector costs were assumed to be $10/ft^2.

IV. RESULTS

The estimated costs of the different heating and cooling technologies are presented in Tables 2 and 3 for the winter and summer peaking service areas, respectively. As indicated in Table 2, the storage and bivalent systems are the most efficient heating systems in terms of overall cost. Presenting the utility with electric loads only during the off-peak hours, these systems do not contribute to the utility's coincident peak demand.

The ripple-controlled bivalent heat pump is especially attractive. Entailing a small customer capital cost penalty - approximately $500 over the cost of a heat pump with electric resistance backup — the heat pump with oil furnace backup achieves substantial savings through the virtual elimination of the on-peak electrical load.

As shown in Table 2, the costs of energy supply to the solar resistance and the solar-assisted heat pump systems are lower than for direct resistance heating; however, the only solar system offering supply costs comparable to those for the storage and bivalent heating systems is the solar resistance system operating in the second mode. By the very nature of the design of this system - essentially a storage resistance system plus a solar collector - the customer costs for this system are always greater than for a simple storage resistance heating system. As this system comparison makes clear and as pointed out in an earlier paper, the addition of a solar collector can be justified only in terms of the value of the off-peak utility supplied energy that it displaces. For Service Area A, the total cost of the solar storage technology becomes comparable to the cost of electric storage heating at a collector cost of about $\$4.50/\mathrm{ft}^2$, if it is assumed that the collector is financed at the utility cost of money. If lower cost home mortgage money is used to finance the solar system (as well as the competing, storage heating system), the collector breakeven cost is $\$7.00/\mathrm{ft}^2$.

Although the total cost of supplying space heating services with the solar-assisted heat pump is less than the total costs for the solar/resistance heating systems, the breakeven cost of the collector component of the solar-assisted heat pump is lower than for the solar/resistance system in Service Area A. If the storage heat pump is chosen as the reference technology and if utility financing is assumed, the breakeven cost of the collector component of the solar-assisted heat pump is $\$1.00/\mathrm{ft}^2$. If home mortgage financing is assumed, the breakeven cost of the solar collector is $\$1.50/\mathrm{ft}^2$, a difficult cost target indeed.

For the service area supplied by a summer-peaking utility, the entire heating season is off-peak so that the benefits of storage and bivalent heating systems are greatly reduced. The conventional heat pump is the most economical

Table 2. Cost of Supply, Service Area A

System	System Characteristics	Contribution to Utility Peak (kW/Customer)	Average Utility Cost (c/kWh)	Costs ($/Yr/Customer) Energy Supply Utility				Device[c]		Total	
				Generating[a]	T&D	Total	Supplemental Fuel[b]	Util. Rate	Mort. Rate	Util. Rate	Mort. Rate
Space Heating											
Resistance											
Direct	Central Electric Furnace	16.6	9.0	1125	820	1945	--	240	140	2185	2085
Storage	8 hour Central Storage	0.0	1.7	365	0	365	--	535	320	900	685
Bivalent	Ripple Controlled Oil Furnace Backup	0.0	2.9	580	0	580	45	610	380	1235	1005
Heat Pump											
Conventional	2.5 ton (SPF = 2.06)	15.0	11.8	730	740	1470	--	325	200	1795	1670
Storage	8 hour Resistance Storage	0.0	2.9	305	0	305	--	575	350	880	655
Bivalent (Mode 1)	Oil Furnace Backup	3.3	6.4	360	165	525	65	430	280	1020	870
Bivalent (Mode 2)	Ripple Controlled Oil Furnace	0.0	3.0	230	0	230	100	460	300	790	630
Solar											
Resistance	330 ft^2 (50% solar)	10.8	9.6	395	530	925	--	1300	760	2225	1685
Storage Resistance	330 ft^2 (50% solar)	0.0	1.6	155	0	155	--	1360	800	1515	955
Heat Pump	270 ft^2 (SPF ≃ 2.3)	9.1	9.0	365	450	230	--	1110	650	1340	880
Air Conditioning											
Conventional	2.5 ton Heat Pump	0.0	4.3	95	0	95	--	255	175	350	270
Storage	8 hour Ice Storage	0.0	1.6	35	0	35	--	475	310	510	345

[a] Includes generation capital, fuel, cycling, and maintenance costs.

[b] Cost of fossil fuel for bivalent system.

[c] All heat pump device costs are net an air conditioner capital cost credit of $1050.

Table 3. Cost of Supply, Service Area B

System	System Characteristics	Contribution to Utility Peak (kW/Customer)	Average Utility Cost (¢/kWh)	Costs ($/Yr/Customer) Energy Supply Utility Generating[a]	Costs ($/Yr/Customer) Energy Supply Utility T&D	Costs ($/Yr/Customer) Energy Supply Utility Total	Costs ($/Yr/Customer) Energy Supply Supplemental Fuel[b]	Costs ($/Yr/Customer) Device[c] Util. Rate	Costs ($/Yr/Customer) Device[c] Mort. Rate	Costs ($/Yr/Customer) Total Util. Rate	Costs ($/Yr/Customer) Total Mort. Rate
Space Heating											
Resistance											
Direct	Central Electric Furnace	0.0	4.2	805	0	805	--	235	140	1040	945
Storage	8 hour Central Storage	0.0	1.9	370	0	370	--	415	245	785	615
Bivalent	Ripple Controlled Oil Furnace Backup	0.0	2.9	450	0	450	20	605	380	1075	850
Heat Pump											
Conventional	2.5 ton (SFP = 2.0)	0.0	2.7	260	0	260	--	325	200	585	460
Storage	8 hour Resistance Storage	0.0	2.3	220	0	220	--	440	270	660	490
Bivalent (Mode 1)	Oil Furnace Backup	0.0	2.5	185	0	185	60	430	280	675	525
Bivalent (Mode 2)	Ripple Controlled Oil Furnace	0.0	2.3	165	0	165	90	460	300	715	555
Solar											
Resistance	300 ft^2 (50% solar)	0.0	2.0	180	0	180	--	1200	710	1380	890
Storage Resistance	300 ft^2 (50% solar)	0.0	1.5	135	0	135	--	1280	750	1415	885
Heat Pump	270 ft^2 (SPF ≃ 2.4)	0.0	2.4	200	0	200	--	940	550	1140	750
Air Conditioning											
Conventional	2.5 ton Heat Pump	5.5	23.3	415	265	680	--	255	175	935	855
Storage	8 hour Ice Storage	0.0	2.1	60	0	60	--	475	310	535	370

[a] Includes generation capital, fuel, cycling, and maintenance costs.

[b] Cost of fossil fuel for bivalent system.

[c] All heat pump device costs are net an air conditioner capital cost credit of $1050.

heating technology. Storage and bivalent technologies are 10-20% more expensive in terms of overall cost and suffer the disadvantage of being more complicated technologies. Solar/storage-resistance heating becomes cost competitive with storage resistance heating at collector costs of \$2.75/ft^2 (utility financing) and \$6.00/ft^2 (customer financing). Under either utility or customer financing, the breakeven cost of the collector component of the solar-assisted heat pump is less than \$1.00/ft^2.

Figures 1 and 2 display annualized energy supply costs (utility capital and fuel and bivalent fuel costs) and device (customer) capital costs for each of the heating technologies. The dashed lines represent constant total cost curves. As shown in the figures, storage and bivalent systems are the most efficient technologies in the winter-peaking service area, while the conventional heat pump is the lowest cost technology in the service area supplied by the summer-peaking utility.

In the summer peaking service area, the conventional heat pump is the most cost-effective means of supplying heating services. This result, combined with the finding that storage air conditioning is a low cost method of providing summer space conditioning, indicates that a heat pump, using diurnal ice storage during the summer months, is an efficient technology for year round space conditioning.

V. FUTURE WORK

Future work will cover the following major task areas:

- comprehensive, region-specific comparison of customer TES with utility storage
- evaluation of the technical and commercial feasibility of seasonal TES for solar space heating
- comparison of electric and electric-assisted TES systems with oil- and gas-fired heating systems.

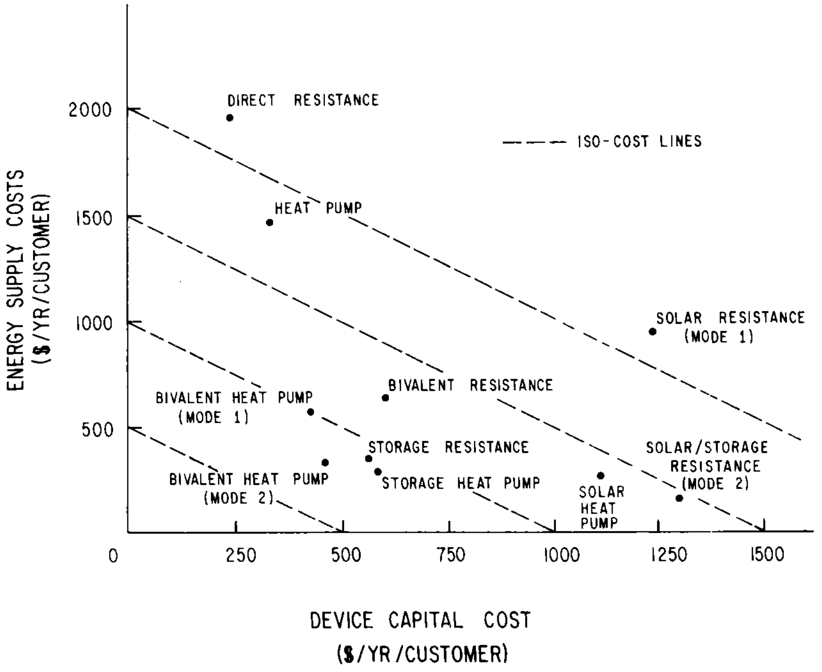

Fig. 1. Annualized Costs for Different Electric Heating Technologies, Winter Peaking Service Area, Utility Cost of Money on Both Sides of Meter.

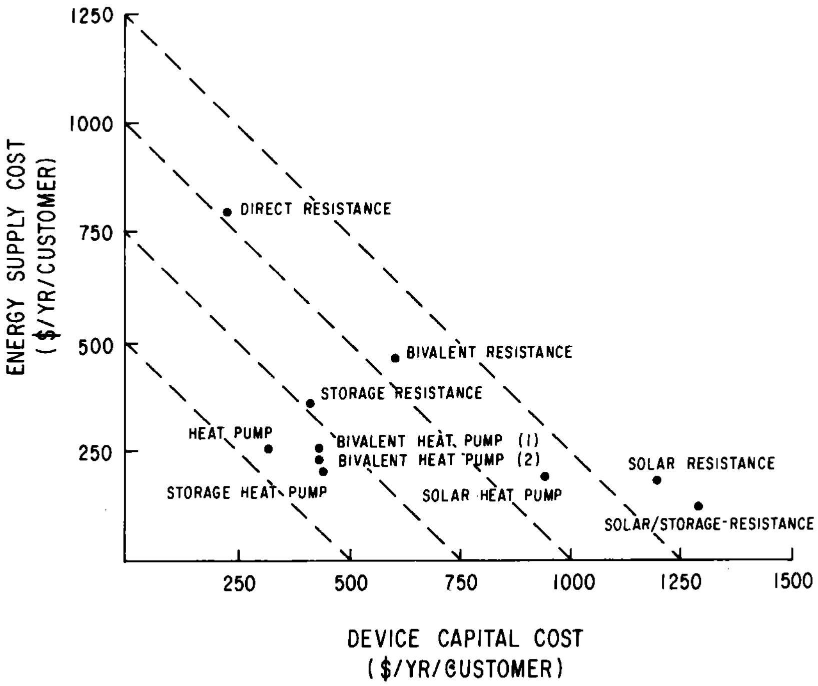

Fig. 2. Annualized Costs for Different Electric Heating Technologies, Summer Peaking Service Area, Utility Cost of Money on Both Sides of Meter.

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PROJECT SUMMARY

ORGANIZATION: Water Resources Research Institute, Auburn University

ADDRESS: Auburn University, Auburn, AL 36830

PROJECT TITLE: Subsurface Waste Heat Storage, Experimental Study

PRINCIPAL INVESTIGATORS: James C. Warman
Fred J. Molz

TELEPHONE NO: (205) 826-5075

CONTRACT NO: E-(40-1)-5003

CONTRACT PERIOD: 8/15/75-6/30/77

CONTRACT AMOUNT: ERDA $ 95,000.00
OTHER $155,000.00

PROJECT GOALS:

The idea of pumping a volume of heated water into an aquifer, storing it there for a period of time and then pumping it back out is called the Heat Storage Well Concept. The goals of the present project were to begin actual testing of this concept and to provide data for the calibration of mathematical models describing the transport of heat in ground water.

PROJECT STATUS: Complete

I. Purpose

The Water Resources Research Institute of Auburn University performed a field experiment in which a volume of heated water was pumped into a confined aquifer and recovered. The purpose of the field experiment was to begin testing the Heat Storage Well Concept and to provide data (hydraulic heads and ground water temperatures) for the calibration of mathematical models describing the transport of heat in ground water.

II. Background Information

The possibility of using confined aquifers (saline or fresh) as natural containers for fluids such as gas, fresh water or a water-based solution has been considered seriously for the past decade [Esmail and Kimbler, 1967; Katz and Tek, 1970; Kimbler, 1970; Kumar and Kimbler, 1970; Moulder, 1970; Kazmann, 1971, 1974; Kazmann, Kimbler and Whitehead, 1974; Smith and Hanor, 1975]. More recently, however, much attention has been focused on the use of aquifers as temporary storage reservoirs for thermal energy in the form of moderate to high temperature water (140F°-400F°; 60C°-204C°) [Meyer and Todd, 1973; Hausz and Meyer, 1975; Meyer, 1976; Molz et al., 1976; Warman, Molz and Jones, 1976; Molz and Bell, 1977].

Studies of the Heat Storage Well concept by the General Electric Company [Meyer, 1976] have as their interrelated principal objectives the conservation of large amounts of heat now wasted in generating electricity and the reduction of thermal pollution caused by discharge of this waste heat. Others have considered the possibility of using aquifer storage of heated or cooled water in conjunction with very large solar energy systems [Martin, Harris and Davidson, 1975]. The Heat Storage Well concept appears to make large-scale total-energy systems feasible. According to Meyer (1976), "Some 600 small total-energy systems are now in operation in the United States, but their total electrical generating capacity is only 0.4 percent of the national total. The technological innovation needed to make large-scale total-energy systems feasible is a means for storing large amounts of high-temperature water or steam for long periods of time--several months--at low cost and low loss. With such storage technology available, large thermal electric generating systems could produce high-temperature water as a joint product with electricity; storage of heated water makes possible the matching of electrical generation, which must instantaneously satisfy the demand for electricity, with the demand for heat."

Development of an adequate understanding of the hydraulics, heat transfer and geochemistry of Heat Storage Wells is essential if the concept is to be applied successfully. Therefore, in the early seventies the U.S. Geological Survey initiated an effort to develop a series of sophisticated mathematical models for describing the time-dependent transport of water and heat in a ground water system [Appel and Bredehoeft, 1976; Mercer et al., 1975]. In parallel with the modeling effort was an experimental study conducted by Auburn University. Funding for the experimental work was provided by the U.S. Geological Survey and the Energy Research and Development Administration. The objectives of the experimental program were to begin actual testing of the Heat Storage Well concept and to provide data for calibration of mathematical models.

III. Project Description

The research program was composed of four phases. Phase I consisted of the drilling of an exploratory well at the selected field site by the Alabama Power Company. Phase II involved the construction of the central injection well, three observation wells, and the performance of preliminary pumping tests. Phase III was devoted to the construction of the remainder of the observation well field, performance of final pumping tests, and the measurement of aquifer thermal properties; while Phase IV was devoted to a cycle of warm water injection, storage and recovery.

IV. Results

1. In selecting a site for a heat storage well, care must be taken to ascertain that natural movement of the ground water is very small. If a sufficiently large pore velocity exists, the site will be unacceptable unless the gradient is controlled artificially [Molz and Bell, 1977].

2. Long operation of a heat storage well will require use of heated water with extremely low suspended solids. (A hundred million gallons (3.785×10^8L) of water with suspended solids of 1 part per million contains 836 lbs (379 kg) of suspended material.) It is likely that clogging will be one of the most serious problems concerning the intermediate to long-term operation of heat storage wells.

3. If a storage aquifer contains even small amounts of clay, one must not inject a fluid that will cause the clay fraction to swell. The pH and ion content of the water must be compatible with the particular clay mineral. Exposure to distilled water can cause some clays to swell [Mitchell, 1976]. Also, the injected water must not precipitate any chemical compounds in the storage aquifer or onto the aquifer matrix.

4. Care must be taken not to create hydraulic conditions capable of causing the failure of a confining stratum if a confined aquifer is to be used for storage purposes. It may be that high temperature water will weaken aquitard materials or increase their permeability. The effect of temperatures in the 140 to 400F° (60 to 204C°) range on mechanical and hydraulic properties of aquitard materials should be studied.

5. Considering the relatively small injection volume and a partially penetrating injection well, the thermal recovery factor of 0.68 is considered encouraging. Simulation studies [Papadopulos and Larson, 1977] predict high recovery factors for storage wells involving hundreds of millions of gallons of heated water.

6. Anomalous cooling effects can lead to errors in observation wells intended to measure ground water temperatures. The effects appear to be due to mixing between the hotter water in the lower portion of the well penetrating the storage formation and the cooler water in the casing above the formation.

7. One procedure for minimizing the possibility of chemical or mechanical clogging of an injection well is to use formation water as an influent to the heating system. Ground water tends to be low in suspended solids, and the main difference between the injected water and the native water will be temperature.

8. In order to further develop the heat storage well concept, additional experimental studies are needed involving larger volumes of water and higher injection temperatures. The geochemistry problem must be studied carefully, and the effect of high temperatures on the mechanical and hydraulic properties of clay confining layers must be determined.

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PROJECT SUMMARY

ORGANIZATION: Brookhaven National Laboratory

ADDRESS: Upton, New York 11973

PROJECT TITLE: Encapsulation of Phase Change Materials in Concrete Masonry Construction

PRINCIPAL INVESTIGATOR: L. E. Kukacka TELEPHONE NO.: (516) 345-3065

CONTRACT NO.: 19Y-14279V CONTRACT PERIOD: 27 months

CONTRACT AMOUNT: ERDA $302,000

PROJECT GOALS:

The encapsulation of phase change materials (PCM) in masonry offers a method for producing a low-cost energy storage system which can be manufactured with only small modifications to existing processes. If thermal storage is used in conjunction with other space conditioning system modifications which provide increased overall efficiency of heating and cooling devices, the use of improved thermal management practice, and the optimum use of national electric generating capacity, national savings that substantially exceed the Btu equivalent of millions of barrels of oil annually can be derived.

The most efficient place to provide substantial thermal storage is in the structure and components which immediately surround a building's occupants.

Normal weight concrete consists of ∿ 80 wt % aggregate. Therefore, the greatest and most uniform concentration of PCM can be attained by using the material as a partial replacement for the normal fine and coarse aggregate. To accomplish this, the PCM must be immobilized and capable of interacting with the binder to produce a high strength and low permeability concrete. It is also essential that the PCM not react chemically with the aggregate and be non-corrosive to steel reinforcement.

For several years Brookhaven National Laboratory has been developing a series of composites called "Concrete Polymer Materials". These materials are high strength, impermeable, and have other properties which make them excellent candidate materials for use with PCM in energy storage systems.

The goals of the work will be the development of techniques for incorporating PCM, identified primarily by other organizations, into concrete and concrete polymer building materials and to characterize them by measuring the appropriate mechanical, physical and chemical properties. Economic studies will also be made.

PROJECT STATUS:

The project was initiated in August 1977. To date concrete and concrete polymer specimens have been prepared in which a PCM ($CaCl_2 \cdot 6H_2O$) has been used as a partial replacement for stone aggregate. Experiments to determine the maximum concentration of PCM that can be incorporated into the materials and to determine the optimum PCM concentration with respect to the properties of the composites and energy storage characteristics are commencing.

PROJECT SUMMARY

ORGANIZATION: Clemson University

ADDRESS: Clemson, SC 29631

PROJECT TITLE: Immiscible Fluid - Heat of Fusion Heat Storage System

PRINCIPAL INVESTIGATOR: D. D. Edie TELEPHONE NO.: 803-656-3055

CO-INVESTIGATORS: S. S. Melsheimer
J. C. Mullins

CONTRACT NO.: E-(40-1)-5190

CONTRACT AMOUNT: $139,000 ERDA PERIOD: 6/1/76 - 5/30/78

PROJECT GOALS:

The primary goal is to evaluate the feasibility of direct contact heat transfer in phase change energy storage using aqueous salt systems. This concept promises to alleviate the heat transfer and phase segregation problems encountered in earlier heat of fusion energy storage systems, yielding a practical, compact energy storage unit. A secondary goal is improved knowledge and understanding of heat and mass transfer in direct contact heat transfer in aqueous crystallizing systems.

PROJECT STATUS:

Review of the literature (1, 2, 3, 4) has identified a number of aqueous salt systems with suitable properties (phase change temperature, heat of fusion, and cost being the primary factors). Identification of heat transfer fluids with desirable properties (immiscibility, nonflammability, nontoxicity) has proved more difficult, with no fluids meeting all requirements located to date.

Crystal growth rates of selected salts have been determined as a function of undercooling. These growth velocities were determined in an apparatus specifically designed to eliminate fluid boundary layer mass transfer resistance. This information will be used in analyzing the dynamic performance of the direct contact-latent heat storage system to ascertain the rate-limiting processes.

Preliminary studies of energy storage efficiency have been conducted using a bench scale unit. The results appear to confirm the viability of the basic concept, though indicating that phase segregation problems have not been completely eliminated with the current apparatus. A larger, pilot scale unit with design improvements is being placed into operation currently. This unit will provide data on interphase heat transfer as well as facilitate determination of the effect of extended cycling on energy storage efficiency.

PURPOSE

The object of the study is the evaluation of direct contact heat transfer to aqueous crystallizing salt systems for phase change energy storage applications. Direct contact heat transfer, using an immiscible fluid, promises to alleviate heat transfer rate and phase segregation problems encountered with surface heat transfer systems.

BACKGROUND

The need for energy storage systems for such applications as solar heating systems and as a load-leveling device for heat pumps has become quite evident in recent years. The advantages of utilizing latent heat as opposed to sensible heat storage have been discussed many times (e.g., Telkes (1, 2)) and will not be repeated here. An optimum system should have a high energy storage per unit volume, provide an adequate rate of heat transfer, and be economical. The materials used should be noncorrosive, nontoxic, and inflammable. In addition, the storage of energy must be at the desired temperature level. With the possible exception of water storage (if the temperature of interest is $0^{o}C$) no system appears to have all of the desired attributes. For many of the applications of energy storage it is desirable to store the energy over the temperature range, $25\text{-}50^{o}C$. Materials with suitable phase changes in this range have been suggested by Telkes (2, 3) and Lane et al. (4).

PROJECT DESCRIPTION

After carefully reviewing various storage systems and the problems associated with each, it became clear that the use of direct contact heat exchange offered solutions to many of these problems. A schematic diagram of the proposed system is shown in Figure 1. The essence of this technique is that a fluid lower in density and immiscible with an aqueous salt solution is used as a heat transfer medium. It is introduced at the bottom of the storage vessel as a dispersed phase, and transfers heat to or from the aqueous solution as it rises through the solution. Agitation is provided by the rising bubbles. This agitation alleviates phase segregation and poor heat transfer associated with the majority of phase change storage systems. The heat transfer fluid is then pumped through the remainder of the heat transfer loop.

The use of direct contact heat transfer in energy storage is not a new concept. It appears to have been proposed first by Etherington (5) as a method of storing energy for heat pumps. Etherington used a light mineral oil as a transfer fluid and an aqueous solution of disodium phosphate as the phase change material in his study, with mixed results.

To determine the feasibility of the direct contact-heat of fusion energy storage system, several distinct areas require investigation: (1) identification of suitable heat transfer fluids and phase change materials; (2) bench scale studies of apparently feasible systems; (3) studies of heat and mass transfer rates, and of agitation achieved by immiscible fluid injection; (4) incorporation of the above information into a pilot scale study including cycling over an extended period of time under conditions representative of potential applications.

RESULTS

Identification of suitable heat transfer fluids and phase change materials is the first problem at hand. Lane et al. (4) have suggested a list of promising inorganic salt systems for latent heat of fusion energy storage. Telkes (2, 3, 6) has studied a number of inorganic salt hydrates for use in energy storage. Based on these findings and on our own analysis the two salts chosen for initial investigation were $Na_2SO_4 \cdot 10H_2O$ and $Na_2HPO_4 \cdot 12H_2O$. Several other salts appear to meet the key selection criteria (low cost, appropriate transition temperature, and high heat of fusion), and may be studied in the later stages of the project. Generally, however, the conclusion at this point is that a number of inorganic salt hydrates are suitable, with the optimum salt for a given application depending primarily on the transition temperature of interest.

The situation with respect to heat transfer fluids is more complex. The fluid must meet a number of criteria:

(1) immiscibility with the aqueous salt solution;
(2) density well below that of the salt solution (Sp.Gr. of 1.0 or less);
(3) chemically stable in contact with water and the inorganic salts;
(4) no phase change (freezing or boiling) over the operating range of either the heat source (such as a solar collector) or storage system.

Additional criteria that should be met if a generally acceptable storage system is to be developed are:

(5) good toxicity and corrosion properties;
(6) good flammability properties (flash point of 260°C or higher for domestic solar applications);
(7) low cost.

The initial calorimetric studies of the direct contact-phase change system (7, 8) used Exxon Varsol 18, marketed as a solvent rather than as a heat transfer fluid. It generally meets all the specifications above except the flammability requirement. Several commercial heat transfer fluids which also apparently met the criteria above, including good flammability attributes, were then investigated. These include Dow Corning Silicone Oil Q2-1132, and several paraffinic hydrocarbons (Exxon Terresstic 32, Terresstic 68, Terresstic 100, and Exxon Marcol 72). All of these were found to form an emulsion with the aqueous salt solution, and with water, leading to carry-over of the salt solution.

The most obvious difference between these fluids and Exxon Varsol 18 was their considerably higher viscosity. Experiments using equal amounts of heat transfer fluid and water in an agitated flask showed the tendency to form an emulsion was clearly viscosity dependent. The flask was agitated, and the temperature level gradually raised until the emulsion broke. For each fluid tested, emulsions began to disappear at a heat transfer fluid viscosity of approximately 4.5 cp (determined using a Contraves Viscometer). Similar experiments with Na_2HPO_4 solution replacing the water verified this result, though indicating a slightly higher break point (5.2 cp). Viscosity less than 4.5 cp at the lowest temperature of interest is thus an additional criterion to be used in screening prospective heat transfer fluids.

A list of 110 different fluids has been compiled from references in previous direct contact heat transfer work and from manufacturers information. Using the viscosity criterion in conjunction with other physical properties requirements quickly trims this to 20 prospective fluids, however none appear to have flammability properties as good as desired. Work is in progress to develop missing information on some of these fluids, and efforts to identify additional prospective fluids are continuing. The five fluids with the best combination of properties will be tested using the bench scale energy storage unit to determine their suitability in practice.

Bench scale studies of selected feasible systems are conducted using an apparatus similar to the schematic in Figure 1, with a 1.5 liter cylindrical plexiglas storage container. A gear pump is used to circulate the heat transfer fluid through an auxiliary heat exchanger (heat is added or removed to provide heating and cooling cycles) and into a conical diffuser fitted into the base of the storage container. Two salts (Na_2SO_4 and Na_2HPO_4) and several heat transfer fluids have been tested to date. Of the latter, only Varsol 18 has provided acceptable performance in operation (though its flashpoint of 43°C makes it clearly unsuitable for use in most applications of the storage system.)

The Na_2SO_4 system involves two solid phases, a decahydrate ($Na_2SO_4 \cdot 10H_2O$) and anhydrous Na_2SO_4. Upon melting decahydrate crystals in a heating cycle, anhydrous Na_2SO_4 crystals and a solution are formed. On the cooling cycle, the anhydrous Na_2SO_4 must go into solution, then recrystallize as the decahydrate. As the density of the anhydrous salt is quite high ($2.8 g/cm^3$), it settles to the bottom of the vessel unless extremely high flow rates of Varsol are used to maintain it in suspension. Consequently, mass transfer rates are very slow. For this reason Na_2SO_4 has been discarded as a feasible storage medium with the present system design.

Na_2HPO_4 has proved much more promising, however. Technical grade anhydrous salt was used to prepare the solution corresponding to the hydrated crystalline form $Na_2HPO_4 \cdot 12H_2O$ (39.6 mass percent Na_2HPO_4). The lower grade salt was mixed with tap water ensuring the presence of seeds needed for nucleation. Although nucleating agents have been reported (6), no problems associated with lack of nucleation have been observed. A calibrated difference thermocouple measures the temperature difference between the outlet and inlet Varsol streams. Flow rates of the Varsol were determined volumetrically and the temperature of the exit stream was measured with a thermocouple. These data (measured as a function of time) allowed the calculation of a heat flux between the Varsol stream and the aqueous salt solutions. Integration of the flux over the duration of the cycle gave the total heat transferred between the Varsol and the phase change material. The temperature of the contents of the tank was monitored by a thermocouple near the center of the tank. This temperature was used to obtain the initial and final temperatures and to correct for relatively small heat losses to the surroundings. The results of 10 cycles are shown in Table I. The "efficiency" reported for each run is calculated relative to amount of energy that could have been stored or removed from the storage medium assuming equilibrium existed at the start and finish of each heating or cooling run. For example, in the heating run of Cycle 1 the energy stored was 76.5 percent of that theoretically possible. Figures 2 and 3 depict the temperature and heat flux obtained in typical runs.

Table I
Efficiency of Na_2HPO_4 Energy Storage

Cycle No.	Mean Varsol Flow cc/sec	Efficiency	
		Cooling	Heating
1	11.9	74.6%	76.5%
2	11.6	75.4	74.9
3	11.5	74.0	71.7
4	11.6	78.7	77.0
5	11.8	69.8	72.9
6	11.4	80.6	77.9
7	11.8	81.8	79.5
8	11.5	78.0	76.0
9	11.0	78.7	77.1
10	11.3	76.4	77.9
Avg	11.5	76.8	76.1

This set of heating and cooling runs was conducted as consecutive cycles with the same salt solution. Note that no degradation of efficiency with time is observable. The fluctuations in efficiency between runs is attributed to experimental uncertainties (8). The criterion for ending a run was reduction of the heat flux to a predetermined minimum value, indicated by a Varsol temperature difference of 2°C. This was chosen to avoid difficulties in measurement of very low temperature differences, as well as to recognize practical limitations on usable heat flux.

A second set of ten cycles has been conducted at a lower nominal flow rate, 8.0 cc/sec. Similar results were obtained, with average efficiences of 69.9% on heating and 70.6% on cooling. The slightly lower efficiency presumably results from the poorer agitation obtained at the lower flow rate. In any event, the overall storage efficiency averages over three times that of a water storage system operating over the same temperature limits.

The third area of study preliminary to the final system test is determination of heat and mass transfer rate limitations in this complex, multi-phase system. The most fundamental aspect of this, the basic crystal growth rate data, was addressed first. The apparatus constructed for this purpose is shown in Figure 4, with an enlarged view of the crystal holder in Figure 5. Three small seed cyrstals are placed in the crystal holder and lowered into the supersaturated salt solution. The crystals are allowed to grow for a period of 10 minutes and the increase in mass determined. Details of the experimental procedure are given elsewhere (8).

The crystal growth velocity was calculated assuming that the crystals were cubic. In Figure 4 are shown the results for the growth velocity of $Na_2SO_4 \cdot 10H_2O$ as a function of R.P.M. for an undercooling of 1.75°C. The three values at a particular rotation speed are obtained in a single run and thus the undercooling should be exactly the same for each. The scatter of a set of three points presumably represents errors in mass determinations and irregularities in growth due to differences in the seed crystals. Note that at low velocities where mass transfer through the fluid controls, there is less scatter. After determining that the growth velocity of $Na_2SO_4 \cdot 10H_2O$, $Na_2HPO_4 \cdot 12H_2O$ and $Na_2HPO_4 \cdot 7H_2O$ was essentially free of mass transfer effects above 240 R.P.M., the growth velocity for all three solids was determined as a function of undercooling. The results are shown in Figure 5. Extrapolations of the growth velocity versus temperature to a zero velocity produced the equilibrium temperatures in Figure 5. These values are in excellent agreement with values from the literature (9).

The investigation of heat transfer in the direct contact system is presently in the preliminary stages. A pilot scale apparatus, similar to the schematic of Figure 1, has been constructed. It has a storage vessel volume of 11 liters, and is fully instrumented to allow calculation of interphase heat transfer coefficients. Initial testing of the system has been conducted using water as the storage medium. Heat transfer coefficient data compare well with similar data from the literature. Study of the heat transfer coefficient in the aqueous salt system is currently beginning.

FUTURE ACTIVITIES

Studies will be continued in all areas described above, with emphasis on the search for an acceptable heat transfer fluid and on identification of the interphase heat transfer coefficients. In the latter regard, the effects of system geometry and fluid flow rates on system performance will receive particular attention. The accumulated information of the preliminary studies will then be applied in conducting a pilot scale study of the direct contact-heat of fusion system cycling over extended periods of time. Important points to be addressed will include performance degradation due to gradual segregation of the phases, salt carryover into other portions of the loop, and development of operational techniques for various applications.

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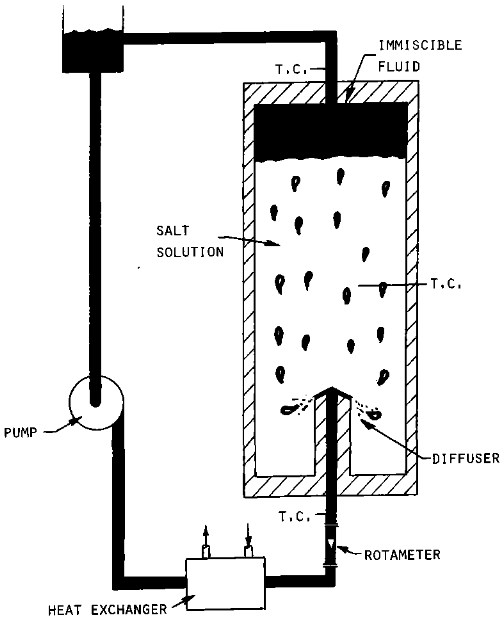

FIGURE 1. IMMISCIBLE FLUID-HEAT OF FUSION STORAGE SYSTEM

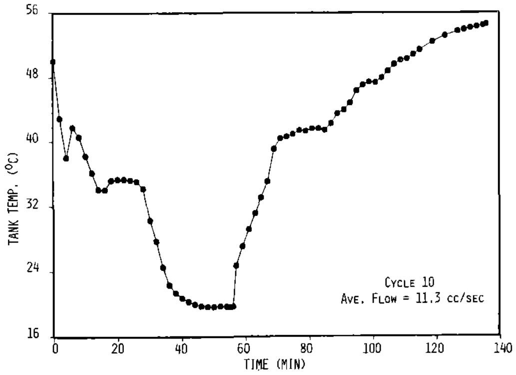

FIGURE 2. TEMPERATURE VERSUS TIME FOR Na_2HPO_4 - VARSOL SYSTEM

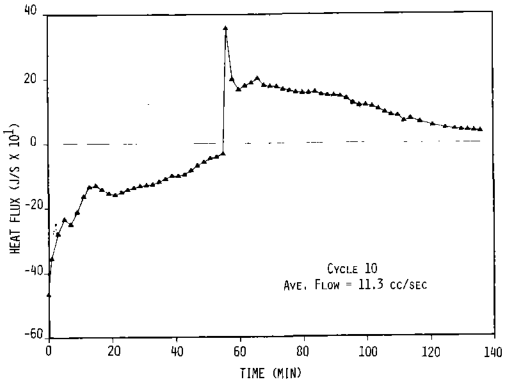

FIGURE 3. HEAT FLUX VS. TIME FOR Na_2HPO_4 - VARSOL SYSTEM

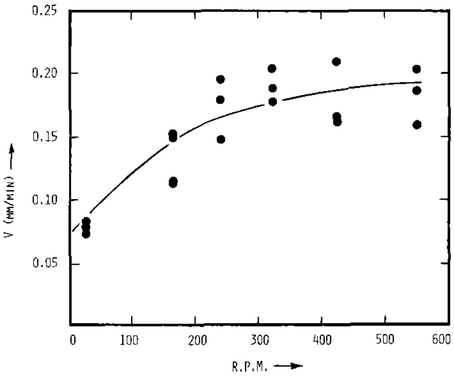

FIGURE 4. GROWTH RATE OF $Na_2SO_4 \cdot 10H_2O$ VERSUS RPM OF CRYSTAL SEED HOLDER

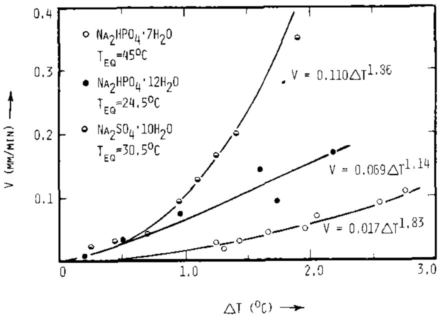

FIGURE 5. CRYSTAL GROWTH VELOCITY VERSUS UNDERCOOLING

PROJECT SUMMARY

ORGANIZATION: Atmospheric Sciences Center, Desert Research Institute

ADDRESS: Reno, NV 89507

PROJECT TITLE: "Studies of a Salt Hydrate Heat Storage System"

PRINCIPAL INVESTIGATOR: John Hallett TELEPHONE NO.: (702) 972-1676

CONTRACT NO.: AER 75-19601 CONTRACT PERIOD: 1 JUL 1975-
1 DEC 1977

CONTRACT AMOUNT: ERDA - $176,000
OTHER

PROJECT GOALS:

To develop a system for utilizing heat of fusion of salt hydrates for energy storage ∿ 10^6 B.T.U. in ∿ 100 ft^3 space to give almost constant heat flux during the crystallization cycle. The system concept to be developed involves a continuous crystallization process, whereby crystals are continuously generated in a supersaturated solution, grow and sediment, giving an essentially unchanged heat transfer geometry during the crystallization cycle. Physical criteria for crystal growth and secondary crystal production are developed and applied to the design and operation of a pilot system capable of one and two component operation. Materials examined are $Na_2SO_4 \cdot 10H_2O$, $CH_3COONa \cdot 3H_2O$ and $Na_2S_2O_3 \cdot 5H_2O$.

PROJECT STATUS:

Approaching completion.

I. Purpose

Thermal storage systems which utilize latent heats in general possess the attribute that the heat tends to be released at a fixed temperature, which is particularly desirable from the engineering point of view. Phase transformations of salt hydrates have the added advantages that the heat stored per unit volume is reasonably large, through the hydrogen bonding of the water in the salt, and that the phase transition temperatures are appropriate for numerous solar energy applications.

The study undertaken at the Desert Research Institute has been designed to investigate the feasibility of developing a practical means for utilizing the significant latent heat of fusion of salt hydrates, aiming to lessen problems which had arisen in several earlier systems. The specific purpose of the current project has been to devise a concept that would enable energy to be withdrawn from or put into the storage system at constant flux, to identify and investigate the parameters pertinent to that concept, and implement the findings in a workable pilot system.

II. Background Information

Energy storage by melting and crystallization of Glauber's salt was investigated over 20 years ago by Telkes. This material has a melting temperature of 32.5 ^{o}C and a latent heat about one half that of the water-ice transition, a volume $\sim$ 100 ft^3 providing sufficient storage volume for a small residence. The material is non-toxic and inexpensive. Two problems arose in the initial system. First, the solution tended to substantially supersaturate; when crystallization did occur, it was often rapid throughout the volume. Secondly, after a series of melt-crystallization cycles, the dense anhydride which formed on melting separated at the base of the tank and was overlain by less dense solution. This failed to mix satisfactorily with successive cycles and the effective thermal capacity fell. Improvements to this system were to add a nucleating agent to initiate nucleation at modest supersaturation and a thickening agent to prevent anhydride sedimentation. The problem of falling heat flux with time, as the solution crystallized from the surface inwards, was partly solved by using a number of small units. Heat transfer was achieved at the surface of the container or by pipes within the system.

An alternative process of heat transfer was described by Edie (1976, TES Conference), whereby a second fluid, immiscible in the solution, was bubbled through from the base. This served to transfer heat more efficiently, and also, in the absence of surfaces, to enable crystals to grow more effectively in the fluid bulk. Despite certain technical problems, this concept of a fluid heat exchanger has considerable merit and has been investigated further in the project described here.

III. Project Description

As a means of achieving the goal of constant heat flux in a practical energy storage system, a concept utilizing the fallout of "spent" crystals has been developed. In such a system very small secondary crystals are generated by agitation and allowed to grow in response to the thermal needs of the heat exchanger (which may be either of the standard finned type near the top of the storage tank or of the immiscible fluid type bubbling through the entire depth). Once large enough to have a significant fall speed, the matured crystals sediment to the bottom of the tank where they are in effect removed from the subsequent operation of the system. In this way the heat transfer characteristics of the system is largely unaffected by the depletion of stored energy and the system as a whole can achieve the ideal of a "flat" response over the range of storage capacity.

To implement such concepts optimally in any real system it is imperative that certain microphysical characteristics of crystallization be investigated and thoroughly understood. These include nucleation, the crystal growth velocity and habit as functions of supersaturation, along with the crystal fall speed and its dependence on crystal size and habit. An understanding of the microphysical mechanisms by which secondary crystals are produced from parent crystals is certainly appropriate, but so far it has been possible only to outline the macroscopic conditions under which such breeding takes place. As an integral part of this energy storage project, each of the microphysical parameters has been investigated in context with each of three salt hydrates, $Na_2SO_4 \cdot 10H_2O$, $Na_2S_2O_3 \cdot 5H_2O$ and $CH_3COONa \cdot 3H_2O$, chosen for the appropriateness of their respective transition temperatures of 32.5, 48, and 58 °C to solar systems utilizing flat-plate collectors.

Nucleation characteristics of each salt hydrate were studied by thermally cycling test tube samples (10 ml of solution saturated at the transition temperature) from above the transition temperature to some 40 °C below, the nucleation temperature being taken as that temperature at which a sudden warming of the embedded thermocouple junction occurred. Saturated borax was also added to some of the samples of $Na_2SO_4 \cdot 10H_2O$, as were bits of Teflon, to test their effects on the nucleation temperature.

Crystallization velocities, crystal habit and fall speeds, as well as the conditions for secondary crystal production were all investigated in various temperature-controlled baths. In particular, measurements of the fall speeds of individual crystals and studies of their ability to breed new crystals were made photographically in a Schlieren set up such that the natural convection currents, initiated by the density and temperature differences associated with the growth of the falling crystals, were revealed.

To test the composite of ideas in a workable system a two-liter tank of each of the three salt hydrates was constructed around both the solid heat exchanger and the immiscible fluid heat exchanger concepts. In the first case, cooled fluid was circulated through a finned heat exchanger coated with Teflon to inhibit nucleation and growth on the solid surfaces. In the second case, kerosene was used directly as heat exchange fluid and circulated through an external bath and then allowed to bubble into the bottom of the denser salt solution. When the in-coming kerosene was relatively cool, supersaturations were developed locally within the solution volume which caused both primary crystallization and secondary nucleation to proceed in steady fashion. Circulation patterns and nucleation effectiveness were observed visually through the transparent walls of the tank, while kerosene flow rates and inlet and outlet temperatures were monitored continuously.

IV. Results

(a) Nucleation and Supercooling

It was found that for all three hydrates, substantial supercooling could be reproducibly achieved in small samples (10 cm^3). It was obviously necessary to carry the melting process to completion, so that all traces of previous crystal were removed. Deliberate contamination by borax enabled nucleation of Glauber's salt to be obtained reproducibly at 24 ± 1 °C; no satisfactory nucleant was found for the other two salts. At extreme supercoolings, Glauber's salt would supersaturate to $\sim$ -10 °C, when nucleation of ice and hydrate would occur separately. Both sodium acetate and hypo could be cooled to very low temperatures without crystallization, forming a high viscosity glass. Larger systems (∿ one liter) could be supercooled somewhat, but could not be systematically supercooled after nucleation had once taken place. Evidently there was some retention of crystals or impurities in physical defects in the container or heat exchanger surface which could not be removed by meltdown. This finding led to the abandonment of the concept that a one component supersaturated system could be utilized for a controlled continuous crystallization system since crystallization would eventually occur somewhere in the system and prevent further operation.

(b) Crystallization Velocity and Habit

Crystallization velocity, measured from ciné film, increased approximately as ΔT^2 ($\Delta T \equiv$ supercooling ∿ 10 to 20 °C), the velocity at $\Delta T = 10$ °C being 0.6 cm s^{-1} (Glauber's salt), 0.005 cm s^{-1} (Na-thiosulfate), and 0.1 cm s^{-1} (Na-acetate). The latter two hydrates formed a glass on cooling to low temperatures. The crystallization velocity of sodium acetate was constant over a significant range of supercooling (Fig. 1) and fell to low values at temperatures below ∿ -60 °C. The habit of the crystals was strongly dependent on supercooling, with a tendency for finer crystals at larger values.

(c) Secondary Crystal Production and Convection

Crystals falling at terminal velocity in a supersaturated solution grow at a higher rate than when stationary. More important, with supercooling greater than ∿ 6 °C, copious secondary crystals are produced in the path of the falling crystal (Fig. 2). At large supercooling the crystallization velocity for Glauber's salt is large and the solution rapidly becomes slush. This event is significantly influenced by solution flow and stirring, processes which rapidly distribute secondary crystals throughout the fluid. Natural convection around growing crystals influences this process and could be made visible in a Schlieren optical system (Fig. 3).

(d) Pilot System

Fig. 4 shows heat flux measurements from a run in the 2-liter pilot system. Under optimum operating conditions, crystals grew and fell out as the heat was removed by the circulating kerosene, with new secondary crystals being generated at a rate that just balanced the removal rate, such rates being dependent on the flow characteristics.

Technical Problems

(a) Too high a flow rate and hydrodynamic instability at the immiscible fluid interface lead to incorporation of supersaturated solution droplets in the kerosene. As these drops circulated, they accreted on protrusions in the external system and eventually froze solid, blocking the flow. The flow rate was kept below a critical value to prevent this problem.

(b) Too high a supercooling of solution could give rise to an excess of small crystals in the system which failed to sediment; the effective viscosity increased and a higher circulation pressure differential was required. This problem could be solved by ensuring that local supercoolings were not excessive; when the inlet fluid was cold the initial flow rate was reduced.

(c) The anhydride sedimentation could occur in all systems, but could be reduced by utilizing the circulating kerosene to stir the system. This was least successful for Glauber's salt where the anhydride density is much higher than in the other cases.

In summary, a pilot system has been devised and constructed which can be used to store heat by the melting of salt hydrate crystals in contact with warm kerosene and made to give up the heat continuously to relatively cold kerosene as the crystals are subsequently reformed.

Parameters to be controlled for optimum performance are flow rate and maximum local supercooling. The system could be operated until > 0.9 of the solution had crystallized. In an appropriately designed pilot system the crystal numbers adjust themselves to the supercooling, higher supercooling leading to the production of more crystals. Too large a supercooling, on the other hand, gives an excess of crystals which fail to sediment in a realistic time.

V. Future Activities

Fundamental studies are still required on the effect of fluid flow on crystal growth habit, on the crystallization velocity and, most important, the production of secondary crystals. The detail of the flow, the level of turbulence, and its influence on the crystallization are important in determining the behavior of the system. Optimizing flow rate, local supercooling and turbulence level is required for a thermally efficient system which utilizes a large fraction of the salt and does not permit sedimentation of the anhydride.

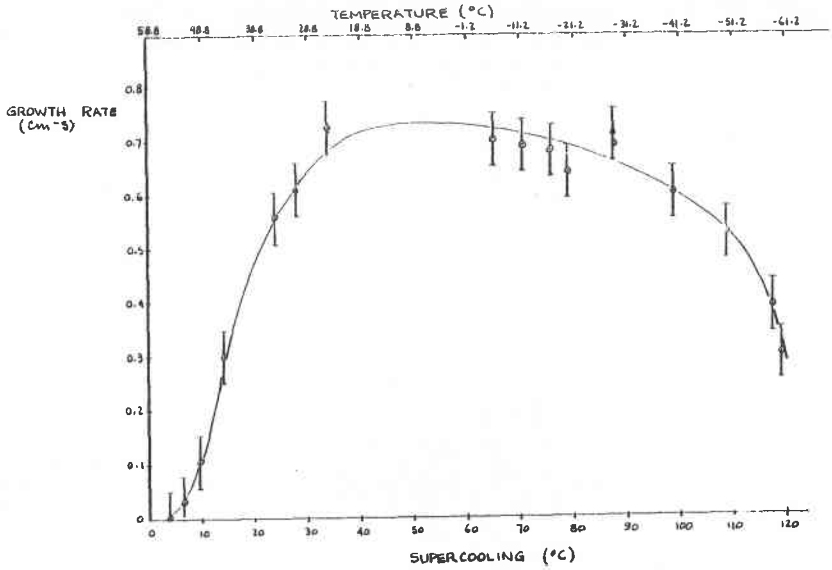

Fig. 1. Crystallization velocity of Na-acetate$\cdot 3H_2O$ as a function of supercooling.

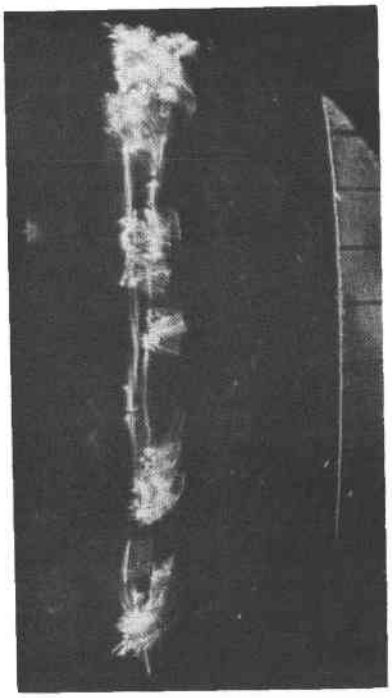

Fig. 2. Secondary crystal production in stationary sodium sulfate.

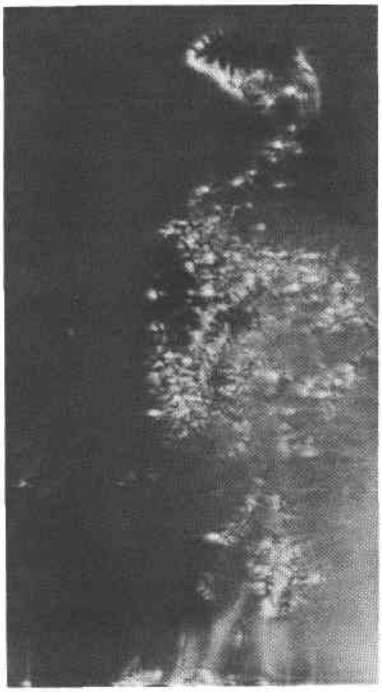

Fig. 3. Natural convection around a falling crystal revealed by examination in a Schlieren optical system.

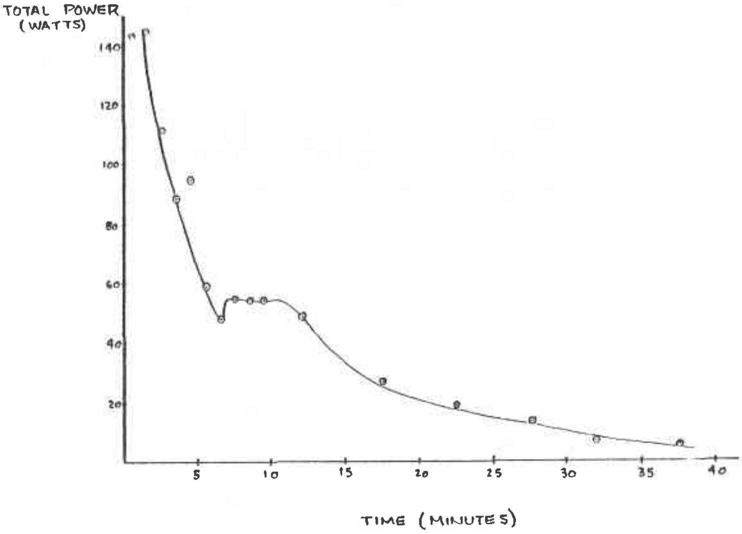

Fig. 4. Power output from the two-liter Na-acetate$\cdot 3H_2O$ pilot system.

PROJECT SUMMARY

THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

MACRO-ENCAPSULATION OF HEAT STORAGE PHASE-CHANGE MATERIALS

PRINCIPAL INVESTIGATOR: George A. Lane

TELEPHONE NO.: (517)636-0292

CONTRACT NO.: E(40-1)-5217

CONTRACT PERIOD: 9-29-76 to 3-29-78

CONTRACT AMOUNT: ERDA $175,000

PREPARED FOR PRESENTATION AT THE: Annual TES Contractors' Information Exchange Meeting, September 29 & 30, 1977, Gatlinburg, Tennessee

The general objectives of our program are: 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.

The project involves three tasks:

Task 1 - Materials selection, including a limited literature search, selection of candidate phase change materials, and selection and characterization of encapsulating materials.

Task 2 - Procurement of phase-change and encapsulating materials, encapsulation studies, and testing of the encapsulated material.

Task 3 - Preliminary design and economic evaluation of a residence-sized heat storage sub-system.

I. SELECTION OF PHASE CHANGE MATERIALS

No single phase change heat storage material will satisfy the requirements of all residential solar systems. Substances with various different melting points are needed, for example, for hydronic heating, hot faucet water, forced air heating, heat pump systems, or absorption air conditioning. We have selected for this program five different storage media with melting points ranging from 27° to 89°C., which should satisfy the requirements of the heating systems.

A. Hydronic Heating, 70-90°C.

Current practice is to circulate water at 60-80°C. through baseboard heaters. Storage at 70-90°C. is needed to allow an adequate heat transfer rate from the storage media to the working fluid. Systems could be designed to operate at considerably lower temperatures, but much larger room heaters would be required, increasing system cost.

The suitable materials identified under Contract NSF-C906 for this application were subjected to further tests, and using criteria of heat of fusion, freezing behavior, and cost, the selection was narrowed to the substances shown in Table I.

TABLE I

MOST PROMISING MATERIALS FOR HYDRONIC HEATING APPLICATION

Material	m.p., °C	ΔH, cal./g	Cost, ¢/lb.
$Mg(NO_3)_2 \cdot 6H_2O$	89	38	15
Naphthalene	80	35	10
Urea + NH_4Br	79	36	30
$Ba(OH)_2 \cdot 8H_2O$	76	64	30

1. Barium Hydroxide Octahydrate ($Ba\{OH\}_2 \cdot 8H_2O$) - This material has a very high heat of fusion, a high density (2.2 g./cc.), good freezing behavior, and no supercooling. Its disadvantages are that barium compounds are more expensive than more common salts, barium hydroxide is toxic upon ingestion, and that $Ba(OH)_2 \cdot 8H_2O$ reacts with atmospheric carbon dioxide to form barium carbonate, which is unsuitable for heat storage.

2. Urea-Ammonium Bromide Eutectic (Urea + NH_4Br) - This material exhibits excellent freezing behavior with no supercooling, and good density (about 1.8 g./cc.). The fire retardant properties of the bromide are a favorable factor. However, bromides are more expensive than the more common salts.

3. Naphthalene - This is an inexpensive, widely available organic compound. It has excellent freezing behavior with no supercooling. The "moth ball" smell would be objectionable if it escaped into a residence. A major disadvantage is its open cup flash point, 88°C., only a few degrees above the melting point. This could represent a fire hazard.

4. Magnesium Nitrate Hexahydrate ($Mg\{NO_3\}_2 \cdot 6H_2O$) - This compound exhibits good freezing behavior, except that it supercools as much as 15°C. Recent Dow-funded research has discovered several practical nucleating agents which will eliminate this problem. Safety tests so far have shown no fire or deflagration hazard, even when mixed with fuels such as grease, glycol, cellulose, cardboard, or iron powder.

This material seems the best candidate for this application, so it has been chosen for encapsulation studies.

B. Water Heating, 60-70°C.

Since water below about 55°C. will not remove grease in a dishwasher, 60°C. is the lower feasible limit for heat storage for this application. The storage materials discussed in the previous section could also be used. However, it is usually desirable to store heat near the lowest practical temperature for an application -- to minimize heat loss, and to maximize solar collector efficiency.

On the basis of laboratory tests of freezing behavior, heat of fusion, and cost, the suitable materials identified under Contract NSF-C906 were reduced to the three materials listed in Table II.

TABLE II

MOST PROMISING MATERIALS FOR
WATER HEATING APPLICATION

Material	m.p., °C	ΔH, cal./g.	Cost, ¢/lb.
Naphthalene + Benzoic Acid	67	29	15
Paraffin Wax	64	42	10
Stearic Acid + Palmitic Acid	60	48	25

1. Paraffin Wax - Many different inexpensive paraffin waxes with different melting points can be obtained. These are under study by several groups at present. These materials typically melt over a temperature range of 5-10°C., rather than isothermally. These waxes have a lower density than most other heat storage candidates.

2. Stearic Acid + Palmitic Acid - The fatty acids can be obtained in a variety of mixtures with different melting points. They have excellent freezing properties and no supercooling. The cost is higher than for other candidate materials. We elected to pursue encapsulation studies with the stearic acid mixture melting at 60°C.

3. Naphthalene + Benzoic Acid Eutectic - This organic substance has good freezing behavior, except for supercooling of about 2°C. The flash point (open cup) was determined to be 95°C., providing a margin of safety of 28°C. above the melting point. The "moth ball" odor would be objectionable, but would be a ready indicator of a leaking capsule. Encapsulation studies will be started on this material.

C. Air Heating, 40-60°C.

Most forced-air heating systems are designed to discharge air above 30°C. To provide a heat exchange gradient, the storage temperature must be about 40°C., or more. The list of potentially suitable materials discovered under Contract NSF-C906 was narrowed to the candidates shown in Table III through laboratory freezing tests, and consideration of heat of fusion, cost, stability, and hazard.

TABLE III

MOST PROMISING MATERIALS FOR
AIR HEATING APPLICATION

Material	m.p.,°C.	ΔH, cal./g.	Cost, ¢/lb.
p Dichlorobenzene	53	30	25
$Mg(NO_3)_2 \cdot 6H_2O + NH_4NO_3$	52	30	10
EPAL 1618 Alcohol	47	40 (est)	30
Pinacol $\cdot 6H_2O$	45	70	--
Urea + NH_4NO_3	44	--	5

1. p Dichlorobenzene - This chlorinated organic compound has excellent freezing behavior, no supercooling, and fair density (1.5 g./cc.); however, the cost is higher than desired.

2. Urea-Ammonium Nitrate Eutectic (Urea + NH_4NO_3) - This material is quite inexpensive and has acceptable freezing behavior. It was rejected because some NH_4NO_3 - urea mixtures are explosive. While there is no evidence that this eutectic is hazardous, we feel it best not to take the risk.

3. Pinacol Hexahydrate - This organic hydrate has a very good heat of fusion. It supercools excessively, however, and is not commercially available.

4. EPAL 1618 Alcohol - This mixture of primary, straight chain, aliphatic alcohols has good freezing behavior and is available commercially. The cost is somewhat high for this application.

5. Magnesium Nitrate Hexahydrate - Ammonium Nitrate Eutectic ($Mg(NO_3)_2 \cdot 6H_2O + NH_4NO_3$) - This substance is inexpensive and has good freezing behavior, except for supercooling a few degrees. Recent Dow-funded research has uncovered a few nucleating agents which minimize supercooling.

The oxidizing nature of nitrates might represent a safety problem. Initial tests have not uncovered a hazard, however.

This material was selected for encapsulation studies for the air heating application.

D. Heat Pump Applications, 20-40°C.

Phase change materials can be used to store low level solar energy as a source for a heat pump. The isothermal storage property is very beneficial to the COP (coefficient of performance) of the heat pump. The materials identified during Contract NSF-C906, through consideration of freezing behavior, cost hazards, commercial availability, and heat of fusion, were reduced to those shown in Table IV.

TABLE IV

MOST PROMISING MATERIALS FOR
HEAT PUMP APPLICATION

Material	m.p., °C	ΔH, cal./g.	Cost, ¢/lb.
$Na_2HPO_4 \cdot 12H_2O$	35	67	20
Methylnaphthalene	24	35(est.)	--
$CaCl_2 \cdot 6H_2O$	27	46	5

1. Disodium Phosphate Dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) - This inorganic hydrate salt has a very high heat of fusion. Potentially, the cost could be much lower than at present. Its principal drawback is the freezing behavior. In addition to severe supercooling, there are a multiplicity of hydrates and phases. Several researchers have attacked this problem, with no adequate solution.

2. Methylnaphthalene - This organic compound has excellent freezing behavior. It is not available in bulk, but should be plentiful as new naphtha-cracking plants are built.

3. Calcium Chloride Hexahydrate ($CaCl_2 \cdot 6H_2O$) - This material has good freezing behavior if nucleators, discovered under Contract NSF-C906 and recent Dow-funded work, are used. This substance is inexpensive and readily available commercially. It was chosen for encapsulation work.

E. Absorption Air Conditioning

No storage materials were selected for this application, since it is believed the development of solar units is further in the future than solar heating systems.

F. Properties of Phase Change Materials

The PCM's under study are listed in Table V.

TABLE V

PHASE CHANGE MATERIALS
SELECTED FOR STUDY

Materials	m.p., °C	ΔH, cal./g	Cost, ¢/lb.
$Mg(NO_3)_2 \cdot 6H_2O$	89	38	15(est.)
Naphthalene + Benzoic Acid	67	29	15
Stearic Acid Mix	60	48	25
$Mg(NO_3)_2 \cdot 6H_2O + NH_4NO_3$	52	30	10
$CaCl_2 \cdot 6H_2O$	27	46	5

The heat capacities of both liquid and solid PCM's were measured. Data are shown in Figure 1. The thermal conductivities of the crystalline PCM's were also determined, as displayed in Figure 2. For comparison, the thermal conductivity of crystalline $CaCl_2 \cdot 6H_2O$ was previously found to be 26.0×10^{-4} cal. cm.$^{-1}$ sec.$^{-1}$ °C^{-1}.

II. CONTAINER SELECTION

The containers considered in this program have been restricted to materials, shapes, and sizes which are commercially available from manufacturers' stock or based on standard tooling and stock materials.

Although the prototype thermal storage unit to be constructed in Phase II of this project will not be full-size, the container sizes, internal geometry, flow rates and heat transfer rates will be as close to those of a practical, commercial unit as possible. The container and heat exchanger parameters have been chosen on the basis of computer studies, based on a simple mathematical model of a thermal energy storage unit suitable for a small commercial building or a medium-sized residence.

A. Container Sizes and Shapes

Three basic container shapes are being considered: cylinders, tetrahedra, and pillows. Cylindrical containers include metal cans, glass and plastic bottles, and chub-type flexible film packages. Tetrahedra and pillows must be fabricated from plastic film.

The sizes and shapes for each container candidate were based on trade-offs between calculated heat transfer effectiveness, the magnitude of pressure drops in air heat transfer systems, costs, and the volumetric efficiency of the total heat transfer unit. In general, the container costs, pumping losses, and floor space associated with a specific mass of heat of fusion (HOF) material are improved as container size increases but the heat transfer rates and efficiency are degraded.

1. Model Heat Exchangers - The trade-offs used to specify containers were based on a simple computer simulation of a hypothetical heat of fusion thermal energy storage heat exchanger. Three types of exchanger were designed and modeled. They included conventional hot air and hot water systems, and a heat pump system. The hot air and hot water systems passed air or water over encapsulated HOF materials, heated the fluid, then pumped the fluid directly to the load space. The heat pump was assumed to pass HOF-warmed air past the evaporator coils and load space air past the condenser coils. Table VI lists the flows, pressure drop, and cut-off temperatures used in the models.

TABLE VI

DESIGN PARAMETERS OF
MODEL HEAT EXCHANGERS

	Hot Air	Hot Water	Heat Pump
Flow	1200 CFM	7.5 GPM	1200 CFM
Pressure Drop	1" H_2O	--	1" H_2O
Discharge Temperature at Termination	95°F	150°F	35°F
Load Air Temperature	65°F	65°F	65°F
Minimum Permissible Output BTU/HR	38,880	30,000	30,000

Container	Container Dimensions Inches
Cylinder	
Tall No. 3 Can	4.25 x 7
No. 300 Can	3 x 4.4375
16 oz. Plastic Bottle	2.5 x 7
Pillow	8 x 5.5 x 1.25
Tetrahedron	4 x 4

Two capacities were simulated. A one day storage system was assigned a capacity of 300,000 Btu of latent heat, a three day system required 900,000 Btu. These values correspond with approximately 60% of the heating system demand in a 1500 square foot (medium sized) northern home during the coldest months and 100% of the demand at the beginning and end of the heating season.

The dimensions and capacities of standard sized commercial containers were used to design model heat exchangers for each HOF material and package type. A representative design is illustrated in Figure 3.

The effects of sizes, shapes, and spacing of the containers on the heat transfer rates, pressure drops, and theoretical efficiencies of the exchanger were calculated.

2. Computer Model - A simple computer model was used to simulate performance. The model attacked the extreme nonsteady state behavior of an HOF storage unit by following slugs of heat transfer fluid through the heat exchanger and assuming that groups of HOF material-filled containers experienced steady state heat transfer as the slugs flowed past. Temperatures, heat transfer coefficients and frozen-molten HOF material ratio were recalculated as each slug passed each group of containers in order to approximate the time dependent, location dependent heat transfer behavior of an actual HOF heat storage device.

The model follows an 18 to 27 second slug of heat transfer fluid through the heat exchanger. The exchanger is mathematically divided into 12 to 15 sections. Heat transfer rates, and temperatures are calculated for each section on the assumption that each container in the section behaves identically, and each is momentarily experiencing steady state heat transfer. Coefficients are determined from classical steady state equations based on the assumption that the frozen or molten core retains the original shape of the container. Heat transfer fluid flows continuously. The discharge mode is assumed to be controlling.

3. Computer Results - Simulation of model heat exchanger behavior indicates that the concept of encapsulating HOF materials in commercial containers is viable. Although restricted by the assumptions of the model, the calculations predict that:

1. Heat transfer rates are acceptable. Most designs could deliver considerably more than the 20,000 to 30,000 Btu/hr estimated residence load. Delivery curves tended to be flat until near exhaustion.

2. Efficiencies appear acceptable. Convenient designs delivered approximately 90% of the stored heat before output temperatures fell below the 95°F ASHRAE guide.

3. Standard commercial containers, with minor axis less than 2.5-3.0 inches and capacities of 7 to 90 in^3 per container were acceptable.

4. It was possible to manipulate designs so that pressure drops in air systems were limited to 1 inch of water or less. Blowers of 1 HP or less would be required. Although larger than those of most home heating systems, the size would be reasonable.

5. Macroencapsulated HOF heat exchangers display behavior similar to stratification in sensible heat systems. Containers near the entrance deplete rapidly. Containers near the exhaust retain capacity. Therefore, large capacity units are more efficient than small units.

6. As expected, container material has little effect on heat transfer. Film coefficients and crystal conductivities dominate heat transfer coefficients.

Table VII lists the HOF materials, container sizes, and calculated fractions of latent heat discharged.

TABLE VII

PREDICTED EFFICIENCIES OF MODEL SYSTEMS

MATERIAL	MELTING TEMPERATURE °F	EXCHANGER CAPACITY 10^5 Btu	CONTAINER	PERCENT DISCHARGED
$Mg(NO_3)_2 \cdot 6H_2O$	192	3	Cylinder 2.5 in. dia.	87[1]
Napthalene-Benzoic Acid Eutectic	152	3	Cylinder 3 in. dia.	95
			Pillow 8 X 5.5 x 1.25 in.	95
Stearic Acid - Palmitic Acid	146	8.4	Cylinder 4.25 in. dia.	96
		3	Cylinder 4.25 in. dia.	87
		3	Cylinder 3 in. dia.	93
		3	Tetrahedron 4 X 4 in.	95
		3	Tetrahedron 4 X 4 in.	93[2]
$Mg(NO_3)_2 \cdot 6H_2O$ - NH_4NO_3 Eutectic	125	3	Cylinder 3 in. dia.	75
		3	Cylinder 2.5 in. dia.	85
		3	Tetrahedron 4 x 4 in.	91
		3	Pillow 8 X 5.5 X 12.5 in.	82
$CaCl_2 \cdot 6H_2O$	80	3	Cylinder 2.5 in. dia.	97[3]

[1] Water as heat transfer fluid

[2] Air film heat transfer coefficient arbitrarily reduced 45%

[3] Exhaust air at 35°F, heat pump output 3000 Btu/hr.

a. Cylinders - The dimensions of "Tall No. 3" sanitary cans, "No. 300" sanitary cans, and a standard 16 oz. plastic bottle were used to model units based on cylinders. The curves are applicable to chub-type film packages since the diameter and length of film packages are essentially unrestricted.

Output curves for representative air systems are presented in Figures 4 through 8. Figure 4 illustrates the behavior of a "Tall No. 3" can storing 840,000 Btu at the 147°F (64°C) fusion temperature characteristic of a stearic acid-palmitic acid mixture. Over 95% of the stored heat was discharged before the output temperature fell to 95°F. The degree of stratification is illustrated in Figure 5.

The 300,00 Btu unit required smaller cans to improve heat transfer. Figure 6 illustrates the behavior of two 300,000 Btu, 147°F (64°C) units containing "Tall No. 3" and "No. 300" cans. "No. 300" cans appear adequate for service in this temperature range.

When the pronounced effect of capacity on output curves illustrated by Figures 4 and 6 was observed, designs were restricted to 300,000 Btu units as a worst case.

As expected the temperature of fusion has a pronounced effect on the behavior of HOF storage systems. A different sized container may be desirable for each temperature range. As Figure 7 illustrates, the 153°F (67°C) Naphthalene-Benzoic Acid eutectic performs well in 3" diameter cans. The lower temperature Magnesium Nitrate Hexahydrate-Ammonium Nitrate eutectic requires a smaller container, 2 inches in diameter, perhaps.

A 2.5 inch diameter container appears suitable for use in $CaCl_2 \cdot 6H_2O$ - heat pump systems. Figure 8 illustrates calculated discharge temperatures and Coefficients of Performance (COP) of such a system. The simulation was based on the performance curves of a Westinghouse Model HP030D heat pump. Heat of fusion warmed air was passed over the evaporator coils of the heat pump, then returned to the storage unit.

The simple model used to predict air system performance is not well suited to water systems. The assumption of steady discharge in an air system is feasible because of the negligible heat capacity of the stationary air held in a real exchanger experiencing intermittent demand.

The presence of a significant mass of water in an exchanger requires a model capable of predicting non-steady state heat transfer. When coupled with the time dependent, position dependent treatments needed for HOF exchangers, this computation is beyond the scope of this program.

The simple model was used to generate a curve for a Magnesium Nitrate Hexahydrate-water system. The performance curve is illustrated in Figure 9. The calculated 87% efficiency is acceptable, but the data are interpreted to indicate that the storage system can supply the load with greater efficiency.

The 300,000 Btu exchanger design corresponding to Figure 9 contains over 400 gallons of water in the 0.75 inch spaces between containers. The water could supply a 30,000 Btu/hr. load with a 9°F temperature swing. Conduction between the containers and the water during the stagnant portions of the discharge cycle of a real world installation probably would supply a significant fraction of the load demand. The 87% efficiency predicted by the constant discharge, forced convection model probably represents a minimum value.

b. Film Pillows - Simple flat pouches formed by heat sealing the ends of a cylindrical tube of packaging film would appear as pillows if laid flat on a support. Package costs and heat exchanger assembly costs would be among the lowest of any design.

Unfortunately, heat transfer in this configuration is believed poor. The pillows would approximate flat plates.

Heat tranfer rates between plates and air flowing parallel to the plates suffer from the formation of laminary boundary layers at the surfaces. Film coefficients are about half those of air flowing normal to surfaces or banks of tubes.

Film coefficients of 1.47 Btu/hr-ft^2-°F are reported for the flat pan system used in the University of Delaware "Solar One" house.[1] Heat transfer surfaces in a pillow-filled exchanger exhibit hills and valleys corresponding to the bulges at the centers of the pillows, improving heat transfer coefficients (h).

Figure 10 illustrates the simulated discharge curves of two heat exchangers based on differing HOF candidates. Two film coefficients, 1.47 and 1.9 Btu/hr-ft^2-°F, were used in the model.

Heat exchangers containing higher temperature HOF materials are not affected by variations in film coefficients. The short heat transfer path in a pillow exchanger dominates efficiency. Both Napthalene-Benzoic Acid eutectic (152°F, 67°C) simulations produced efficiencies of 95%.

Pillow designs containing lower temperature HOF materials are sensitive to film coefficients. A design based on Magnesium Nitrate Hexahydrate-Ammonium Nitrate eutectic would exhibit an unsuitable 73% efficiency if the 1.47 coefficient prevailed. The higher 1.9 coefficient would increase efficiencies to 82%, a marginally acceptable value.

c. Film Tetrahedra - If the two ends of a short tube of flexible packaging material are heat sealed so that the axes of the seals are at right angles, the package approximates the shape of a tetrahedron. Commercial machinery capable of filling and sealing tetrahedra is available. Standard equipment can process tubes of up to 4 inch diameter and 7 inch length.[2] Tetrahedral geometry minimizes the amount of film needed to package a given volume.

The tetrahedral concept produces superior heat transfer. Figure 11 illustrates the simulated performance of exchangers based on differing fusion temperature HOF candidates. The geometry of the package is so conducive to heat transfer that efficiencies are not significantly reduced if the air film coefficients are arbitrarily reduced.

B. Container Materials

A variety of containers is being examined under this program. They include aluminum and steel cans, plastic bottles, and flexible plastic film packages.

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[1] Telkes, Maria "Thermal Energy Storage", IECEC '75 Record, p. 111-115.

[2] Personal Communication, R. Ohren, Hayessen Manufacturing Co., Des Plaines, Illinois

1. Films - Film packages potentially are the lowest cost packaging material for an encapsulated HOF heat exchanger. The selection of suitable films is an important goal of this project.

The major criteria used in selecting films are:

i) cost of the finished package
ii) permeability
iii) mechanical strength at elevated temperature
iv) chemical resistance
v) ease of reliable manufacture using state-of-the-art techniques

Fifteen commercial types of packaging film were considered as candidates for HOF storage devices. None is wholly suitable. Multi-layer laminations are needed to supply the necessary combination of strength, permeability, and inertness.

An economical and universally applicable film is the high density polyethylene/aluminum/polyester combination. It possesses maximum barrier properties, and is an item of commerce, useful in commercial markets other than HOF storage. The raw material costs are lower than those of other combinations. Long production run lamination economics apply.

Two commercial types of high density polyethylene/aluminum/polyester film have been identified. Reynolds Metals Company and Continental Can Company produce R-2 Retort Film. The film is a laminate of 3 mil polyethylene, 3.5 mil foil and .5 mil Dupont Mylar brand polyester. The product has been tested at Natick Laboratory for over 14 years. The film is designed for long term storage followed by boil-in-the-bag preparation of military rations. The film is used commercially overseas for the storage and cooking of foodstuffs. Physical property data are given in Table VIII.

TABLE VIII

PHYSICAL PROPERTIES OF R-2 FILM

PROPERTY	ROOM TEMPERATURE	160°F	TEST
Tensile Strength, psi			ASTM D882-67
Machine Direction	7320	4550	
Transverse Direction	6785	4575	
Elongation, %			ASTM D882-67
Machine Direction	85	120	
Transverse Direction	80	215	
Tensile Modulus, psi (2% Secant)			ASTM D882-67
Machine Direction	163500	114500	
Transverse Direction	151700	105400	
Water Vapor Transmission g. Loss/24 hr./100 sq. in./mil at 100°F, 90% RH		<0.01	

St. Regis Paper Company manufactures the Alure series of aluminized Mylar brand polyester film and polyethylene laminations. Grade CX contains 0.5 mil aluminized polyester laminated to 2 mil high density polyethylene. Although not as effective a barrier as the three part R-2 film, barrier properties are reputedly good.

The American Can Company produces Glaminate® film, a laminate of polyethylene, aluminum foil, paper,and polyethylene, for use in consumer containers such as toothpaste tubes. The major advantage of Glaminate film over Retort film is that the low density polyethylene on both sides allows a strong lap seam rather than a weak pouch seam. Tubes are presently made up to 1 15/16" diameter and 8" long.

2. Cans - Aluminum cans were originally proposed as the material of choice for metal containers. Consultation with can manufacturers[4] and packaging specialists[5] indicates that steel cans will be superior. When compared with steel cans, aluminum cans are:

i) more susceptible to internal corrosion
ii) weaker
iii) subject to size restrictions
iv) expected to be more expensive

Steel cans are expected to be suitable for calcium chloride hexahydrate and magnesium nitrate hexahydrate. Aerosol cans are stronger than regular steel cans, and manufactured to stricter tolerances. Standard aerosol sizes more nearly fit needs for the narrow, tall can desired for more efficient heat transfer. Therefore, aerosol cans were chosen for our study.

3. Bottles - Four types of plastic were considered as candidates for plastic bottles, high density polyethylene, high density polyethylene-saran laminates, polypropylene, and high barrier styrene-acrylonitrile. The high density polyethylene and high density polyethylene-saran laminates are considered the most promising.

Calculations based on the equilibrium vapor pressure of water over calcium chloride hexahydrate indicate that 2.4% of the contained water would be lost after 20 years storage in a standard 25 mil wall thickness, 16 ounce polyethylene or polyethylene-saran laminate bottle.

Carbon dioxide diffuses through a polyethylene bottle rapidly, and it could not protect a carbon dioxide absorbent HOF material such as barium hydroxide octahydrate. Saran-high density polyethylene laminate bottles exhibit carbon dioxide permeabilities reduced by a factor of 300 when compared to polyethylene. A 16 ounce, 25 mil wall thickness laminate bottle could allow about 7 grams of carbon dioxide to enter during a 20 year exposure.

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[4] Personal Communication, R. J. O'Brian, Aluminum Company of America, Pittsburg, Pennsylvania

[5] Personal Communication, G. Brockman, Continental Can Corporation, Chicago, Illinois

Aromatic hydrocarbons attack polyethylene at elevated temperatures. The rate through a standard 25 mil wall thickness bottle could approach 0.8 grams per day.

Surface sulfonation of high density polyethylene greatly reduces hydrocarbon permeance. Published data[7] state that sulfonation protects the resin from attack by gasoline and can reduce diffusion to 0.002 grams per day or 4% of the net contents of a 16 ounce bottle after 20 years.

C. Containers Costs

Costs for a variety of filled containers are presented in Tables IX and X. The costs are based on distributor prices and estimates of filling expense. Mark-ups and the cost of HOF materials are not included. The costs of a cubic foot of containment are rounded to the nearest $0.05. Values show for containment of 300,000 Btu latent heat are rounded to the nearest $5.

As expected, film container estimated costs are lower than those of other containers. The cost of packing a given amount of material increases as the container size decreases.

TABLE IX

FILM CONTAINER COSTS

Film Containers

Material	Polyester/Aluminum Foil/Polyethylene			
Container	Tube	Tube	Pillow	Tetrahedron
Dimensions, in.	48 X 4	24 X 2	8 X 5.5 X 1.25	4 X 4
Area, in.^{2}	600	164	124	28
Film Cost, $	0.265	0.065	0.05	0.011
Fill Cost, $	0.100	0.03	0.01	0.005
Mesh Bag(2), $	0.05	0.025	----	-----
Total, $	0.415	0.12	0.06	0.016
Volume-Ft^3	.347	.043	.033	0.0043
Cost/Ft^3, $	1.20	2.80	1.80	3.70
Cost for 300,000 Btu $CaCl_2 \cdot 6H_2O$, $	40(1)	95	60	125

(1) 4-inch diameter not suitable for 300,00 Btu unit
(2) Mesh bag used as exterior support for tube

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[7] Ziemba, G. P., Thomas, L. S., Parsons, C. P., Hollo, R. A., "Surface Sulfonation-A Practical Solution to Eliminating The Hydrocarbon Permeation Problem with HDPE Fuel Tanks". Society of Plastics Engineers National Technical Conference, "Plastics. . .Serving Man in Motion", Nov. 12-14, 1974, Detroit, Michigan.

TABLE X

BOTTLE AND CAN CONTAINER COSTS

BOTTLES

Material	Glass	Glass	Plastic	Plastic
Size - oz.	48	16	48	16
Capacity - in^3	87	29	87	30
Cost, $	.23	.10	.18	.08
Cost/Ft^3, $	4.60	6.00	3.60	4.60
Cost for 300,000 Btu				
$CaCl_2 \cdot 6H_2O$, $	155 (1)	205	120 (1)	160
Stearic Acid	320 (1)	390	230 (1)	300

CANS

Type	Sanitary	Sanitary	Aerosol
Style	No. 3 Tall	No. 300	202 X 708
Dimensions, in.	4.25 X 7	3 X 4.43	2.125 X 7.5
Capacity - in^3	83	25	22.5
Cost, $	.18	.07	.10
Cost/Ft^3, $	3.75	4.85	7.70
Cost for 300,000 Btu $CaCl_2 \cdot 6H_2O$	130 (1)	165	265

(1) 4 inch diameter not suitable for 300,000 Btu unit.

Although the data presented are tentative, a limited comparison with conventional systems indicates that containment costs are reasonable. At $0.75 a gallon the containment cost for a 300,000 Btu sensible heat water system with a 40°F swing would be about $675. The most expensive macroencapsulation estimate is considerably lower.

III. MATERIALS COMPATIBILITY

A. Film Evaluation

The compatibility of PCM's with laminated plastic films was tested by fabricating 3 1/4" x 5 3/4" pillows or 1 11/16" x 6 1/2" cylinders filled with the molten PCM's, and storing them at a temperature 5-15°C above the melting point of the PCM. As shown in Table XI, the lower-melting inorganic materials proved compatible, while the higher-melting materials tended to attack the heat sealed areas at the seams.

TABLE XI

EVALUATION OF PLASTIC FILMS WITH PCM'S

Materials	R-2 Retort Film	Glaminate® Film	Alure Film
$Mg(NO_3)_2 \cdot 6H_2O$, 100°C.	Seams Leak in 7 days	Embrittles	Seam Failed, 1-3 days
Naphthalene + Benzoic Acid, 90°C.	PCM migrates thru seam, 1 day	Film Delaminates	--
Stearic Acid mix, 75°C	Leaked out, 13 days	--	Seam rupture, 1 day
$Mg(NO_3)_2 \cdot 6H_2O + NH_4NO_3$, 70°C	OK, 32 days	OK, 28 days	OK, 32 days
$CaCl_2 \cdot 6H_2O$, 45°C	OK, 32 days	OK, 28 days	OK, 32 days

B. Plastic Bottle Evaluation

The compatibility of PCM's with high density polyethylene was studied by cutting 4" long "dog bone" test bars 1/8" wide in the test area. These specimens were formed from the sides of the plastic bottles and selected to be similar in thickness. Tensile strength was measured before exposure, after dry exposure to the test temperature, and after immersion 4 weeks at the test temperature in the liquid PCM. Test temperatures were the same as used for the plastic films. As outlined in Table XII, only the two lower-melting PCM's are compatible with the bottle material.

TABLE XII

EVALUATION OF PLASTIC BOTTLES WITH PCM'S

Materials	Storage Temp.,°C	Tensile Strength, Psi
None	20	2660
None	100	Failed: brittle
$Mg(NO_3)_2 \cdot 6H_2O$	100	3200; brittle
None	90	2860
Naphthalene + Benzoic Acid	90	2200; 8-13% wt. gain
None	75	2820
Stearic Acid Mix	75	2800; 5% wt. gain
None	70	2860
$Mg(NO_3)_2 \cdot 6H_2O + NH_4NO_3$	70	2940
$CaCl_2 \cdot 6H_2O$	45	2870

The two next higher-melting materials will not weaken the bottles, but dissolve into the plastic. No conclusion can be drawn about the highest-melting PCM, since the bottle itself fails at this temperature.

Sulfonated polyethlene bottles were tested, as the surface layer of sulfonated plastic resists chemical migration. Results are outlined in Table XIII.

TABLE XIII

EVALUATION OF SULFONATED
PLASTIC BOTTLES WITH PCM'S

Materials	Storage Temp., °C	Tensile Strength Psi	Wt. Change,%
None	20	2610	0.00
None	85	2720	-0.09
Naphthalene + Benzoic Acid	85	2750	+0.09
Stearic Acid Mix	85	2750	+0.09

The sulfonated bottles showed negligible uptake of naphthalene-benzoic acid eutectic or stearic acid mixture, in contrast to weight gains of 5-13% observed for the unsulfonated bottles. In spite of the low uptake of PCM, a few tiny crystals of naphthalene were found on the outside of the bottle in an area where sulfonation apparently was spotty. These bottles should be satisfactory for encapsulation of the two organic PCM's.

C. Steel Can Evaluation

To determine the compatibility of PCM's with metal cans, 1" x 3" coupons were cut from the sides of seamed and drawn aerosol cans. No surface treatment, other than washing with acetone, was used. The coupons were immersed in molten PCM's for 31 days and the corrosion rate determined by weight loss. Table XIV shows the results.

Either type of can is suitable for encapsulating calcium chloride hexahydrate, if air is excluded during filling. The corrosion rates for reagent grade magnesium nitrate hexahydrate and its eutectic with ammonium nitrate are higher, but should be acceptable for either type of can. The technical grade magnesium nitrate hexahydrate and the stearic acid mixture are marginal, and further tests should be run, if encapsulation in steel cans is to be recommended. The corrosion rate for the eutectic of naphthalene and benzoic acid is too high for this PCM to be used in steel cans. A corrosion rate of 15×10^{-6} lbs./ft.^{2}/day is equal to about 0.1 mil/yr., or 2 mils in 20 years. The seamed aerosol can is 10 mil thick, and the drawn can 7.5 to 8.5 mil thick. In actual use, corrosion will be non-uniform, and further tests with cans filled with molten PCM's should be run.

D. Material Selection

Table XV summarizes the present status of the materials compatibility work. For $CaCl_2 \cdot 6H_2O$ and the $Mg(NO_3)_2 \cdot 6H_2O$ - NH_4NO_3 eutectic, all the encapsulating materials appear usable. For naphthalene/benzoic acid and stearic acid, the sulfonated

TABLE XIV

EVALUATION OF STEEL CANS WITH PCM'S

Materials	Temp. °C	Corrosion Rate, lbs./ft.^{2}/day Seamed Cans	Drawn Cans
$Mg(NO_3)_2 \cdot 6H_2O + NH_4NO_3$	70	9.1×10^{-6}	6.6×10^{-6}
$CaCl_2 \cdot 6H_2O$	50	1.2	1.0
$CaCl_2 \cdot 6H_2O$*	50	1.1	0.8
$Mg(NO_3)_2 \cdot 6H_2O$	100	3.1	9.6
$Mg(NO_3)_2 \cdot 6H_2O$**	100	17.5	16.5
Stearic acid	75	21.3	14.3
Naphthalene/benzoic acid	90	123.	113.

*0.2% corrosion inhibitor added.

**Technical grade material.

TABLE XV

SUMMARY OF MATERIAL COMPATIBILITY WITH PCM'S

	PCM MATERIAL				
Encapsulant Material	$CaCl_2 \cdot 6H_2O$	$Mg(NO_3)_2 \cdot 6H_2O + NH_4NO_3$	Stearic Acid	Naphthalene + Benzoic Acid	$Mg(NO_3)_2 \cdot 6H_2O$
Polyethlene Bottle	OK	OK	Weight Gain	Weight Gain	Embrittles
Sulfonated Polyethylene Bottle	-	-	OK	OK	-
R-2 Retort Film	OK	OK	Seam Leaks	Seam Migration	Seam Leaks
Alure Film	OK	OK	Seam Rupture	-	Seam Leaks
Glaminate Film	OK	OK	-	NG	Embrittles
Drawn Steel Can	OK	OK	Marginal	NG	OK
Seamed Steel Can	OK	OK	Marginal	NG	OK

polyethylene bottle is the only fully satisfactory encapsulant. For magnesium nitrate hexahydrate, steel cans are the encapsulating material of choice.

On the basis of the compatibility data, we have made a tentative pairing of PCM's with encapsulant materials, as given in Table XVI. Calcium chloride hexahydrate in high density polyethylene bottles is the first encapsulated PCM evaluated in the heat storage test device. A choice will be made among the several

TABLE XVI

TENTATIVE SELECTION OF PCM-ENCAPSULANT PAIRS

Phase Change Materials	Encapsulating Medium
$CaCl_2 \cdot 6H_2O$	High Density Polyethylene Bottle
$Mg(NO_3)_2 \cdot 6H_2O/NH_4NO_3$ Eutectic	R-2 Retort Film
Stearic Acid	Sulfonated Polyethylene Bottle
Naphthalene/Benzoic Acid Eutectic	Sulfonated Polyethylene Bottle
$Mg(NO_3)_2 \cdot 6H_2O$	Drawn Steel Aerosol Can

films under study before the magnesium nitrate hexahydrate-ammonium nitrate eutectic is evaluated in the test device.

IV. HEAT STORAGE TEST DEVICE

A thermal energy storage (TES) test device (Figure 12) has been constructed, and tests have started on macro-encapsulated $CaCl_2 \cdot 6H_2O$. Shake-down runs were made using empty 16 oz. plastic bottles (see Figure 13), and a constant air flow rate and inlet temperature were achieved at both the high and low set points. A half-dozen melting-freezing cycles have been run with the apparatus, which is functioning very satisfactorily.

Figure 1

HEAT CAPACITY OF PCM'S

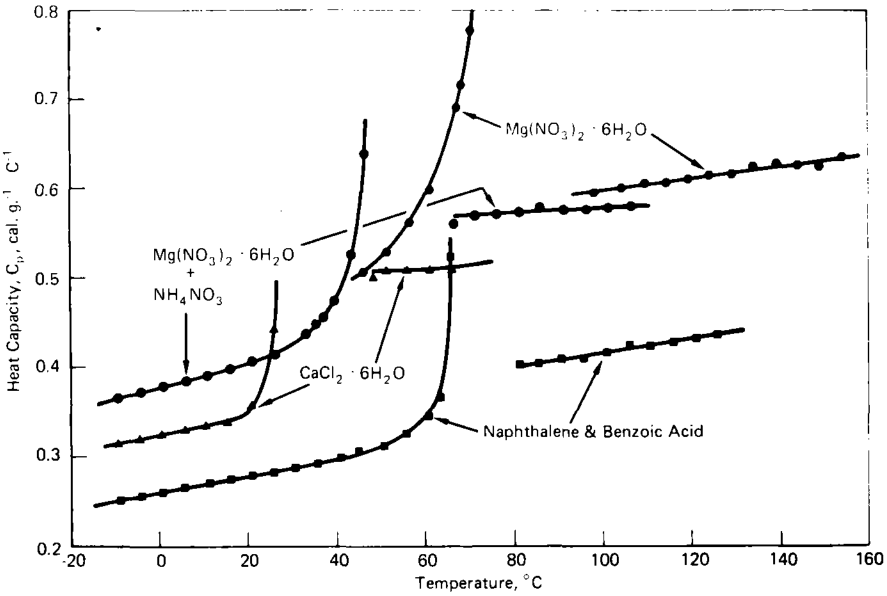


Figure 2

PCM Solid Phase Thermal Conductivity

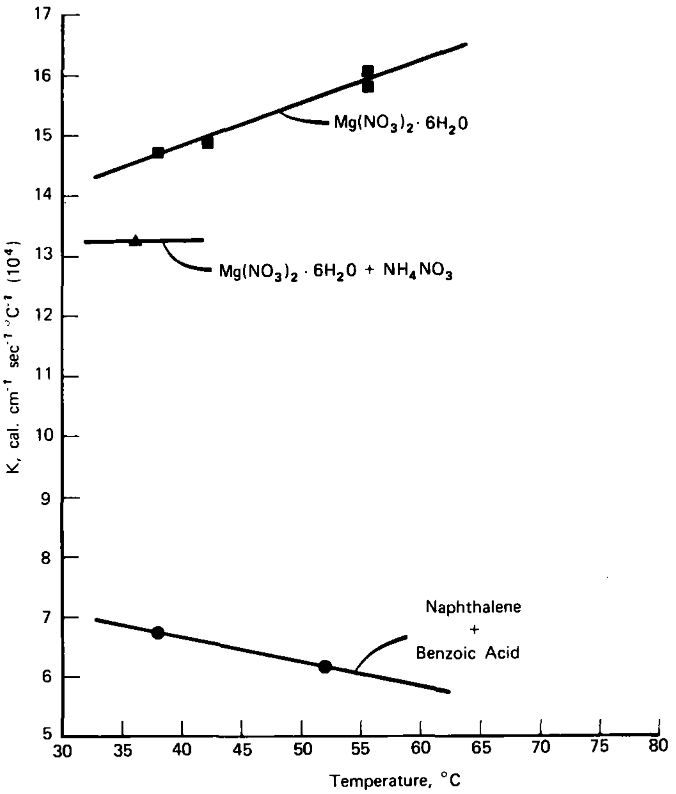
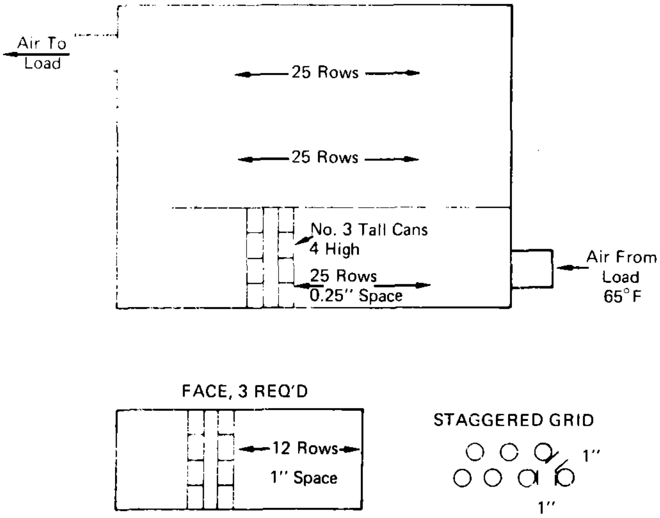


Figure 3
EXAMPLE OF CONCEPTUAL DESIGNS, STEARIC – PALMITIC ACID, 3 DAY STORAGE



Cans Total	3600
Mass Total	11016 Lb
Heat Transfer Area	2332.5 Sq Ft
Air Flow	1200 Cu Ft^3/Min.
Velocity (Interstitial)	8 Feet/Sec.
h_f (Air Film Coeff)	3.9 Btu/Hr.-Sq Ft - °F
ΔP (Pressure Drop)	0.7 – 0.8 In. Hg

Figure 4 TALL #3 CANS, STEARIC – PALMITIC ACID, 3 DAY STORAGE, 840,000 BTU

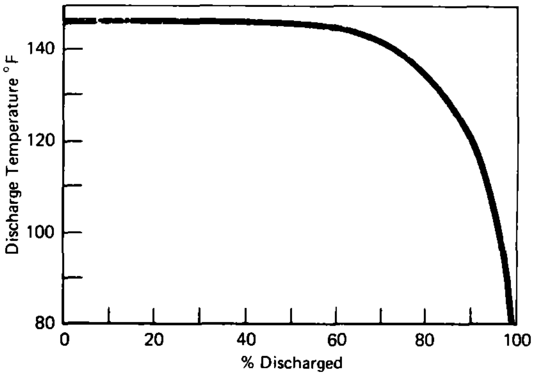


Figure 5 TALL #3 CANS, STEARIC – PALMITIC ACID, 3 DAY STORAGE IN BED, 840,000 BTU

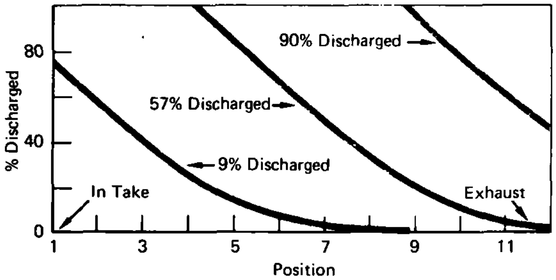


Figure 6.

300,000 BTU STEARIC – PALMITIC ACID SYSTEM

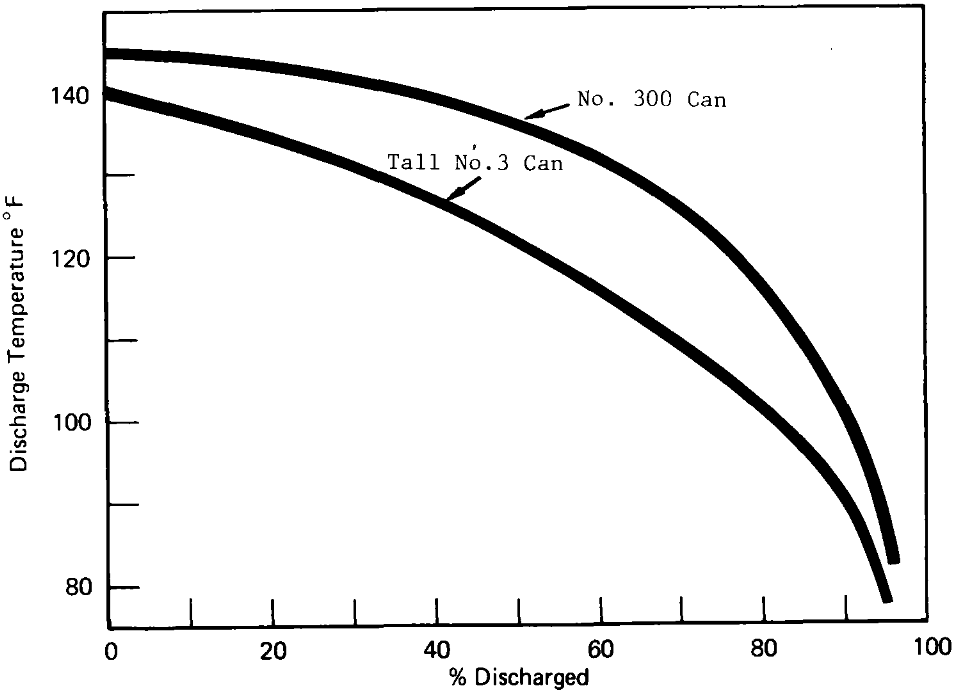


Figure 7.

EFFECTS OF CONTAINER SIZE AND MELTING TEMPERATURE ON DISCHARGE CURVES – 300,000 BTU

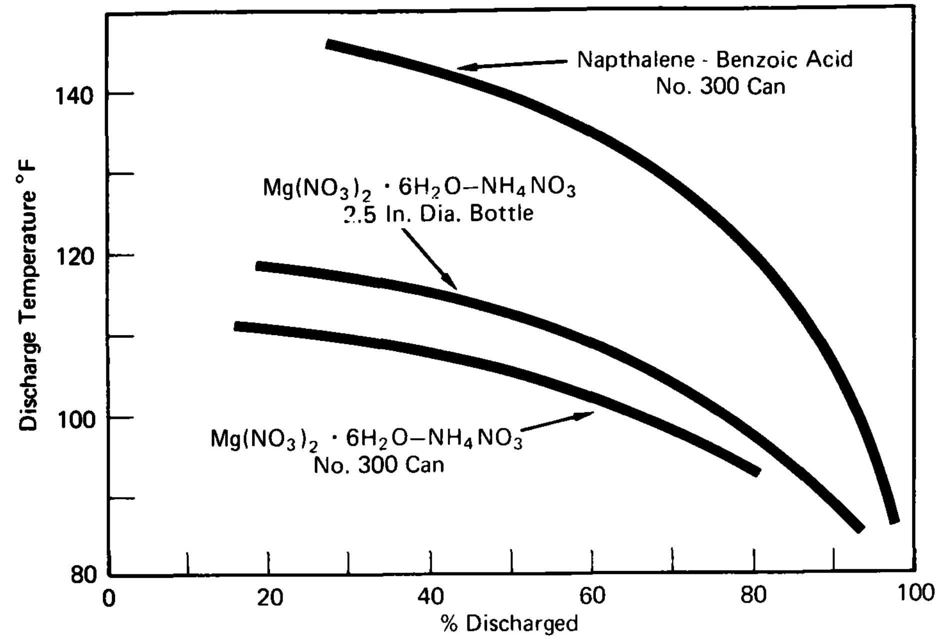


Figure 8.

2.5 IN. CYLINDERS $CaCl_2 \cdot 6H_2O$ – HEAT PUMP SYSTEM

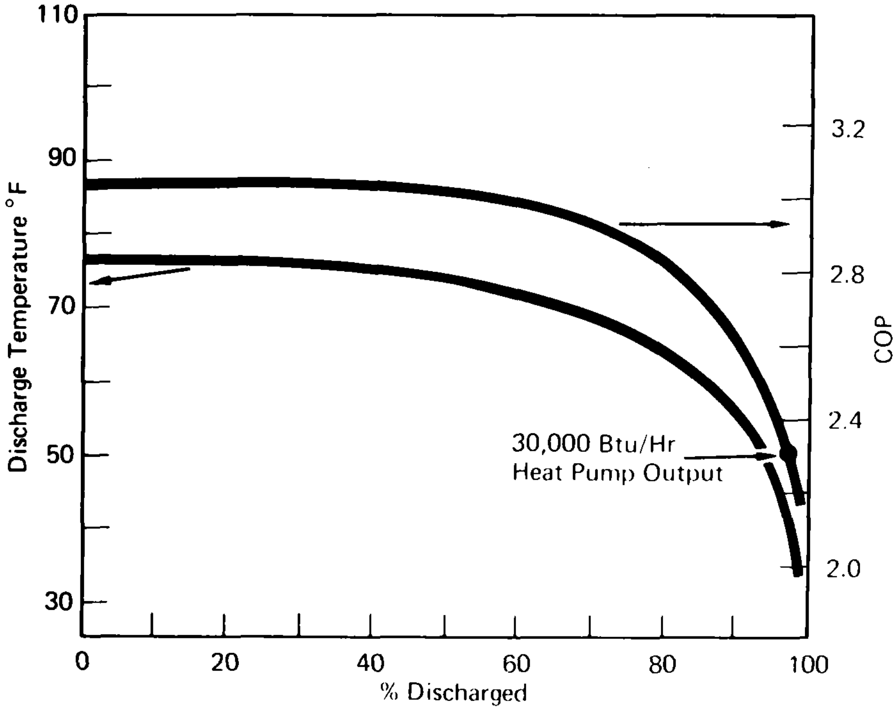


Figure 9.

$Mg(NO_3)_2 \cdot 6H_2O$ 300,000 BTU HYDRONIC HEATING SYSTEM, 2.5 IN. CYLINDERS

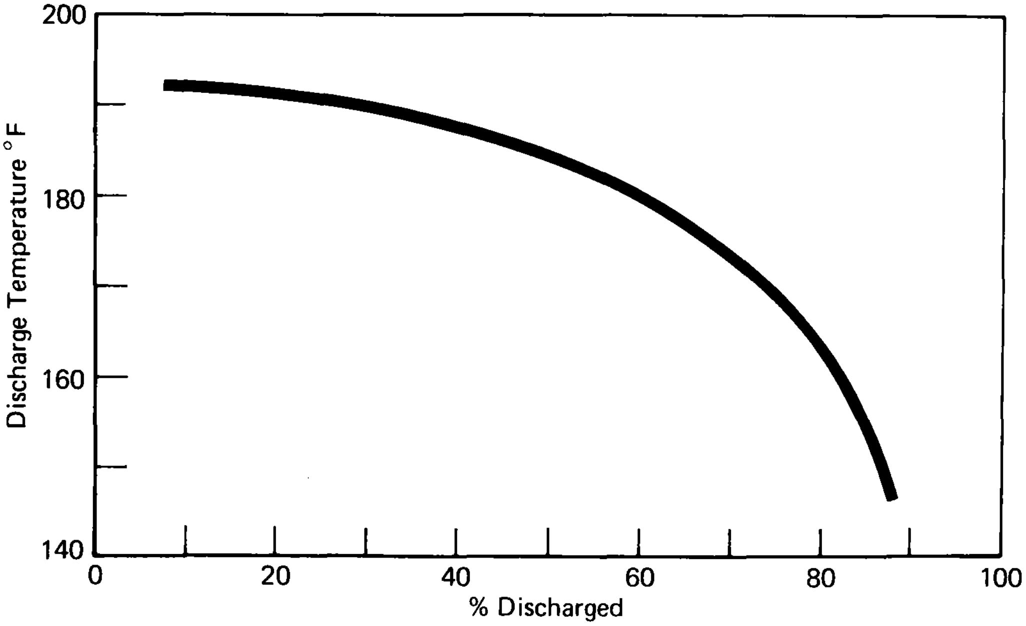


Figure 10.

EFFECTS OF MELT TEMPERATURE AND FILM COEFFICIENTS ON PILLOW DISCHARGE CURVES

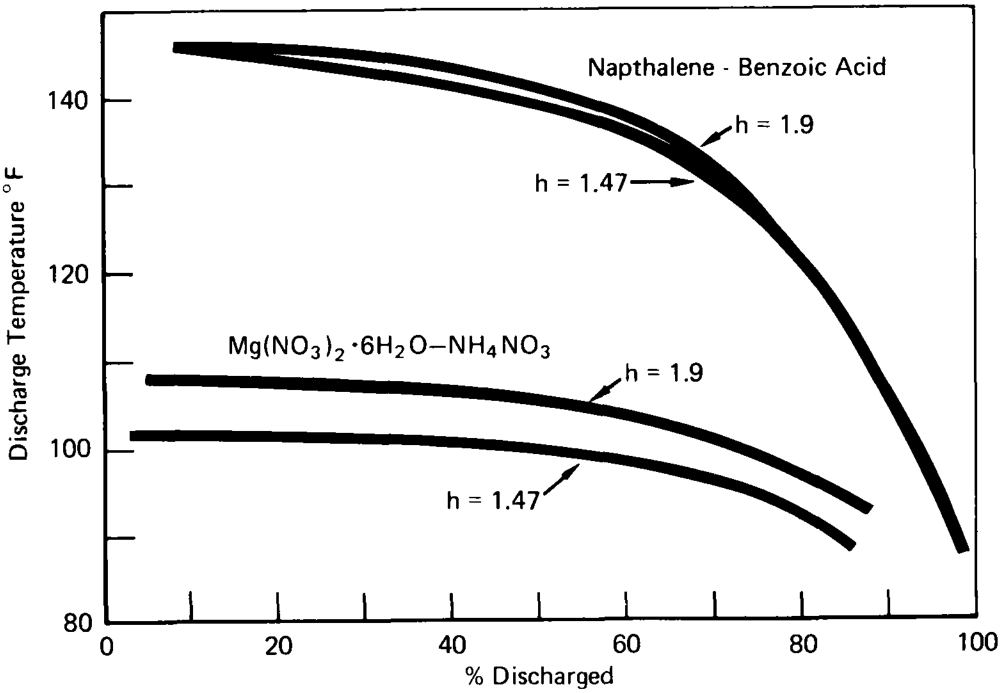
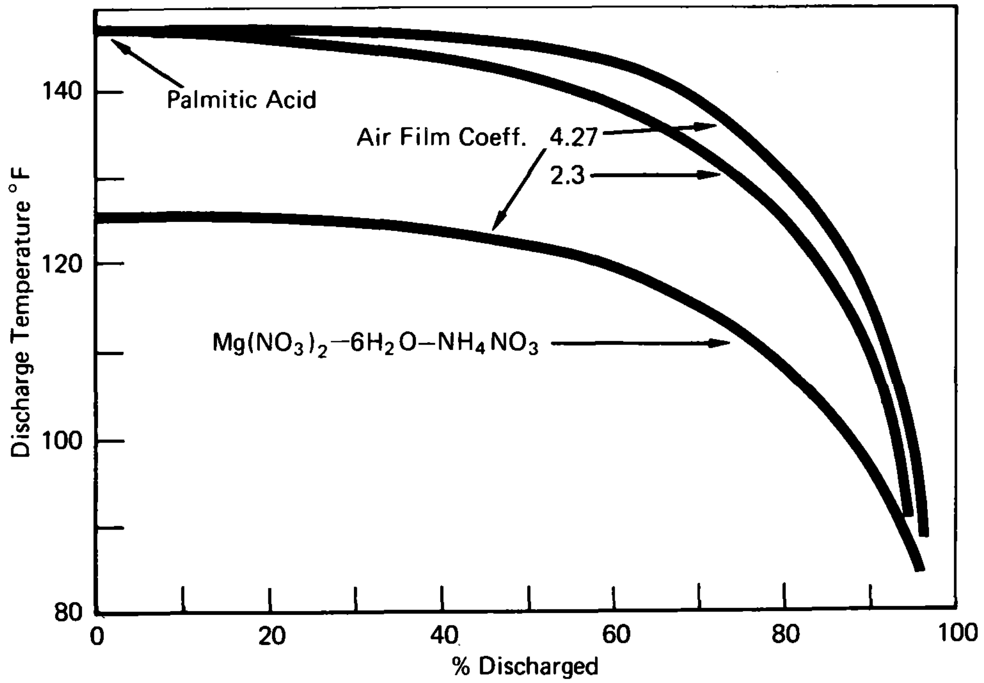
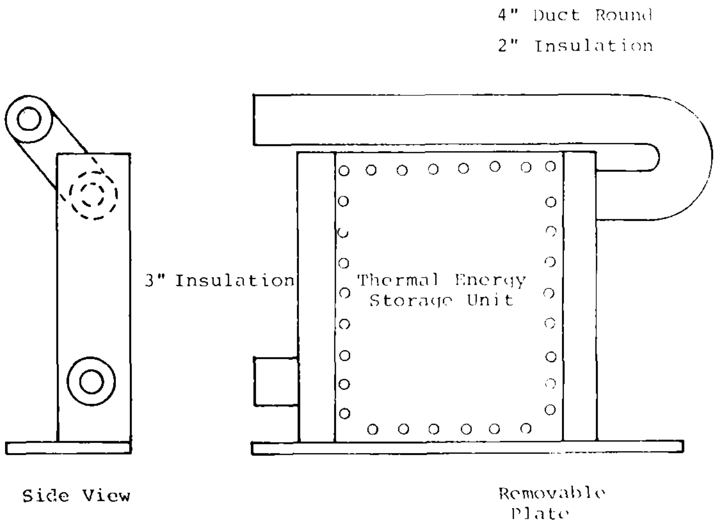


Figure 11

300,000 BTU – 4" X 4" TETRAHEDRA





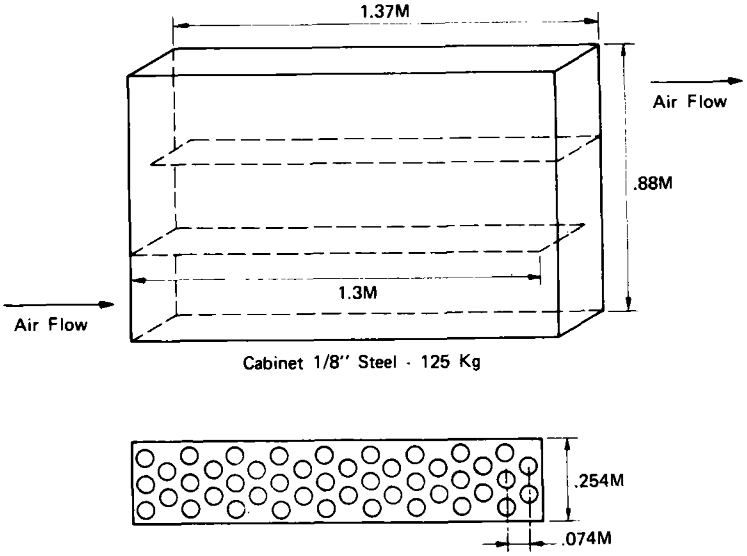
Front View

Figure 12

Test Apparatus for Encapsulated Phase Change Materials.

Figure 13

Calcium Chloride Hexahydrate Storage Medium, Air - Heat Transfer Fluid, Thermal Energy Storage Unit



Containers	.061M Dia .180 HT Bottles Walls .74 mm HDPE
Layout	.024M Spacing Triangular Pitch Minimum Possible Void Fraction .876

THERMAL ENERGY STORAGE BY MEANS OF HEAT OF SOLUTION

by

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July 1976 to September 1977

Contract No. E(49-1) 5158

1. INTRODUCTION

The Franklin Institute Research Laboratories (FIRL) have been investigating thermal energy storage (TES) by means of the latent heat of crystallization of solutes from saturated aqueous solutions. A preliminary technical and economic analysis for various thermal storage applications has been presented (1,2). The methodology promises the advantages of smaller volume, and therefore lower tank costs than storage in water or other liquids. Smaller heat exchanger costs could be expected than are typical for phase change media encapsulated in plates or tubes.

The work to be described emphasizes the development and performance of a prototype thermal storage device. The object is a compact, low cost, and zero or low maintenance design for residential off-peak air conditioning.

2. SELECTION OF SOLUTIONS FOR TES APPLICATIONS

The results of experimental determination of heats of crystallization, densities and other property data for commercial grade salts were used to construct Table 1. In that table the costs include the storage medium and tank for 200,000 Btu theoretical storage capacity. Temperature swings of 27°F (15°C) were used for the calculations in each case. A smaller allowable temperature swing or higher tank costs (0.75 $/gallon in Table 1) would economically penalize the salt solutions relatively less than storage in water.

TABLE 1. MEASURED PROPERTIES OF SOLUTIONS

	STORAGE DENSITY REL. WATER	CORROSIVE TO MILD STEEL?	TOXICITY	COST OF MATERIAL AND TANK REL. WATER
SODIUM SULFATE	1.61	YES		0.58
SODIUM CARBONATE	2.93	NO	SKIN IRRITANT LD_{50} ORAL, 4000 MG/KG	0.49
TRISODIUM PHOSPHATE	2.70	NO	SKIN IRRITANT	0.64
SODIUM TETRABORATE	1.71	NO	BORISM LD_{50} ORAL, 1700 MG/KG	0.66
BORIC ACID	2.17	YES	BORISM	0.91

The final selection of salts was made for various TES applications. The selections and the most important criteria on which they are based are presented in Table 2. A detailed description of the experimental results and the selection process is given in Reference (3).

TABLE 2. SOLUTES SELECTED FOR VARIOUS APPLICATIONS

APPLICATION	SELECTED SOLUTE	SELECTION CRITERIA
• OFF-PEAK ELECTRIC OR COOL SIDE SOLAR AIR CONDITIONING	• SODIUM CARBONATE (TRIMETHYLAMINE CLATHRATE HYDRATE)	• LARGE HEAT OF CRYSTALLIZATION • LARGE SOLUBILITY CHANGE WITH TEMPERATURE
• SOLAR SPACE AND HOT WATER HEATING	• TRISODIUM PHOSPHATE	• LOW COST/TES CAPACITY • NON-CORROSIVE TO MILD STEEL (CARBONATE, PHOSPHATE AND AMINE) ALUMINUM (BORIC ACID OR AMINE) OR COPPER (ALL EXCEPT AMINE WITH INHIBITORS)
• HOT SIDE SOLAR AIR CONDITIONING	• BORIC ACID	• LOW TOXICITY (EXCEPT BORIC ACID AND TRIMETHYLAMINE)

Trimethylamine clathrate hydrate (Table 2) was recently added to the list of aqueous solutes selected for consideration.* Particular advantages may be realizable for the off-peak and solar air conditioning applications because of both economic and performance factors (4,5,6). The energy savings with off-peak air conditioning are realizable by employing higher than normal evaporator temperatures, consistent with the requirement of a maximum storage temperature of 55°F (12.8°C) for acceptable dehumidification performance. Additionally, water cannot be easily stratified thermally in the air conditioning storage application because the thermal expansion coefficient is small in that temperature range and reverses sign below 38°F (4°C).

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*Trimethylamine hydrate possesses a higher latent heat of fusion per unit volume than sodium carbonate decahydrate and has a very high coefficient of solubility with temperature. The amine is only slightly soluble in water below its melting point of 53°F (11.7°C) and is miscible with water at or above the melting point. It is noncorrosive to aluminum or mild steel, but is toxic, in a manner similar to ammonia, and the warmed solutions of the amine have high vapor pressures. The amine may also not be compatible with most oils, sealants, and gasket materials.

3. HEAT EXCHANGER DESIGN

Since completion of the selection task, the program has concentrated on the storage subsystem development and on the design of a reasonable cost, reliable, and energy efficient heat exchanger. The heat exchanger concepts explored are presented in Table 3. Immiscible liquid/liquid heat exchanger methodology has been most encouraging, as well be discussed.

TABLE 3. HEAT EXCHANGER DEVELOPMENT

- PUMP AQUEOUS SOLUTIONS DIRECTLY
  - TUBE-IN-SHELL
  - ANTI-NUCLEATION COATINGS
- TUBE-IN-BATH
- LIQUID/LIQUID

Tests were first performed in which the aqueous medium was pumped directly through the shell of a tube-in-shell heat exchanger. Typical results are shown in Figure 1. The construction and operation in this mode is described elsewhere (3). Heat exchanger performance and thermal efficiency are poor because of salt deposition on the tubes. Nucleation on the tubes could not be prevented despite anti-nucleation coatings on the heat exchanger tubes, low or high fluid velocities, and using a relatively high heat sink temperature of 40°F (4.4°C). The tube coatings which were tested are Teflon, a non-stick spray rubber, polypropylene, and a chlorinated polyether. Teflon anti-nucleation performance was marginally superior to the other coatings.

A second heat exchanger tested employed a tube-in-bath design. A 1/8 HP stirrer and a 16-foot copper coil were suspended in solutions of sodium carbonate or sodium sulfate. This was designed in analogy to devices used in commercial crystallizers. The results, see Figure 2, were similar to those from the tube-in-shell heat exchanger testing. Even with the maximum stirrer velocity, a build-up of salt crust on the tube was not prevented. Various means of dislodging the salt or preventing the build-up with vibrators, scrapers, or thermal pulsing were rejected because of mechanical complexity or uncertain reliability, and also because of the expected high auxiliary energy consumption. A possible solution to the heat exchanger fouling problem is to abandon the heat exchanger tubes for a direct contact immiscible heat transfer fluid.

4. LIQUID/LIQUID HEAT EXCHANGER/STORAGE DEVICE

Liquid/liquid heat exchanger methodology has been investigated for applications to desalination (7,8), geothermal energy utilization (9), thermal energy storage in water (10) or in phase change media (11), and for the direct crystallization of aqueous solutes with evaporating refrigerants (12). The criteria for the selection of an immiscible fluid for use with aqueous thermal storage media are shown in Table 4.

TABLE 4. CRITERIA FOR OIL SELECTION

- FLASH POINT
- TOXICITY
- OPERATING EFFICIENCY
  - VISCOSITY
  - SPECIFIC HEAT
  - DENSITY
- CHEMICAL STABILITY
  - OXIDATION
  - COMPATIBILITY SOLUTION
- EMULSIFICATION
- COST

The concept is illustrated in Figure 3 for the off-peak air conditioning application. The refrigerant evaporator for charging the device is located in an oil layer floating on the storage medium, and fouling by the crystallizing aqueous solution is prevented. Discharge of the "stored cold" is accomplished with a finned coil immersed in the aqueous solution. Since the coil is always warmer than the solution, there is no fouling. During both charging and discharging the oil pump located on the top of the tank is running at rates less than 1 gpm (63 cm^3/sec).

The oil transfers heat from the solution to the evaporator with about 1°C temperature difference on reaching the oil/solution interface. During discharge the oil provides sufficient agitation to stir the crystal bed slowly. Maintaining the solution in a constantly saturated state is desirable during discharge, since the thermal availability is thereby maximized. It is not yet apparent that sufficient agitation can be provided with the oil pump alone. Attempting to increase the rate of dissolution by increasing the oil velocity results in emulsification of the oil/solution and salts can then deposit on the evaporator coil. If a stirrer were used, the oil pump would be off during discharge.

Stand-by losses to ambient are minimized by allowing the storage medium to naturally stratify. Because the solution layers near the crystal bed become more concentrated and denser as the temperature rises, the salt is effectively isolated from the bulk of the solution and the two components, solution and salt, may be made to interact at will by agitation. When the sodium carbonate decahydrate dissolves, the temperature of the solution is lowered. Thus, stand-by losses are less than would be the case for an equally well insulated water tank.

5. RESULTS OF LIQUID/LIQUID STORAGE DEVICE TESTING

A solution of sodium carbonate saturated at 58°F (14.4°C) on being cooled to 40°F (4.4°C) deposits enough sodium carbonate decahydrate to occupy about 1/3 of the aqueous volume. Over a 10°C temperature swing the laboratory data indicates a volumetric storage density 2.4 times that of water (3). Figure 4 shows a glass storage tank containing 30 gallons (0.11 m^3) of sodium carbonate solution saturated at 54°F which had been cooled to 40°F (4.4°C) using a coil in the oil layer (an alkylated aromatic fluid) and the oil pump as described previously. The solution was then allowed to slowly warm up to 54°F (12.2°C) over a 40 hour stand-by duration. Figure 4 shows that about 60 percent of the sodium carbonate decahydrate does not redissolve under these quiescent conditions. At the same time, the rate of temperature increase was considerably slowed, as shown in Figure 5.

Emulsification at the oil/solution interface was initially not a problem with the device as shown schematically in Figure 3. Over a 5-week period of testing emulsion formation began and worsened. This resulted in the nucleation of salt on the cooling loop in the oil layer. It is suspected that this was caused either by oxidative degradation of the oil in the presence of the strongly alkaline solution containing copper or by the absorption of plasticizers from PVC tubing or the Viton rubber pump impeller. The oxidation products or plasticizers may stabilize such emulsions. It was also thought that fine particles of calcium carbonate, formed from the commercial grade sodium carbonate and tap water, might help stabilize emulsions. However, filtration of the medium through cotton wadding did not reduce emulsification. In fact, nucleation of the decahydrate salt was reduced by that treatment and poorer crystallizing performance was obtained.

6. CONCLUSIONS

The work thus far has highlighted the areas that require particular attention. Two approaches to preventing the emulsion formation are being taken. The oil is being examined in the laboratory for the presence of oxidation products or plasticizers. These are problems which can be solved by a more judicious choice of materials for constructing the device. The tank design may also be modified to include a separator. This may be a steel rack holding tilted polyethylene baffle plates which may be immersed in the storage tank. The oil would flow over the underside of each plate, and agglomeration of the oil would be promoted by such motion. The plates would also cause a longer contact between the oil and the solution.

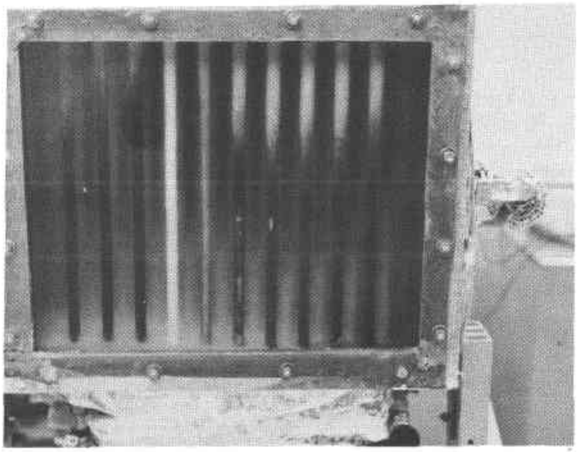


Fig. 1

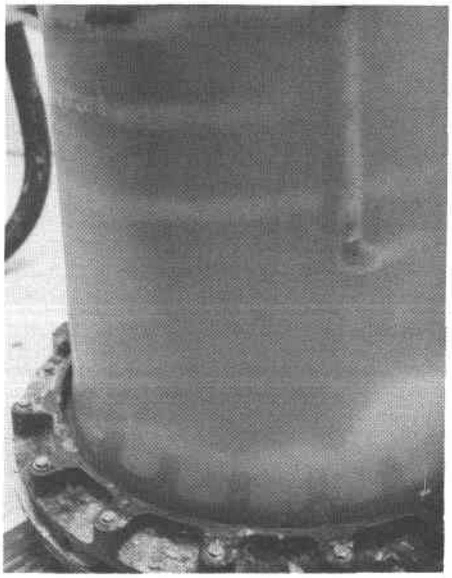
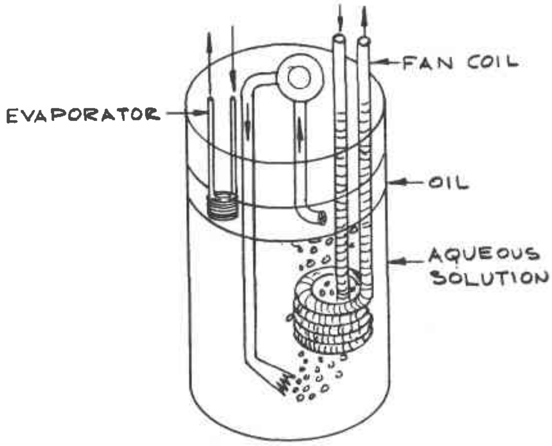


Fig. 2



LIQUID/LIQUID HEAT EXCHANGER
STORAGE DEVICE

Fig. 3

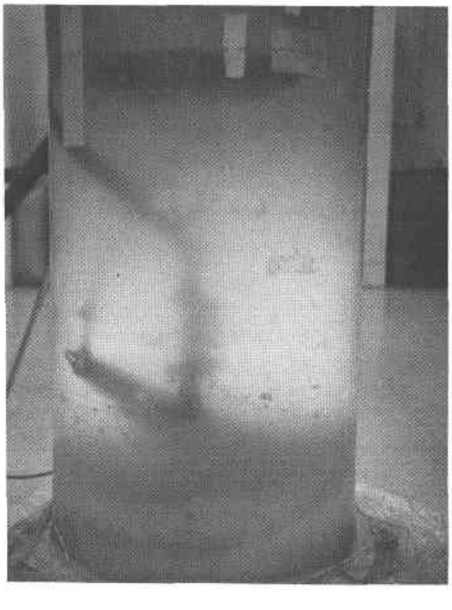


Fig. 4

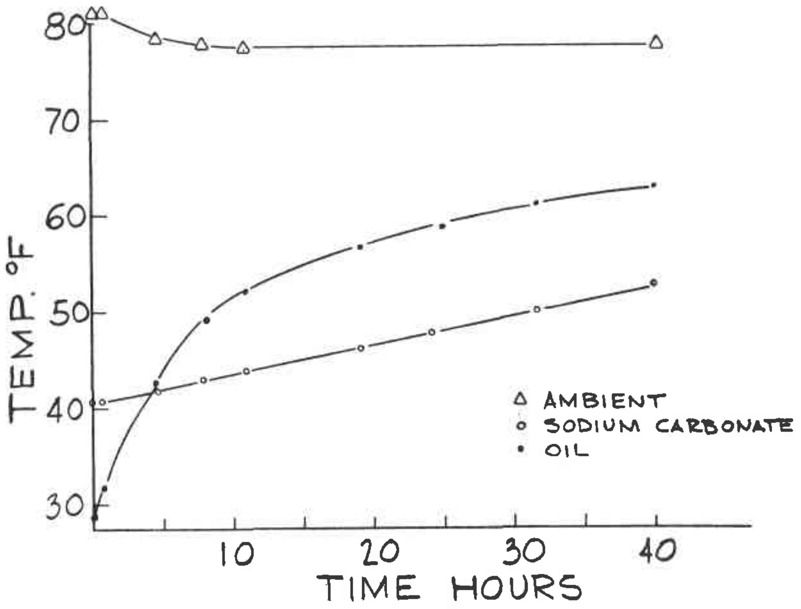

80
70
60
50
40
30
TEMP. °F
10
20
30
40
TIME HOURS
△ AMBIENT
○ SODIUM CARBONATE
• OIL

Fig. 5

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LONG DURATION EARTH STORAGE OF SOLAR ENERGY

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By

S. W. Yuan and A. M. Bloom

Subcontract No. 7349

I. Purpose

To evaluate long term earth storage of solar energy for space and hot water heating.

Specific Concepts: The following will be considered:

A. A system which consists of earth ground with a black plastic cover as the solar collector and buried water piping loops below the ground for both transmission and storage of heat in the system and extraction of heat from the ground storage.

B. A system which consists of solar collectors, water piping loops from the collectors to the ground storage for both transmission and storage of heat in the system, and extraction of heat from the storage ground.

C. A system which consists of solar collectors, heat pipes for transmission, and water pipes for storage and extraction of heat in the system.

A comparative evaluation of the above systems will be made on the basis of an annual cycle.

II. Background Information

The concept of using the earth for seasonal storage of solar energy has been investigated analytically and partially experimentally at the George Washington University under NSF-ERDA Grant (AER 75-18608 A02). The results (see Refs. 1-5) show that the earth can be adequately used as a thermal storage reservoir. In particular, a system consisting of a solar collector for transmission of solar heat through heat pipes or water piping loops to 360 thousand cubic feet of ground storage (e.g., four-tenths of an acre of land twenty feet deep) can provide sufficient space heating for at least twelve average-size houses for year-round hot water and space heating in the Washington-Baltimore area. Furthermore, the results of a theoretical investigation and small laboratory test show that an antigravity heat pipe is feasible for heating the earth storage system. It is believed that some combination of heat pipes and water pipes is an optimum heat exchanger configuration for both solar heating input to earth storage and heat extraction from the storage for space and hot water heating.

III. Project Description

A. Technical Aspect

1. The transient thermal behavior of the earth storage has been analyzed by existing computer programs from previously developed work under NSF Grant AER 75-18608-A02. A correction has been made to the predicted heat storage in order to account for heat losses.

2. The optimum diameter and length of water pipe have been determined as a trade between the thermal efficiency and power required. The configuration is assumed to be a single length of pipe.

B. Economical Aspect

The following consultants have been selected to investigate respective phases of the economics of the earth storage of solar energy.

1. Dr. Ishai Oliker, Burns and Roe, Inc., has been chosen to study the following items:

   (a) Selection of materials of the system
   (b) Preparation costs for storage system
   (c) Costs of storage system installation
   (d) Maintenance costs of the system

2. Dr. Walter Bienert, Dynatherm Corp., has been chosen to study the following items:

   (a) Selection of heat pipes of the system
   (b) Selection of materials related to heat pipes of the system

3. Mr. Gershon Meckler, Gershon Meckler Associates, has been chosen to study the following items:

   (a) Life cycle costs and reliability of the system
   (b) Energy conservation in regard to existing fuel consumption

IV. Results

A. Technical Aspect

1. Introduction

The purpose of this investigation is to analytically investigate three specific concepts of solar energy storage systems.

a. Soil collector with and without buried water pipes for heating and discharging of the ground storage.

b. Flat plate collector with water pipes for heating and discharging of the ground storage.

c. Flat plate collector with heat pipes for heating and water pipes for discharging of the ground storage.

To date, system"a"has been investigated and the study of system "b" is in progress.

2. Analysis of System "a"

The analysis of system "a" was divided into two parts:

a. Soil Collector Without Buried Water Pipes

The soil collector was defined as soil with a black coating on the surface and two plastic covers. The case without water pipes was analyzed first, since it was the simpler of the two cases. For this case, the one-dimensional unsteady heat equation was used with weather data for the Washington-Baltimore area. A typical set of results is shown in Figures 1 and 2 for a unit collector area.

Figure 1 shows a graph of the soil temperature versus depth in the ground storage for various times. The soil temperature is assumed to be 100°F on March 21. The results show that although the temperatures near the surface are high during the summer, only a small amount of thermal storage is preserved throughout the year in the soil region between five and twenty feet. This is believed to be due to the low thermal conductivity of the soil. Figure 2 shows the corresponding results for soil temperature versus time for various depths. It is clear from figure 2 that for depths below 8.5

ft. the soil temperature is almost insensitive to variations in surface temperature. Based on these results it was concluded that some type of earth storage heat exchanger would be required to transfer the high surface temperatures to the lower soil depths.

b. Soil Collector with Buried Water Pipes

The soil collector with buried water pipes was then analyzed. The computer program developed in reference 4 for tube collectors and no storage losses was modified to account for storage losses and to accommodate different types of collectors (flat plate, soil, etc.) A storage volume of 38 ft. x 38 ft. ground surface and a depth of 20 ft. was used. As a test case, 500 ft.^{2} of tube collectors were applied to the storage volume for weather data in the Washington-Baltimore area. The heat exchanger consisted of 2600 ft. of 2 in. water pipe. The house load used in this calculation consisted of 30 x 10^6 BTU for hot water averaged over the entire year and 60 x 10^6 BTU for space heating during the winter. Figure 3 shows the results of this calculation with and without storage losses. The graph in figure 3 is a plot of the bulk fluid temperature, T_B, and outer soil temperature, T_s, at the storage exit versus time (same notation as in reference 4). The case without losses (open symbols) is fictitious since a special working fluid would be required in the water pipe to reach levels greater than 240°F. Furthermore, storage losses are always present. However, both cases are shown as a measure of the effect of storage losses. The results show that for an initial storage temperature of 140°F on October 15, levels of 250°F and 190°F are reached by the end of the summer. Note that the difference between the water and soil temperatures is greater with losses during this period. As the winter load is applied, both levels drop. For the case with losses a level of at least 120°F is maintained throughout the remainder of the winter. It is clear from figure 3 that the effect of losses is to reduce the prediction without losses by about 50% for this size storage. This heat loss is substantially reduced during subsequent years.

The soil collector with buried water pipes was then analyzed. The structure of the soil collector included a black surface, two plastic covers, and one layer of 1 in. water pipes in the first foot of soil (see figure 4). The collector efficiency for this configuration is 50%. One foot of foam insulation was located below the first layer of pipes to limit top losses at night. 2600 feet of 2 in. water pipes was distributed in the twenty feet below the insulation. The results of this calculation are shown in figure 5 for more than a two-year period. The format is the same as in figure 3. An initial temperature of 60°F was used (cold start), and hot water and space heating loads are applied only when the temperature is above 140°F. The results for the first year show that a peak of about 180°F is reached by the end of the summer, and 140°F is reached approximately two months into the winter. During the second year a peak of about 210°F is reached at the end of the summer, and 140°F is reached about three months into the winter. The results for the third year are similar to that of the second year. The relatively rapid drop from the 210°F level during the second year is attributed to the higher losses from the soil collector compared with that during the first year. The following preliminary conclusions can be made for the soil collector:

(1) Buried water pipes are required to distribute the heat collected to the lower depths.

(2) The soil collector has low efficiency for the following reasons:

  a. $F_R = 0.5$
  b. Collector Area = Surface Area
  c. No tilt

(3) A ground storage somewhat greater than 38 ft. x 38 ft. x 20 ft. would be required to handle the complete hot water and space heating load.

B. Economic Aspect

An economic analysis of the system is being made which includes the following aspects:

(1) Life cycle costs and reliability of the system
(2) Selection of materials of the system
(3) Preparation costs for storage system
(4) Cost of storage system installation
(5) Maintenance costs of the system.

Preliminary analysis based on the following results of heating requirements was made.

Heating Requirements	
Hot Water (Summer Months)	13,500,000 BTU
Hot Water (Winter Months)	16,500,000 BTU
Space Heating (Winter Months)	60,000,000 BTU
(a) Solar House with Complete Thermal Storage	
(1) Collector Area	500 ft^2
(2) Summer Solar Collection	60,000,000 BTU*

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*After subtracting 1/3 heat energy for inclement weather and storage losses.

(3)	Summer Heat Storage** Summer collection minus hot water requirements =	46,500,000 BTU
(4)	Winter Solar Collection	30,000,000 BTU
(5)	Winter Space and Water Heating Requirements 60,000,000 + 16,500,000 =	76,500,000 BTU
(6)	Energy Available Summer solar storage plus winter solar collection 46,500,000 + 30,000,000 =	76,500,000 BTU
(b)	Solar House with Only Overnight Storage	
(1)	Collector Area	850 ft^2
(2)	Winter Solar Collection	76,500,000 BTU
(3)	Winter Space and Water Heating Requirements	76,500,000 BTU
(4)	Auxiliary Energy Requirements (assuming 30% of inclement weather) 0.3(76,500,000 + 13,500,000) =	27,000,000 BTU

Figure 6 illustrates annual expenses for solar versus electric space and water heating. The calculations are based on a 1,500 ft^2 house with an annual energy consumption of 90 million BTU. In addition, the following assumptions are made:

(a) Solar House with Complete Thermal Storage

- (1) Initial cost is estimated at \$10 per ft^2 of living area
- (2) Tax Credit: \$2,000

**Thermal earth storage is estimated at 38' x 38' x 20' which is 30% more than required.

(3) Mortgage: 25 years, 8 3/4 percent interest

(4) Homeowner in 50% tax bracket

(5) Zero additional property tax on solar system

(6) Average annual maintenance cost: 2% of initial cost of the system

(b) Solar House with Overnight Storage

(1) Initial cost of the solar system is estimated at 17.50/ft^2 of solar panel

(2) Backup system at no cost

(3) Average annual maintenance cost: 1% of initial cost of the system

(4) Additional heating consumption with backup system is estimated at current electric - 5¢/KWH ($14.7/million BTU) and 6% annual inflation.

(5) All assumptions made in (a-2) through (a-5) are applied in this case

(c) Conventional Heating System

(1) Electricity is estimated at current cost at 5¢/KWH ($14.7/million BTU) with 6% annual inflation.

(2) No annual maintenance cost is assumed.

The results indicate that the earth storage system is economically competitive today with electric assistance systems throughout most of the United States. For countries with considerably lower labor costs, this system would be economically competitive today with the residential-fuel-type heating systems.

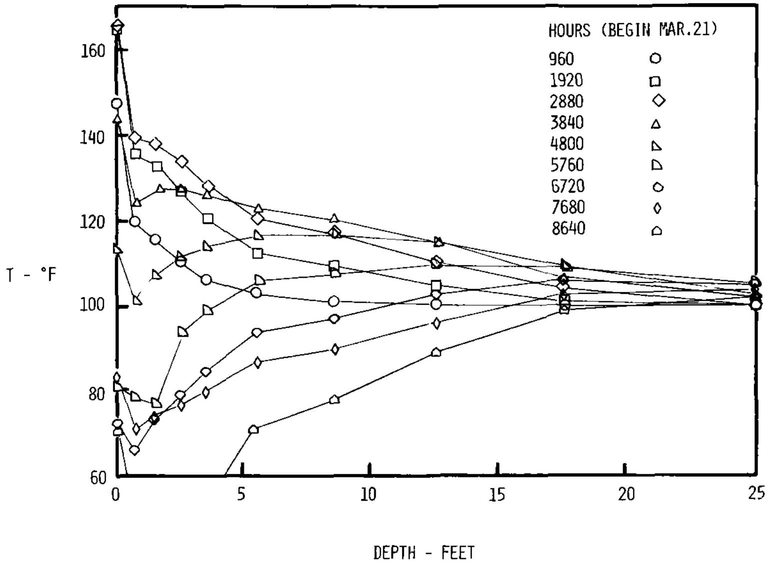

FIGURE 1

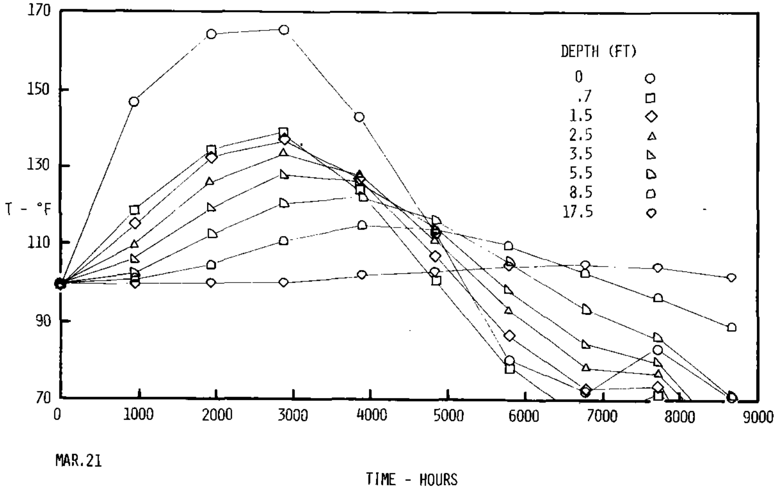

FIGURE 2

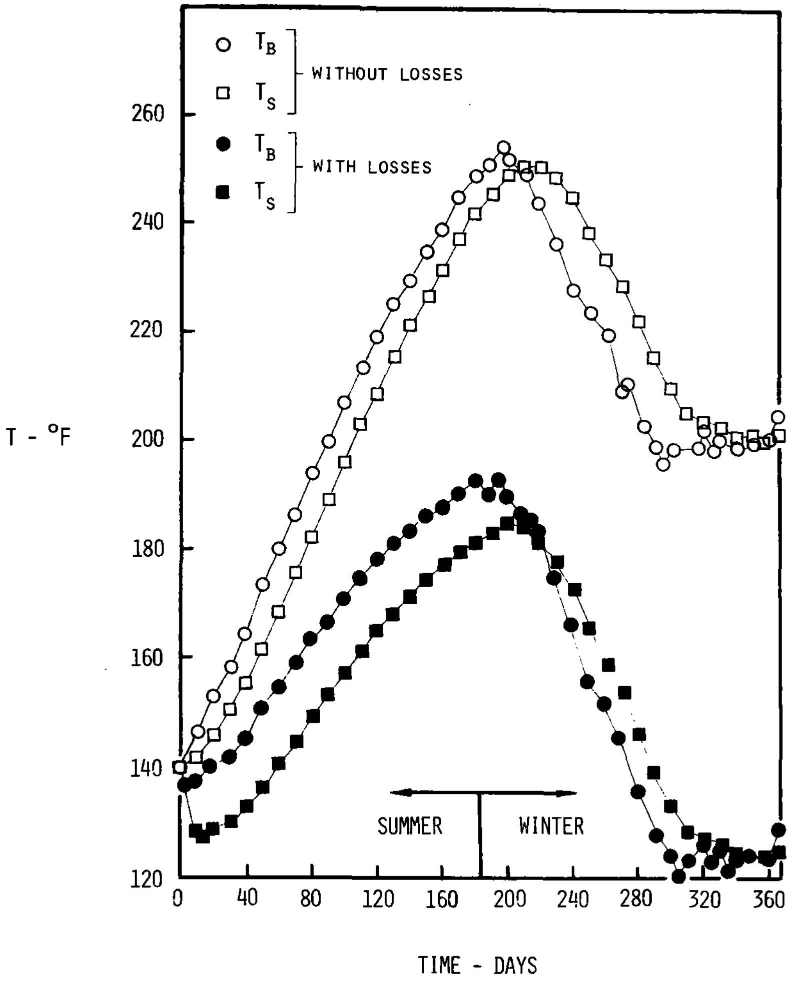

FIGURE 3

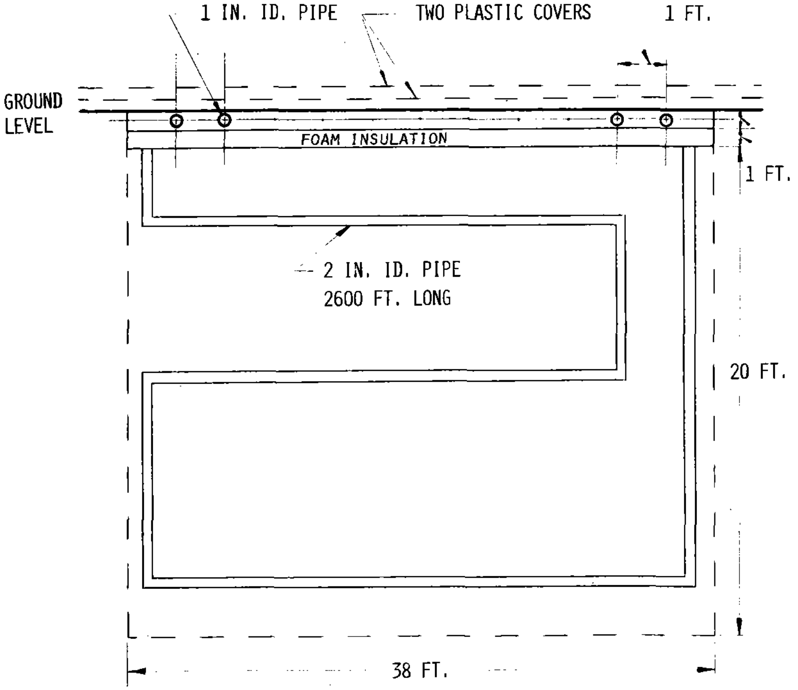

FIGURE 4

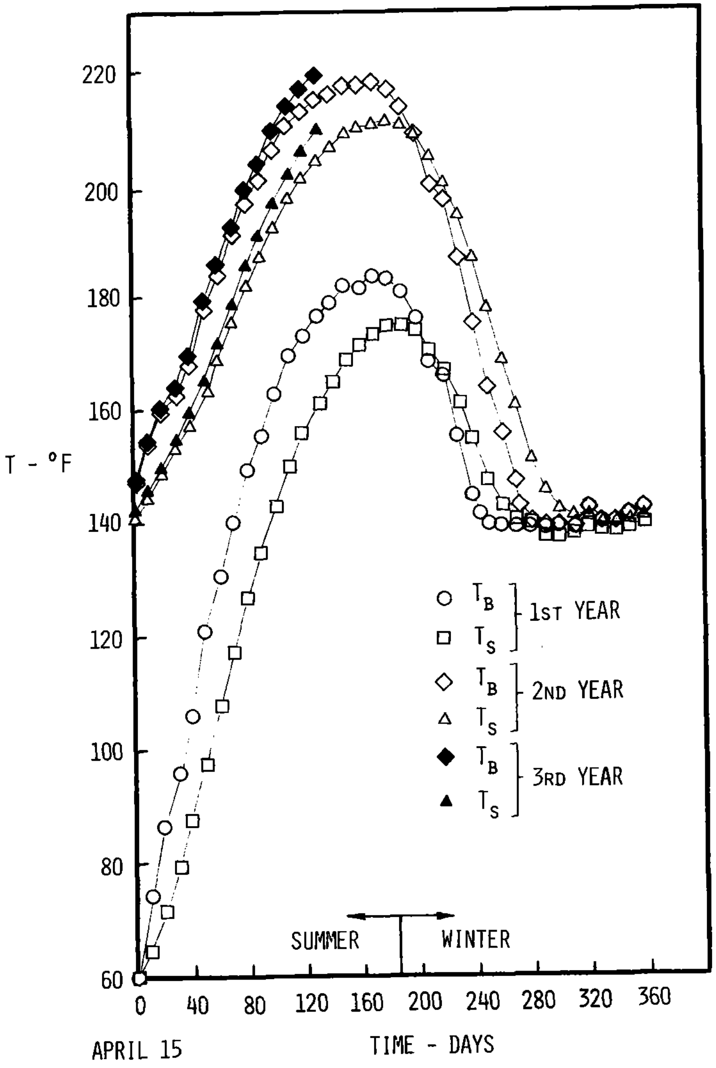

FIGURE 5

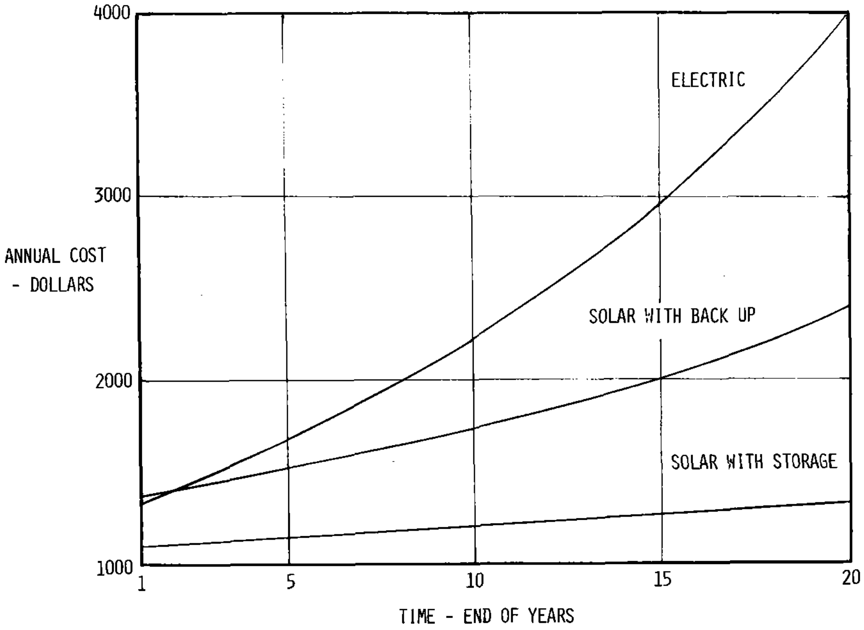

FIGURE 6 - ANNUAL EXPENSES FOR SOLAR VERSUS ELECTRIC SPACE AND HOT WATER HEATING

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2. Yuan, S. W., and Bloom, A. M., "Solar Energy Storage and Utilization," Presented at the 13th Annual Meeting, Society of Engineering Science, Hampton, Virginia, November 1-3, 1976.

3. Yuan, S. W., Bloom, A. M., and Nazli, M., "Long Duration Earth Storage of Solar Energy," Presented at the National Forum of Solar Cooling and Heating, Miami Beach, Florida, December 13-15, 1976.

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5. Kroliczek, E. J., Yuan, S. W., and Bloom, A. M., "Application of Heat Pipes to Ground Storage of Solar Energy," Presented at the AIAA 12th Thermal Physics Conference, Albuquerque, New Mexico, June 27-29, 1977.

PROJECT SUMMARY

Organization:	Lawrence Berkeley Laboratory
Address:	One Cyclotron Road, Berkeley, California 94720
Project Title:	THERMAL ENERGY STORAGE IN UNDERGROUND AQUIFERS
Principal Investigator:	Chin Fu Tsang [Telephone No.: (415) 843-2740 Ext. 5782]
Contract No:	443567-0801 (A7170GA1)
Contract Period:	July 20 - September 30, 1977
Contract Amount:	ERDA $40,000 Other -0-

Project Goals

By means of numerical models or other methods (1) to study and to understand the hydrodynamic, thermal and chemical behavior of an aquifer when used for hot or chilled water storage; (2) to estimate the efficiency of storage and retrieval; and (3) to suggest optimal arrangements for implementation. During the contract period, our goal is to calculate the efficiencies of both hot and cold water storage for an one-well system, and to study the hydrodynamic and thermal behavoir of a two-well system used for hot water storage.

Project Status

The hydrodynamic and thermal behavior of an aquifer under injection and withdrawal of hot water has been studied. The storage and retrieval efficiency has been estimated for daily and seasonal cycles of storage and retrieval. Effects of wells fully or partially penetrating the aquifer were studied. In all cases, calculated energy recovered over energy injected is found to be higher than 80% after only a few cycles.

A similar study has been completed for storing chilled water (4°C) during winter, which is then produced in summer for air-conditioning. Temperatures of produced water are calculated to range from 4-10°C after a few cycles.

We have completed an enlargement of our numerical model, and a calculation of the hydrodynamic and thermal behavior of a two-well system (doublet) has been initiated. In this system, during the storing period, fluid is produced from one well, heated and then injected into the other. During utilization period, the hot water is retrieved from the latter well and cooled used water is reinjected into the former. Some qualitative considerations have also been made for a three-well system. Some hot water storage field data have been obtained from Auburn University, which will be evaluated for their use to verify our numerical model.

I. PURPOSE

The development of practical and low-cost methods for storing a large amount of thermal energy is of fundamental importance for the utilization of solar energy as well as the implementation of total energy systems. The basic function of a storage system is to act as a buffer between time-varying energy inputs and thermal and/or power demands. The present project studies the concept of storing hot or cold water in natural aquifers underground. The purpose is to understand the hydrodynamic and thermal behavior of an aquifer, to estimate the efficiency of thermal storage and retrieval and to suggest optimal arrangements for implementation.

II. BACKGROUND INFORMATION

Aquifers are geologic formations which contain and conduct water. They may be found at depths ranging from a few meters to several kilometers. Confined aquifers are those which are bounded above and below by impermeable layers and are saturated by water under pressure. For many years these types of aquifers have been used for liquid waste disposal and for storing fresh water, oil products and gas. However, their use for hot water storage is a relatively new concept suggested by Robbimov, Umarov and Zakhidov, Kazmann and Meyer and Todd in the early seventies.

The physical basis of the concept lies in: a) the low thermal conductivities of caprock and bedrock materials, b) the large volumes of many aquifers (of the order of $10^7 m^3$), and c) the capability of storing water under high pressures. To estimate the feasibility and efficiency of such a storage system, the behavior during injection and withdrawal cycles must be understood, such as: (1) Thermal behavior of and heat loss from the system during successive cycles of operation, (2) Pressure distribution in the aquifer during the process, and (3) Rock-water chemical reactions and the resulting change in aquifer permeability.

It is only recently that sophisticated computer models have been developed to study these questions using the proper physical conditions and parameters, and to make realistic predictions of the energy recovery efficiency of aquifer storage systems. Furthermore, physical models and field experiments have been initiated to test this concept. These will not only provide data to verify numerical models, but also give an indication of the feasibility and possible problems that may be encountered during the implementation of the aquifer storage concept.

III. PROJECT DESCRIPTION

In the present project, we will make use of a numerical model developed at the Lawrence Berkeley Laboratory to investigate hot and chilled water storage. The numerical model employed is called "CCC" which stands for "Conduction, Convection and Compaction." It is based on the so-called Integrated-Finite-Difference Method. The model computes heat and mass flow in three-dimensional water-saturated porous systems. Concurrent with the mass and energy flow, the vertical deformation of the aquifer system is simulated using the one-dimensional consolidation theory of Terzaghi. Thus the following physical effects can be included simultaneously in the same calculations:

Flow of hot and cold water with large viscosity and density differences.

Effects of temperature on rock and fluid properties (e.g., heat capacity, viscosity and density).

Heat convection and conduction in the aquifer, caprock and bedrock.

Effects of gravity on fluid flow.

Effects of regional groundwater flow.

Combined effects of many injection and withdrawal cycles.

Spatial variations in aquifer properties.

Possible compaction and the associated land subsidence due to pressure changed during the injection-withdrawal history.

Five different cases have been studied:

1. Hot water daily storage: hot water is injected for 12 hours during daytime and produced for 12 hours during nighttime.
2. Hot water seasonal storage, semi-annual cycle: hot water is stored in spring for 90 days, pumped out to use for air-conditioning in summer for 90 days, then hot water is again stored in autumn for 90 days and finally pumped out to use for heating in winter for 90 days.
3. Hot water seasonal storage, annual cycle: hot water is stored in summer for 90 days and used for 90 days in winter for heating. There is no injection or production during spring or fall.
4. Chilled water seasonal storage: chilled water (at 4°C) is stored in winter for 90 days and produced for 90 days in summer to be used for air-conditioning. There is no injection or production during spring or fall.
5. A two-well (doublet) system: during storage period, water is produced from one well, heated and then injected into the other one; during utilization period, hot water is retrieved from the latter and the cooled used water is injected back into the former.

The rates of injection and production are kept the same, equal to 10^6 kg/day.

IV. RESULTS

The initial temperature of the aquifer in all cases is assumed to be 20°C. For cases (1)-(3) we have performed calculations with injection temperature T_i assumed to be 120°C, 220°C and 320°C. It appears that the temperature of the produced water for different injection temperatures approximately scales according to the factor $(T_i - T_0)$. For case (4) only one injection temperature, 4°C, has been used. Some typical results are shown below.

For case 2, seasonal storage, semi-annual cycle, we have performed calculations not only for a well fully penetrating the aquifer (thickness 100 m) but also for a well partially penetrating it for 50 m. Figure 1 displays the temperature contours within the aquifer for the partial penetration case (a) at the end of the injection period of the first cycle and (b) at the end of the production period of the same cycle. The thermal front is not sharp due to heat conduction within the aquifer and with the confining beds.

Figure 2 represents the production temperature at the well during the production period for successive cycles for the case of semi-annual cycle with full penetration. The recovery temperature is increased for each successive cycle as the aquifer is heated up, making it a more efficient hot water storage system. The process will reach quasi-equilibrium when later cycles do not change the temperature appreciably.

The results for semi-annual cycles with full penetration are summarized in Table I. It can be seen the energy recovered (which may be calculated from the integral of temperature over time in Figure 2) improves with each

	CYCLE				
	1	2	3	4	5
ENERGY INJECTED (JOULES)	5.71×10^{13}	5.71×10^{13}	5.71×10^{13}	5.71×10^{13}	5.71×10^{13}
ENERGY RECOVERED (JOULES)	4.96×10^{13}	5.092×10^{13}	5.144×10^{13}	5.18×10^{13}	5.2×10^{13}
ENERGY LOSS FROM AQUIFER (JOULES)	5.34×10^{11}	6.81×10^{11}	7.7×10^{11}	8.41×10^{11}	9.1×10^{11}
ENERGY DIFFUSED TO HEAT UP AQUIFER (JOULES)	7.10×10^{12}	5.5×10^{12}	4.9×10^{12}	4.46×10^{12}	4.2×10^{12}
PERCENTAGE OF ENERGY RECOVERED	86.8%	89.2%	90.0%	90.7%	91.1%
PRODUCTION TEMPERATURE AT END OF CYCLE	124°C	139°C	147°C	151°C	155°C

TABLE I . - FULL PENETRATION -

1 CYCLE = 180 DAYS

$T_i = 220°C$

$T_o = 20°C$

$Q = 1 \times 10^6$ Kg/DAY

$H = 100$m

$\Delta R = 2$m; NO. OF LAYERS = 4

successive cycle. The heat lost is also shown and is two orders of magnitude smaller than the energy recovered. The difference between energy injected and recovered is the energy diffused to heat up the aquifer, making it a better storage system for the following cycle. The last line gives the mimimum recovery temperature during production. This corresponds to the lowest temperature found at the end of each production period, as shown in Figure 2.

For cases (1) - (3) the percentage of energy recovered (i.e., recovered energy divided by total injected energy) during each cycle is plotted against cycle number in Figure 3 which displays surprisingly high values (>80%).

For case 4, where chilled water is stored, the temperature of production during the summer is shown in Figure 4, and the highest temperature during production (at the end of the production period) versus cycle number is shown in Figure 5. Thus after three cycles, the temperature during production is expected to stay below 10°C during the whole production period.

FUTURE ACTIVITIES

During the next fiscal year, the following tasks will be addressed:

1. Further calculations will be done for a "typical" aquifer system, exploring the effects of variations in parameters, such as thickness, permeability, flow rates and boundary conditions.
2. Further calculations will be made for multiple-well systems with the goal of identifying optimal arrangements for heat storage and retrieval.
3. Collection and evaluation of field data collected from thermal storage field experiments (e.g. those of Auburn University). Suggestions may be made to the experimenters for new or additional measurements. We will draw from the LBL expertise in geophysical studies and well-test analysis.

4. Modeling of these field cases will be made using our numerical model. This will (a) validate our model, (b) possibly suggest new crucial experiments that should be done, and (c) may indicate optimal implementation procedures for the hot water storage concept.

5. Preliminary study of chemical precipitation and the consequent change in permeability during injection and production will be made.

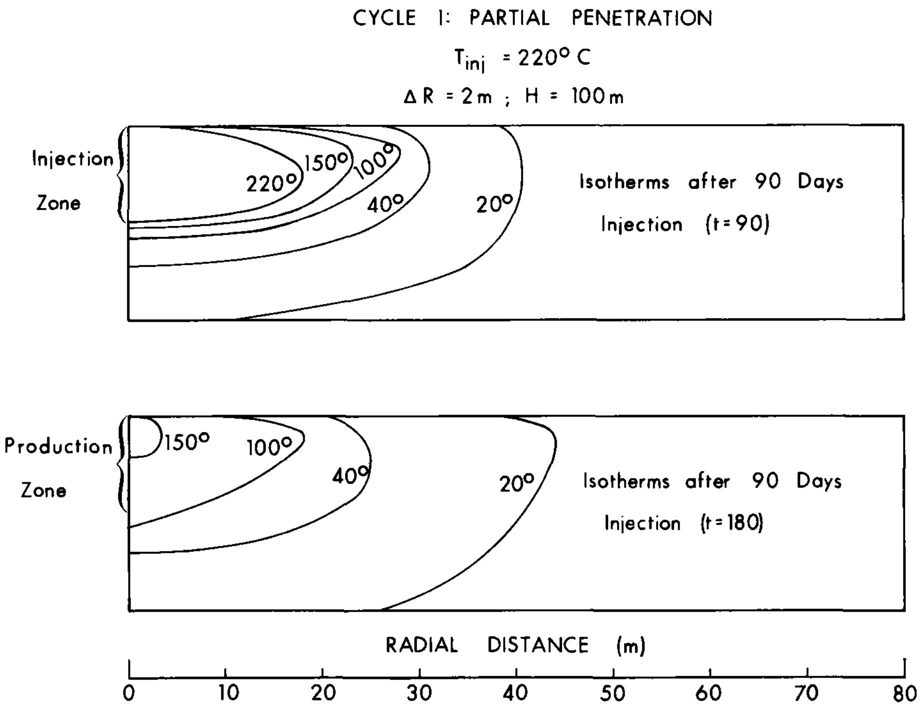

Figure 1. Temperature contours in the aquifer after 90 days of injection; and after 90 days of production in Cycle 1, for the case of semi-annual cycle, seasonal storage. The well penetrates the upper 50 m of the aquifer. Numbers labeling the contours are in degrees Centigrade.

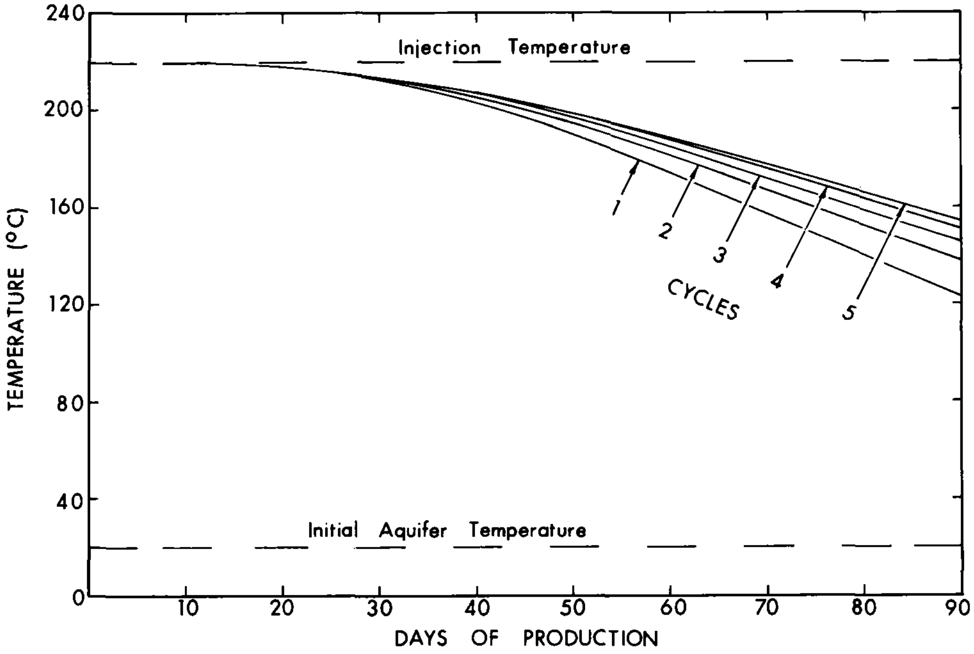

Figure 2. Temperature at the well versus production time for each cycle. The case shown is for seasonal storage with semi-annual cycle, well fully penetrating the aquifer.

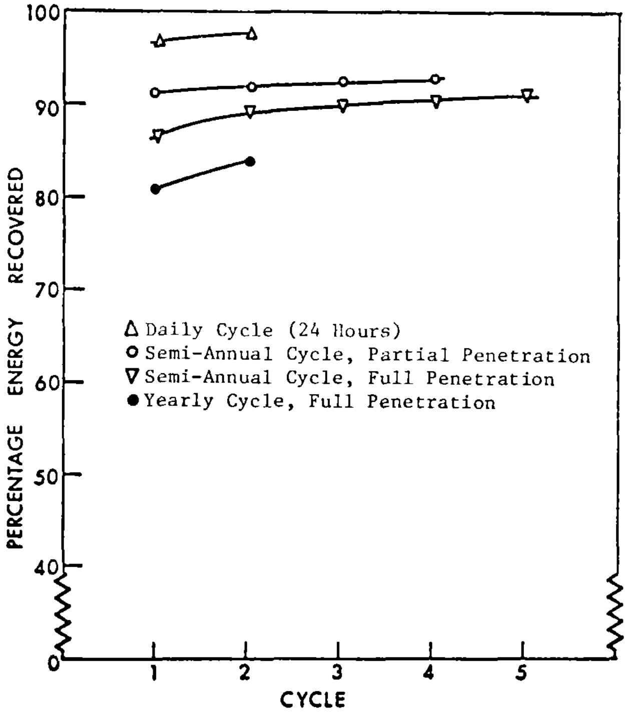

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Figure 3. Percentage of energy recovered over energy injected versus cycle number.

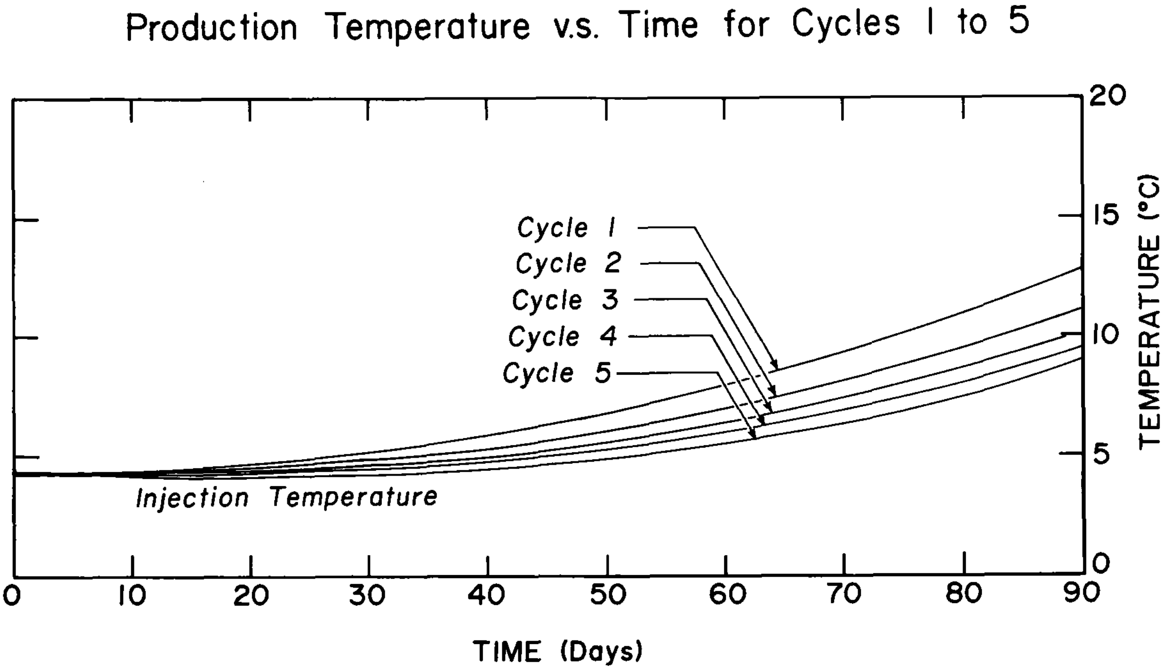

Figure 4. Chilled water storage: Temperature at the well versus production time for each of the Cycles 1 to 5.

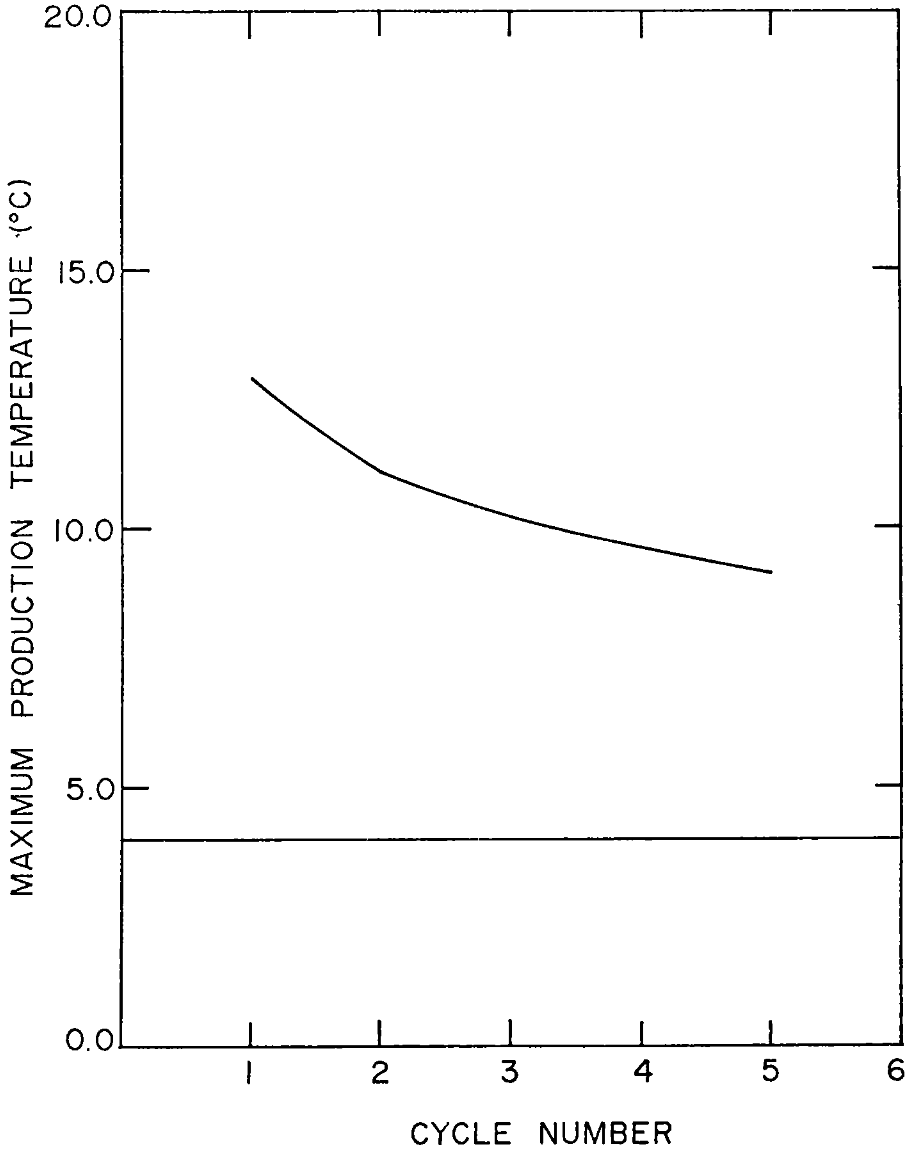

Figure 5. Chilled water storage: Temperature at the end of each production period (maximum production temperature) versus cycle number.

PROJECT SUMMARY

ORGANIZATION: Lockheed Missiles & Space Company, Inc.

ADDRESS: 4800 Bradford Drive, Huntsville, Alabama 35807

PROJECT TITLE: Analysis and Development of a Solar Energy Regenerated Desiccant Crop Drying Facility

PRINCIPAL INVESTIGATOR: D. V. Merrifield, Telephone (205) 837-1800

CONTRACT NO.: UC-7296 CONTRACT PERIOD: 1 April 1977 to 31 December 1977

CONTRACT AMOUNT: $98,849 (ERDA/UCC)

PROJECT GOALS:

The major goal of the project is to develop and demonstrate a cost-effective regenerated desiccant drying system which has more than double the energy efficiency of conventional systems and which can be operated by either solar energy or conventional fuels. The present baseline application is large-scale commercial grain drying. The major goal of the present contractual phase is to investigate methods for system improvement.

PROJECT STATUS:

An evaporative-type desiccant regeneration system is presently being evaluated through a combination of laboratory testing, computer simulation, and design analysis. Major emphasis has been placed on establishing the cost effectiveness potential of this type of system in comparison with a system using a packed column for desiccant regeneration. So far, a 5 lb/hr laboratory system has been tested with good results, math models have been developed to predict system performance, principal system tradeoffs have been identified, and a baseline system design concept has emerged for application to commercial grain drying installations.

ANALYSIS AND DEVELOPMENT OF A SOLAR ENERGY REGENERATED DESICCANT CROP DRYING FACILITY

I. Purpose

The major purpose of the present phase of the program is to establish a specific design approach which will result in the most cost effective overall system, i.e., which tends to minimize the capital equipment cost while maximizing energy efficiency. A promising approach to this, and one which is currently being evaluated, is to regenerate the dilute desiccant with an evaporator and use the latent heat of the steam from the evaporator to perform open cycle thermal drying. Additional objectives of the present contract are to identify the best method of using solar energy with the system, and to identify additional applications for this type of drying system.

II. Background Information

This work was initially begun under ERDA/USDA sponsorship (Ref. 1) with the goal of evaluating desiccant techniques for drying farm crops, with solar energy used for desiccant regeneration. The major motivation for this effort was (and remains) the fact that the nationwide drying of agricultural products prior to storage consumes a large amount of fossil fuel. This initial study resulted in several energy-efficient design concepts for solar regenerated desiccant drying processes, one of which is presently being patented by ERDA (Ref. 2). This study also indicated that energy savings of approximately 50% were realizable compared with conventional low temperature dryers, regardless of the type of energy used. For this reason it became evident that the use of the system could be considered with or without solar energy utilization.

Based on this initial work, a plan was prepared for development and demonstration of the system, and a follow-on phase was funded by ERDA. In the follow-on phase (Ref. 3), completed in March 1977, these accomplishments resulted: A baseline-system concept, using a stripping column for regeneration, was selected and a laboratory scale system was tested and math-modeled. The laboratory tests demonstrated the feasibility of the process and the ability to achieve an energy input of 1100 Btu per pound of water from the crop being dried. Performance predictions for a full-scale system showed an achievable specific energy of 980 Btu/lb, which is approximately one-half of the energy used by conventional dryers. Preliminary cost analysis showed that pay-back periods of less than 10 years were achievable if the system could be utilized at least 3-4 months of the year. The conclusion was that the system will be best suited for large drying installations with high use factor, and that additional R&D studies should be made to seek methods of further reducing system capital cost and possibly increasing system efficiency.

III. Project Description

The present-phase contract, which is aimed at improving system cost effectiveness, has as its central activity the evaluation of an evaporative method for regenerating the desiccant solution (lithium chloride). This encompasses laboratory-scale performance testing, process math modeling, cost effectiveness analysis, conceptual design analysis, and application analysis. Desiccant regeneration with either solar energy or conventional fossil fuel is being considered (two versions of the system). This phase of the project will result in recommendations for the design and demonstration/evaluation of a pilot scale system for application to commercial drying of granular crops such as corn, wheat, soybeans, and rice.

IV. Results

The principal results of the study to date are summarized as follows with regard to: (1) evaporative regeneration system characteristics; (2) laboratory test results; (3) math modeling; and (4) grain drying application analysis.

1. Evaporative Regeneration System Characteristics

The use of an evaporator and steam condenser for desiccant regeneration represents a promising alternative to the use of the stripping column and moist air condenser approach which was studied in the previous contract (Ref. 3) and reported on at last year's ERDA TES meeting (Ref. 4). Although the stripping column approach was found to be technically feasible and capable of providing energy savings of 50%, the evaporator method is under study because of the potential for cost effectiveness improvements and potential operational advantages. Based on our studies to date the evaporative regeneration system can be characterized as follows with respect to the stripping column system:

1. System energy input can be 10 to 15% lower and is insensitive to operating temperature.
2. Operating temperature can be as low as 200 F (3 psia pressure) or at the atmospheric boiling point of the desiccant (and over) depending on the optimum energy supply temperature (solar or fossil).
3. Since a steam-to-water condenser can be used instead of a moist air to desiccant condenser, the condenser size can be reduced by more than a factor of 20.
4. Desiccant flowrates are smaller by a factor of 5 to 6, resulting in a decrease in heat exchanger area.
5. Heat recovery (through steam condensation) can be accomplished at 30 to 40 deg F higher than with a moist air condenser.
6. Less equipment is exposed to desiccant solution; the process flow can be simplified.

Although the evaporator may be required to operate at sub-atmospheric pressure to limit the energy supply temperature, the cost associated with continuous air removal appears to be minimal. Based on preliminary cost estimates it appears that the cost of the evaporator unit could equal or exceed that of a stripping column. It is believed however that cost reductions elsewhere in the system will result in a net cost reduction.

2. Laboratory-Scale Evaporator/Condenser Tests

A 5 lb/hr laboratory-scale evaporative regeneration system was constructed and subjected to performance testing and evaluation. The purpose of this effort is to evaluate performance characteristics, including energy efficiency and heat recovery, and aid in developing design criteria for a large-scale system. A photo of the system, before addition of insulation, is shown in Fig. 1. It includes an electrically heated 3 inch diameter evaporator/separator, a 3.2 square foot water-cooled condenser, a 1.0 square foot heat exchanger, and necessary pumps and piping. During operation heat is removed from the condenser at 150 to 160 F and used to heat a stream of drying air. Due to a normal slight build-up of air in the system when operated at sub-atmospheric pressure, a vacuum pump is used for air removal. When operated at the design capacity of 5 lb/hr, the measured specific energy, in Btus per pound of condensate has been typically around 1440, which agrees well with predicted values. Since each 1000 Btu of recovered heat can be used to remove approximately 0.5 lb of water from the product being dried, the 1440 Btu/lb figure equates to 960 Btu/lb of water removed from the product (includes losses). Figure 2 shows typical test data at near-steady-state conditions. For this test the pressure was maintained at 6.5 psia and the evaporator temperature was 236 ± 2 F. The desiccant concentration increased from 39% to 43% as it passed through the evaporator and gave up water at the rate of approximately 4.9 lb/hr.

In summary, the laboratory system testing has demonstrated that the evaporative process is straightforward, has good operating flexibility, and will provide somewhat better efficiency than can be obtained with a stripping column regeneration system. It is also evident that a second-effect evaporator, operated by steam from the first evaporator, could be utilized, resulting in further energy savings per pound of water removed.

3. Math Modeling and Performance Prediction

Math models for the regeneration system components have been developed for computer simulation to predict performance of the evaporative regeneration system.

For a given desiccant concentration and operating temperature, the rate of water removal from the desiccant in the evaporator can be computed from water-desiccant equilibrium data. The steady state evaporator temperature at a given concentration can be determined by an iterative procedure which matches the evaporation rate and the condensation rate in the condenser at given input system design conditions. For a system where desiccant is continuously reconcentrated by circulation to and from a single storage tank, the tank desiccant concentration becomes a function of time and therefore the evaporator temperature increases with increasing incoming desiccant concentration to the evaporator. For initial and final desiccant concentrations of 36 and 43%, the evaporator temperature ranges from 240 F to 260 F. The corresponding concentrations of regenerated desiccant from the evaporator range from 45 to 53%. When regeneration is accomplished in a continuous manner such as with the use of two storage tanks as shown in Fig. 3, the incoming desiccant concentration to the evaporator is always at the initial concentration and therefore steady state operation of the evaporator can be achieved, which relaxes process control requirements. Typical operating conditions for a steady state system are presented in Fig. 3.

The predicted specific energy requirement of the system for the conditions shown in Fig. 3 is 1380 Btu/lb condensate or 935 Btu/lb moisture removed from the product being dried. The minimum achievable specific energy, using a single-effect evaporator, will be in the range of 850 to 880 Btu/lb.

4. Grain Drying Application

To date, the most promising agricultural drying application for the regenerated desiccant system is commercial grain drying at large fixed installations, at capacities up to 3000 to 5000 bushels/hr, and using either solar or conventional energy, depending on the desired savings in fossil fuel. Figure 4 shows a schematic diagram of the major components of the system, and represents our present baseline approach to design of a large-scale system using the evaporative regeneration process.

V. Future Activities

Future activities include:

1. Conduct parametric analysis of system cost effectiveness for both solar and fossil fueled systems.
2. Visit large commercial grain drying installations to further assess operational requirements. Assess other industrial applications such as lumber drying.
3. Prepare recommendations for design and demonstration of a pilot-scale desiccant dryer.

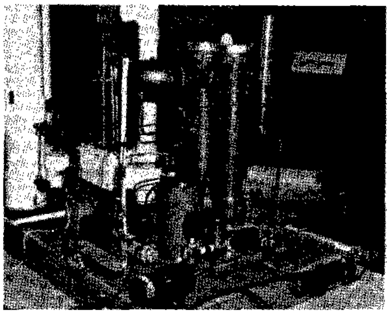

Fig. 1 - Laboratory Evaporator Experiment

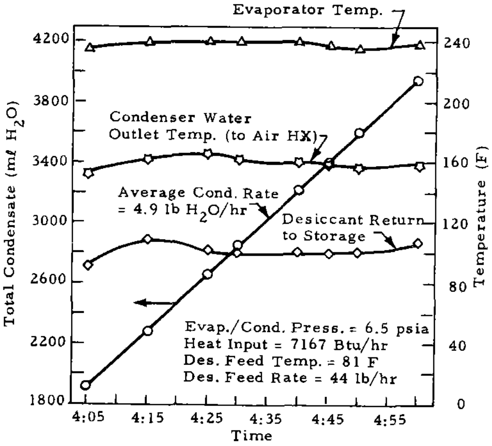

Fig. 2 - Typical Test Data

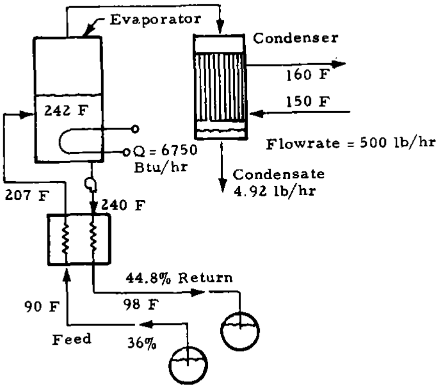

Fig. 3 - Computed Steady State Operating Conditions for Laboratory Scale Evaporator System at 25 lb/hr Feed Rate

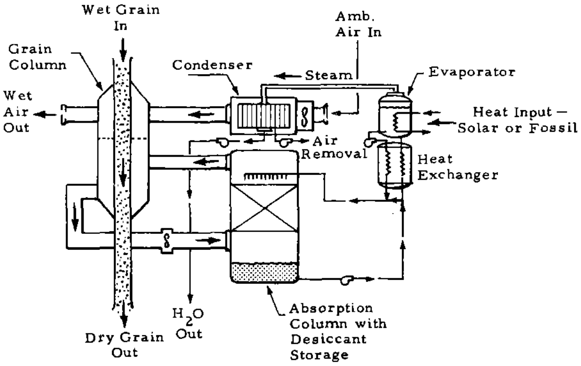

Fig. 4 - Schematic of Desiccant Grain Dryer with Evaporative Regeneration Subsystem

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3. Ko, S. M., D. V. Merrifield and J. W. Fletcher, "Analysis and Development of a Solar Energy Regenerated Desiccant Crop Drying Facility," Phase 1 Study, Final Report, Contract E(40-1) 5157, for U.S. Energy Research and Development Administration, April 1977.

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PROJECT SUMMARY

ORGANIZATION: Monsanto Research Corporation
Dayton Laboratory

ADDRESS: 1515 Nicholas Road
Dayton, Ohio 45407

PROJECT TITLE: Form-Stable Crystalline Polymer Pellets for Thermal Energy Storage

PROJECT PERSONNEL: Ival O. Salyer, Program Manager
George L. Ball III, Project Leader
Ruth A. Botham, Principal Investigator
George H. Jenkins, Research Specialist

TELEPHONE NO.: (513) 268-3411

CONTRACT NO.: EY-76-C-05-5159
CONTRACT PER.: 1 July 1976-1 May 1977

CONTRACT AMOUNT: ERDA - $172,737
OTHER - none

PROJECT GOALS:

The objective of this project was to develop and demonstrate the feasibility of using form-stable, crystalline polyethylene for a thermal energy storage (TES) bed material that is useful in the 120-140°C temperature range suitable for solar absorption air conditioning applications.

PROJECT STATUS:

The objective was achieved by controlled crosslinking of a high density polyethylene (HDPE) in pellet form. This TES material was shown to have a heat of fusion of 46 cal/g ($\sim$98% of the HDPE's heat of fusion prior to crosslinking). These TES pellets retained nearly 100% of their initial heat of fusion through 700 melt/freeze cycles in ethylene glycol, and had excellent form stability characteristics with little or no interparticle adhesion. Tests of this TES pellet material, ranging from analytical differential scanning calorimetry (DSC) to a 60-gallon prototype TES demonstration unit, consistently verified these results.

The feasibility study was completed in May 1977, and a final report issued. A more detailed cost benefit analysis was initiated in September 1977.

I PURPOSE

The major objective of this project was to develop a form-stable (crosslinked), durable, polymer pellet bed material useful for thermal energy storage. The base polymer chosen was high density polyethylene (HDPE), owing to its high initial crystallinity (and hence heat of fusion), low cost, and desirable melting range which was directly applicable to the needs of solar absorption air conditioning.

II BACKGROUND INFORMATION

The development of a cost-effective durable energy storage material is essential to the widespread utilization of solar energy for heating and cooling of buildings. High heat storage efficiency, low cost, retention of heat capacity with time and use, effectiveness around 125-150°C (255-300°F), non-toxicity, non-flammability, and non-corrosivity are desirable characteristics of such a material.

III PROJECT DESCRIPTION

The principal objective of this project was to develop a thermally, form-stable crystalline polyethylene bed material which would retain its high heat of fusion during extended use. The following tasks were undertaken to achieve this objective:

(1) Evaluation and optimization of limited controlled chemical crosslinking techniques on polyethylene;

(2) Evaluation of the heat storage capabilities of the polyethylene crosslinked products;

(3) Optimization of heat transfer to, through, and from the polyethylene, and

(4) Construction and operation of prototype laboratory and pilot heat exchange beds to demonstrate the practicality of this approach to energy storage.

IV RESULTS

Controlled, limited crosslinking of the polyethylene by chemical means was undertaken to produce form-stable, but still highly crystalline, pellets useful as a TES bed material. The achievement of the required form stability is demonstrated in Figure 1, which shows the melt and flow of an uncrosslinked pellet compared to that of form-stable pellets which do not flow on melting.

Two general methods of controlled crosslinking of HDPE were investigated: (1) crosslinking via incorporation and thermal activation of a peroxide to produce primarily C-C crosslinks; and (2) grafting of vinyl triethoxysilane onto the PE backbone, followed by hydrolysis crosslinking through Si-O-Si groups in an aqueous environment.

The method giving products with Si-O-Si crosslinks was found to be preferable. When first prepared on a relatively small scale (∿5 pounds) such crosslinked pellets demonstrated excellent form stability while retaining 91% of the starting HDPE heat of fusion (43 cal/g, as determined by DSC). Even better results were achieved from a 250 pound batch where a heat of fusion of 46 cal/g was obtained by DSC, or ∿98% of the original ΔH_f.

The C-C crosslinked PE products were somewhat inferior to the silane-grafted and crosslinked PE, with respect to both reduced heat of fusion and less form stability (the latter particularly indicated by greater interparticle adhesion). Nevertheless, this type product may also prove to be valuable as a practical TES material.

Evaluation of three prime candidate TES materials was carried out in a lab-scale (1-gallon bed) TES unit (Figure 2) to confirm analytical results. The three candidate materials included two C-C crosslinked PE products and one Si-O-Si crosslinked PE product. Form stability and heat storage capability were evaluated during and at the conclusion of up to 20 melt/freeze cycles in ethylene glycol.

Long-term stability testing was conducted on a smaller scale (<100 g). The silane-grafted/crosslinked HDPE retained ∿100% of its initial heat of fusion after 700 melt/freeze cycles, with excellent form stability and virtually no interparticle adhesion.

The silane-grafted/crosslinked PE was chosen for further scale-up (to 250 pounds) and evaluation in a 60 gallon demonstration TES unit (Figure 3). Testing of the TES material in this unit was continued on an automated basis for up to 170 cycles with no changes in PE performance.

The output of a typical pellet storage unit, in combination with an ethylene glycol heat transfer fluid, was calculated to exceed 0.5 million BTU per 1000 gallons (7000 pounds) at temperatures between 120 and 140°C.

A one-time cost for the materials in a storage bed consisting of the form-stable HDPE with ethylene glycol liquid thermal transfer is projected at ∿0.4¢ per storable BTU. For air thermal transfer, the equivalent would be ∿0.2¢/BTU. Assuming a conservative useful life of 30 years and 333 potential cycles per year for a total of ca. 10,000 cycles, the costs per BTU stored would be 0.00004¢ and 0.00002¢, respectively. These costs were determined using a best foreseeable selling price of 26¢/lb, and a reasonable projected ΔH_f value of 50 cal/g, for these TES pellets.

Assuming that 1 million storage units might be used, each of which has a capacity of one third million BTU, 330 billion BTUs could be stored per cycle. This is equivalent to 56,000 barrels of crude oil per use cycle. Assuming only a very conservative 150 days per year use (approximately 40%) and also a conservative 20-year life, this HDPE-TES material could save 168 million barrels of crude oil in its functional life. This is a savings of 18 pounds of crude oil per pound of the manufactured HDPE material.

A more optimistic usage projection and material life (300 days and 30 years) would make this savings ratio almost 60, for a savings of 560 million barrels of crude oil.

These savings are consistent with the conservation of our petroleum resources, especially over the near term. Importantly, the HDPE-TES material could be made available almost immediately (1978) and in conjunction with solar thermal units could initiate savings of our petroleum resources. Whereas it would be unrealistic to assume that the HDPE-TES material is the only or ultimate answer to thermal energy storage in the long range, it is projected that savings obtainable over the next 20-40 years would more than justify its immediate introduction into the market place.

Storage devices incorporating the HDPE-TES material could also be used immediately for load leveling from a public utility thus reducing capital requirements that in themselves require expending energy. The savings here would not be directly in saving fuel (except that probably more efficient conversion equipment would be used), but in the energy saved in reducing the requirement for additional capital facilities.

A preliminary survey of non-petroleum resources as a basis for the long-term availability of polyethylene was conducted. Potential synthesis routes using established technology were indicated based on starting materials of coal, trees, plants, and/or agricultural residues. More detailed analysis needs to be performed.

V FUTURE ACTIVITIES

Further work to confirm the long-term performance of the TES material system, and to demonstrate its utility in an air heat transfer system, is in order. Significant process improvements (and hence cost reductions) are seen as feasible with the preferred Si-O-Si crosslinked PE TES material and should be investigated. Further development of a C-C crosslinked PE product as an alternative lower cost TES material useful in the same temperature range would also warrant consideration. Finally, defining alternative form-stable polymeric TES materials useful in temperature ranges other than that considered would be most desirable.

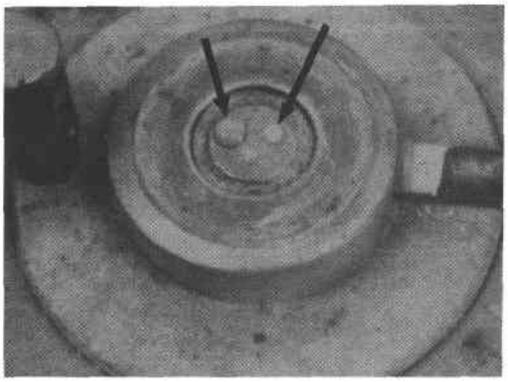

Fig. 1. Normal HDPE (left) flows on melting while modified, form-stable HDPE does not

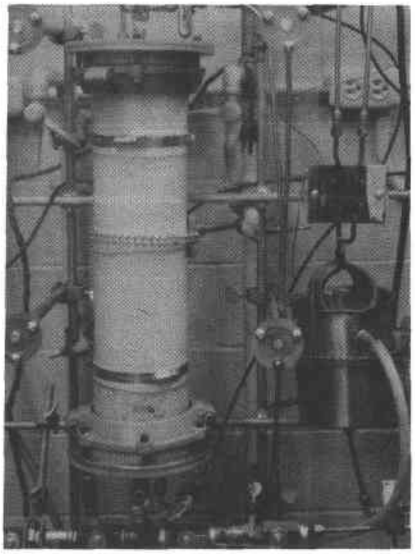

Fig. 2. One gallon lab-scale thermal energy storage unit containing a 5-lb form-stable HDPE pellet bed

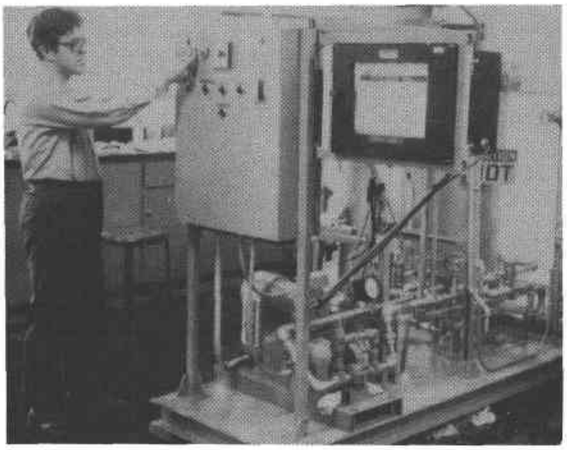

Fig. 3. 60-gallon prototype TES unit containing 250 lb of form-stable PE pellets for automatic cycling durability test

PROJECT SUMMARY

ORGANIZATION: Chemistry Division, Oak Ridge National Laboratory

ADDRESS: P. O. Box X, Oak Ridge, Tennessee 37830

PROJECT TITLE: Crystal Structures of Salt Hydrates for Thermal Energy Storage

PRINCIPAL INVESTIGATOR: William R. Busing

TELEPHONE NO.: (615)483-8611, Ext. 6539

CONTRACT NO.:

CONTRACT PERIOD:

CONTRACT AMOUNT: ERDA
OTHER

PROJECT GOALS:

1) To determine the crystal structures of phase-change materials at the atomic level by neutron diffraction experiments. These studies yield the coordinates and thermal motion parameters of all atoms including hydrogen.

2) To use this information as a basis for the modeling of these materials in terms of atom-atom potential functions. Such models are needed for the eventual understanding of crystal surfaces and interfaces involved in nucleation and growth.

PROJECT STATUS:

The structures of three salt hydrates have been precisely determined by single-crystal neutron diffraction experiments.

CRYSTAL STRUCTURES OF SALT HYDRATES FOR THERMAL ENERGY STORAGE

H. A. Levy   G. C. Lisensky[1]

Glauber's Salt, $Na_2SO_4 \cdot 10H_2O$

Thermal energy storage systems making use of the 32°C incongruent melting transition in Glauber's salt, sodium sulfate decahydrate, have been tested for a number of years. Two sources of difficulty with this working medium are separation of phases on "melting" and supercooling of the "melt" on cooling. To explore the structural chemistry of this material in the hope of understanding the molecular basis for its thermal and crystallization behavior, a neutron diffraction study was undertaken.

An x-ray diffraction study by Templeton and co-workers[2] gave the general nature of the crystal structure, including by inference the approximate hydrogen locations. An explanation of the zero-point entropy of R ln 2 observed from heat capacity studies[3] was postulated as arising from a two-fold statistical disorder in the arrangement of hydrogen atoms in certain hydrogen bonds. Although the two arrangements are crystallographically non-equivalent, the postulated structure required equal populations.

The structure was refined from a three-dimensional set of 2636 unique neutron diffraction intensities. The conclusions of the x-ray study were all confirmed, including in particular the hydrogen bonding scheme and the equal populations required by the postulated explanations of residual entropy. Accurate parameters for the hydrogen atoms, improved accuracy for all other atoms, and a full description of the thermal displacements of all atoms were provided by the refinement. Fig. 1 shows the chain of hydrated sodium ions, each adjacent pair doubly bridged by water molecules, which occurs in the structure. Also shown is a remarkably similar chain as it occurs in the structure of borax.

A new and unusual feature of the structure manifests itself in the apparent thermal displacement of the atoms of the sulfate ion. Figure 2 shows that three of the sulfate oxygen atoms have unusually large thermal displacements in directions suggesting a libration of the ion about the $S\text{-}O_5$ bond direction. An analysis of the data in terms of two distinct equilibrium orientations was carried out: in one orientation, three hydrogen bonds designated in Fig. 2 by dashed lines are formed, and in the other, three alternate hydrogen bonds designated by the opposed solid lines exist. The population ratio for the two orientations is 3:7, from which one may compute an energy difference of $-R\,T\ln(3/7) = 500$ cal/mole. The angular displacement of one orientation from the other is about 29 degrees.

Borax, $Na_2B_4O_7 \cdot 10H_2O$

The utility of borax as a nucleating agent for the crystallization of Glauber's salt from its melt was first suggested by Telkes[4] on the basis of similarity of cell parameters, similarity of chemical formula, and stability of the solid at temperatures above the melting point of Glauber's salt. For this reason, borax is usually incorporated into working media for thermal energy storage which are based on Glauber's salt. As an adjunct to our study of the structure of Glauber's salt, we have examined also, by neutron diffraction, the structure of borax, primarily to gain insight into the structural basis for its nucleating properties for Glauber's salt.

An x-ray study by Morimoto[5] had yielded the general structural arrangement, revealing that its chemical nature is best described by the formula $Na_2(H_2O)_8B_4O_5(OH)_4$. Our neutron diffraction study, based on 2373 unique reflections, furnishes accurate locations of the hydrogen atom positions and improved accuracy for the heavier atoms. The following features appear noteworthy.

The structure contains chains of hydrated sodium ion, adjacent pairs doubly bridged by water molecules, remarkably similar in nearly all details to those found in Glauber's salt (see Fig. 1). The chains in borax contain inversion centers and diad axes of symmetry which are only approximately present in the sulfate, and the intra-chain hydrogen bonds in borax have an ordered rather than disordered arrangement of hydrogen atoms. It seems likely that the close similarity of the cation chains in the two salts is important to understanding the nucleating problem.

The similarity in cell parameters, in particular the monoclinic angle β, between borax and Glauber's salt, presumably also important for the nucleation process, appears to be coincidental. Fig. 3 shows views of both structures in which the cation chains are given corresponding orientations and the shear displacements of neighboring chains are portrayed. It is the magnitude of this shear displacement which fixes the β angle. It is seen that the displacement, while similar in magnitude, is opposite in direction in the two structures. In Glauber's salt, neighboring chains are hydrogen bonded, with disordered hydrogen positions, and in borax they are not.

Sodium Thiosulfate Pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$

Sodium thiosulfate pentahydrate, melting point (semicongruent) 48°C, is considered a candidate material for low-temperature thermal energy storage. The crystal structure has been determined from x-ray data by Taylor and Beevers[6] and from neutron data by Padmanabhan and coworkers.[7] The latter study, from 350 zonal measurements only, indicated a degree of nonuniformity in the bond distances, bond angles, and hydrogen bond characteristics that could not be readily accepted, although apparently significant in terms of the claimed precision. In particular, it was claimed that one hydrogen atom of a water molecule did not participate in hydrogen bonding.

Reported in Table 1 are selected characteristics of the structure deduced from a new neutron diffraction study with 2108 three-dimensional diffraction intensities, with comparison with the earlier results. The present work eliminates the apparent discrepancies of the earlier study and shows that the hydrogen bonding net includes all the hydrogen atoms.

Figure 4 shows a portion of the chain of hydrated sodium ions as it appears in the crystal structure. An unusual feature is the bridging of three adjacent sodium ions by a thiosulfate ion in addition to three shared water molecules.

Table 1. Some characteristic features[a] of the crystal structure of $Na_2S_2O_3 \cdot 5H_2O$.

Water Molecules and Hydrogen Bonds

O—H·····A		Distances (Å) and Angles (deg)			
		O—H	H···A	O···A	H—O—H
O_4	H_1····O_3	.967(4) (.98)	1.863(4)Å (1.76)	2.824(2)Å (2.73)	103.4(3) deg (107.5)
	H_2····O_2	.964(4) (.98)	1.900(4) (1.97)	2.844(2) (2.94)	
O_5	H_3····O_3'	.961(4) (.96)	1.844(3) (1.82)	2.804(2) (2.77)	104.8(3) (106.2)
	H_4····O_3''	.964(3) (.95)	1.951(3) (1.90)	2.904(2) (2.81)	
O_6	H_5····O_4	.963(4) (.94)	1.907(4) (1.88)	2.864(2) (2.73)	104.5(3) (107.6)
	H_6····S_1	.957(4) (.92)	2.401(4) (2.52)	3.352(3) (3.30)	
O_7	H_7····S_1'	.960(4) (.93)	2.392(4) (2.38)	3.338(4) (3.13)	105.3(3) (108.2)
	H_8····O_8	.966(4) (.93)	1.890(4) (1.88)	2.855(3) (2.79)	
O_8	H_9····S_1''	.958(4) (.95)	2.419(5) (2.68)[b]	3.338(4)	106.8(3) (109.8)
	H_{10}···S_1'''	.956(4) (.96)	2.409(4) (2.59)	3.359(4) (3.40)	

[a] Second-line entries in parentheses are from Ref. 7.

[b] Not designated a hydrogen bond in Ref. 7.

Table 1 (Continued)

Sodium-Oxygen Coordination: Distances in Å.

	Present work	Ref. 7		Present work	Ref. 7
Na_1—O_1	2.381(3)	2.25(2)	Na_2—O_1	2.419(3)	2.37(2)
—O_2	2.436	2.64	—O_5	2.365	2.34
—O_4	2.402	2.45	—O_6	2.331	2.46
—O_5	2.429	2.51	—O_7	2.428	2.44
—O_6	2.433	2.36	—O_8	2.380	2.64
—O_7	2.446	2.62			

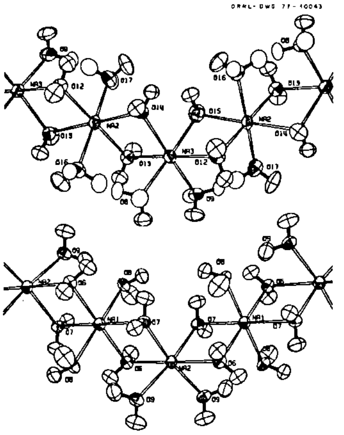

Fig. 1. Portion of the chain of hydrated sodium ions linked by water molecules as it occurs in Glauber's salt (above) and borax (below). The disorder to which the residual entropy is attributed involves the alternate orientations shown for the water molecules labeled O8, O9, O16, and O17 in the upper figure.

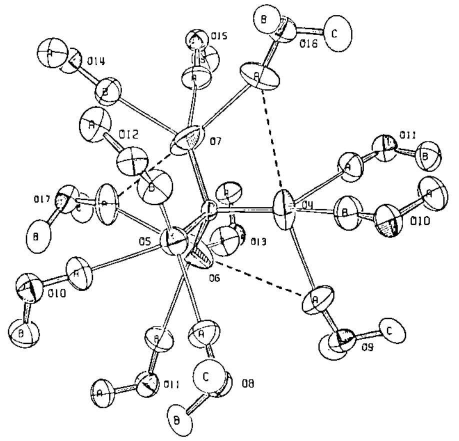

Fig. 2. Sulfate ion and its environment in Glauber's salt. The elongated ellipsoids for O4, O6, and O7 represent the average of two distinct orientations differing by a libration of 29° about the S-O_3 direction. Solid and dashed lines parallel to the long axes of the ellipsoids represent alternate hydrogen bonds. The population of the dashed-line orientation is 30% and is estimated to be 500 cal/mole less stable than the alternate arrangement.

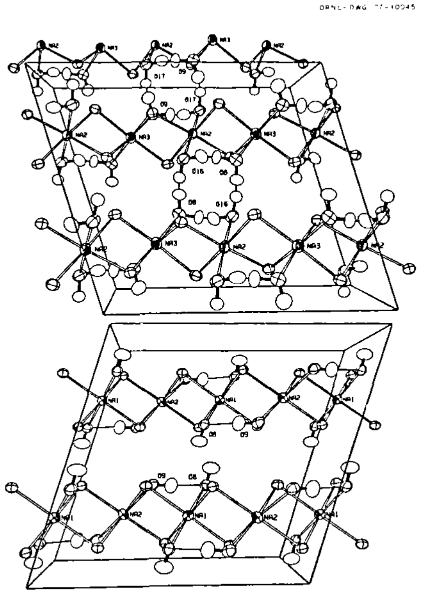

Fig. 3. Views of adjacent chains in Glauber's salt (above) and borax (below).

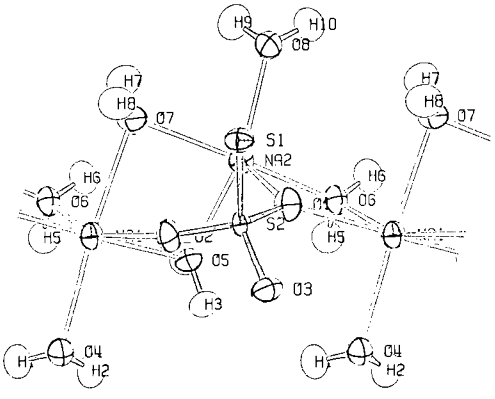

Fig. 4. Portion of the hydrated chain of sodium ions bridged by water molecules and a thiosulfate ion as it occurs in the crystal structure of $Na_2S_2O_3 \cdot 5H_2O$.

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1. Present affiliation: graduate student, California Institute of Technology.
2. H. W. Ruben, D. H. Templeton, R. D. Rosenstein, and I. Olovsson, *J. Amer. Chem. Soc.* **83**, 820 (1961).
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6. P. G. Taylor and C. A. Beevers, *Acta Crystallogr.* **6**, 311 (1952).
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PROJECT SUMMARY

ORGANIZATION: Oak Ridge National Laboratory

ADDRESS: Oak Ridge, TN 37830

PROJECT TITLE: Mathematical Modeling of Moving Boundary Problems

PRINCIPAL INVESTIGATOR: A. Solomon TELEPHONE NO.: (615) 483-8611
Ext. 3-5048

PROJECT GOALS

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

B. The derivation and analysis of methods for the analytical support of other aspects of the TES program.

PROJECT STATUS

I. *Purpose*. The aim of the mathematical modeling effort on the moving boundary problem is to provide qualitative information about the performance of the PCM and a computer simulation of system performance.

II. BACKGROUND INFORMATION

A latent heat thermal energy storage (TES) process can be viewed as one in which a phase change material (PCM) is being melted, and a phase boundary separating the solid and liquid materials, is moving with time. The purpose of this report is to describe current work on the moving boundary problem as it is related to latent heat TES subsystems. We begin with a brief sketch of earlier work in this area.

The moving boundary (or Stefan) problem has been an area of significant interest for almost a century. The early work on Stefan problems is well described in the books of Carslaw and Jaeger [12], Rubinstein [42] and the proceedings of a 1974 conference devoted to this area [35]. The excellent review article of Muehlberger and Sunderland [34] contains an extensive bibliography of papers up to 1965. We may classify work on moving boundary problems as theoretical (e.g. the correctness of the mathematical formulation of the problem), analytical (the derivation of closed form approximations to the solution of the problem), numerical (the development of computational methods for the solution of the problem) and experimental (observing and understanding the phenomenon).

As a mathematical formulation of the TES process becomes more representative of the actual process, its analysis and solution become more difficult. Thus the simplest formulation (a slab geometry and the PCM initially at its melting temperature, heat transfer due only to conduction, and a constant boundary temperature) admits of a simple closed form solution [12]; on the other hand, a formulation in which natural convection, density changes, and additional solid-solid transitions are accounted for, has not been analyzed or "solved" in any manner.

Simple formulations of Stefan problems involving only heat conduction have been subjected to extensive and fruitful theoretical study in recent years. Results of interest to us include the basic facts of existence and uniqueness of solutions to multidimensional problems [18], stable long-time behavior of the process (e.g. [11]) and smoothness of the phase boundary in the simplified formulation (e.g. [45]). These results lend credence to the formulations and their solutions (analytical or numerical) while at the same time hinting at the correctness of more realistic and complex ones. A recent result of a slightly different nature due to Lin [29] permits us under certain conditions to derive simple two-phase approximations using essentially single-phase results.

Work on analytical solutions of moving boundary problems has dominated the literature in recent years. In addition to the known explicit solution of the simplest Stefan problem in slab geometry [12] the early literature contained a variety of techniques such as those based on the use of series expansions and Laplace transforms [16], [37], and conversion to an equivalent integral equation [27].

In recent years analytical techniques have included, among others, the use of perturbation expansion techniques [23], moving heat sources [40], and moment methods [25], but have been dominated by the simple approximation techniques of Goodman [19] and Megerlin [31].

The effective use of computational methods for the solution of Stefan problems dates from the 1955 work of Douglas and Gallie [15]; in the decade following this paper many additional numerical methods were suggested, including changes of variables [30], the method of lines [43], and weak solution approaches [41]. Recent years have seen the development of variational inequality approaches (e.g. [26]), and attempts to apply finite-element techniques to Stefan problems [14]; despite the broad spectrum of numerical methods available to us we can say that few methods are well enough understood or clearly enough extendible to problems which are more meaningful than the simplest ones.

Reliable experimental results pertaining to moving boundary phenomena are neither easily obtained nor widely described. The difficulties encountered in this area are made apparent by the early work of Thomas and Westwater [53] on the melting of a paraffin wax. Effects such as additional solid-solid transitions, super heating (or cooling), free convection, dissolved air bubbles and severe density variation are known to occur in waxes (and other PCM's) (see e.g.[10]) and may result in the irrelevance of the common mathematical formulations.

Research of direct relevance to the TES program began with work on thermal regulation of space vehicle instrumentation. Many of the problems arising in the TES program were addressed in a large number of publications in this area ([54-56], [1,7,8,13,17,20,22,39]). These included the above mentioned phenomena as well as the low thermal conductivity of many acceptable PCM's. The two most important differences between this and the TES program are in the bulk of PCM involved and in the need (or lack of need) of a flexible model of the system.

In recent years activity on TES modeling has grown extensively. Recent work specific to TES includes that of Ozisik [33,36], Shamsundar and Sparrow [47], Bailey [3-6], Schmidt and Szego [46], Tanaka, Tani and Sawata [52], Abhat [1], Lammers [28], Saitoh [44], Yang [57], Hughes [21], Kauffman [24], and Balcomb [9].

III. PROJECT DESCRIPTION

The goals of our TES modeling work are:

a) the development of a computer model of the latent heat TES process;

b) the development of methods for the analytical support of the TES program.

In its initial stage the computer model of a) is to consist of a one-dimensional, time dependent solution to the moving boundary problem, based on pure conduction, and in slab, cylinder or spherical geometry. The model is then to be coupled to various sources and sinks and used to examine the performance of a TES system.

The demands of b) involve the use of analytical procedures for the **qualitative** examination of the TES process.

IV. RESULTS

Let us describe the present state of our work in each area.

SECTION 1. THE COMPUTER MODEL

As of this date the computer program for the model is being written. It is based on a modular type approach in which the temperature and phase state of each distinctive physical region is updated separately through distinct time increments. In this way the user will be able to apply the program to his own desired physical configuration (e.g. PCM capsules, capsule walls, exchange fluids, etc.) with the greatest ease.

The moving boundary problem is dealt with by either of two alternative approaches. The first is the so-called weak solution (or enthalpy) approach in which the explicit location of the phase boundary is avoided; this method has been applied successfully to a growing list of problems (see [2,32,41,48-50]). The second method is a finite element type offshoot of the Megerlin method [31] which allows for a coarse, variable space-time network; this recently developed method is described in [51]. The program will automatically choose that method which is most economical for it, unless the user overrides this choice.

SECTION 2. ANALYTICAL MODELING

Using principally the Megerlin method [31] and variants of the method of moments [25], we have examined a number of one- and two-phase problems in the slab and cylindrical cases. Let us describe our results in turn. In all cases $H, K, C, \alpha, \rho, T_{cr}$ denote the PCM latent heat, conductivity, specific heat, thermal diffusivity, density and melt temperature; t denotes time.

PROBLEM 1. MELT TIME OF A PCM CYLINDER

For a PCM cylinder of radius R_0, initially solid at the melting temperature, T_{cr}, whose wall is set at the (constant) temperature $T_1 > T_{cr}$,

$$(1) \qquad t_f \; (T_1 - T_{cr}) \; \approx \; \frac{HR_0^2}{6\; c\alpha}$$

for t_f the total melting time. Relation (1) was derived by a moment method; upon comparison with crude experiments involving the melting of test-tubes of paraffin wax it was found to predict t_f accurately for small and moderate R_o ($R_0 \approx .033$ ft.). For larger R_0 ($\approx .076$ ft.) it was found to overestimate t_f by a factor of 2; this effect, observed earlier by Thomas and Westwater [53] may be due to free convection in the melt.

PROBLEM 2. THE EFFECT OF A CONTAINER WALL

Consider a PCM region adjacent to a container wall, and initially solid at its melt temperature. If a heat source is applied at the exterior of the wall, how does the wall affect the heat storage performance of the PCM?

Assuming the container wall to be of low thermal resistance as compared to the PCM, expressions were derived via the Megerlin method for the short-time and long-time latent heat storage rate R of the PCM. A typical result is that for a fixed temperature $T_1 > T_{cr}$ at the external container wall in the case of small Stefan number $c\,(T_1 - T_{cr})/_H$. In particular we find for small time that

$$R \simeq \frac{K_c\,(T_1 - T_{cr})}{\ell} \left\{1 + \frac{2\,K_c\,t\,(T_1 - T_{cr})}{H\,\ell^2\,\rho}\right\}^{-\frac{1}{2}}$$

(for ℓ the wall thickness and the subscript "c" indicating a wall property) from which we see the dominance of the container wall on the process. However, for large time

$$R \approx \left\{\frac{K\,\rho\,H\,(T_1 - T_{cr})}{2t}\right\}^{\frac{1}{2}}$$

which is now independent of the container wall.

PROBLEM 3. AN APPLICATION OF THE RESULTS OF PROBLEM 2.

Using the results of the work on problem 2 a number of TES processes were simulated for a paraffin wax PCM and a wall of copper or methylmethacrylate, *for small to moderate times*, (e.g. measured in hours). As time increases the rates tend to agreement. Excellent agreement was obtained by comparing the predicted phase boundary location with earlier experimental data of Ukanwa, Stermole and Golden [54].

PROBLEM 4. COPING WITH DENSITY CHANGES

It is known [10] that the density of solid paraffin waxes changes strongly near the melting temperature. Although this effect will not be incorporated into the computer model at its earlier stages, we do wish to develop a simple method for modeling it. Using a variant of the method of [49] a model has been prepared in which the density is a known function of the specific internal energy. The model is "weak" in the sense that it allow us to ignore the precise location of the phase boundary.

PROBLEM 5. ENHANCEMENT OF CONDUCTIVITY

As has been noted in [56] most attractive PCM's are poor conductors; this in turn prevents rapid heat transfer between the heat source and the region of the phase boundary and hence retards the latent heat TES process. Can we enhance the conductivity of the PCM by adding a suitable good conducting metallic filler material to it?

Two attempts have been made to address this question. Using a formula due to Shuhmeister for the effective thermal conductivity of a fibrous material [38], which is a weighted average of parallel and perpendicular values, the Megerlin method was applied to various combinations of filler and PCM. Rough paraffin-wax experiments indicate that the estimated effective conductivity was too large. With this in mind an analysis of the PCM melting front along a thin good conducting fin, one end of which is at high temperature, has been performed.

We find that an approximation to the extent of the melting process along the fin is given by

$$L(t) = \frac{\sqrt{\ell K^*}}{\sqrt{3}} \left\{ \frac{2t\ (T_1 - T_{cr}}{K \rho H} \right\}^{\frac{1}{4}}$$

where ℓ and K^* are the fin width and conductivity. Similar results are found for a thin wire.

PROBLEM 6. PERIODIC BOUNDARY TEMPERATURE FOR A PCM SLAB

Consider a solid PCM slab initially at the melting temperature T_{cr}. Let its boundary temperature be

$$T = T_{cr} + B \sin \nu t$$

for B, $\nu > 0$ known.

Then the rate of latent heat storage is

$$R = \rho \sqrt{\alpha \, cHB\nu} \quad \cos \frac{\nu t}{2} \; .$$

V. FUTURE ACTIVITIES

Future directions of our work include the following:

a) comparison of the computer model and the above analytical results with available experimental data;

b) coupling of the computer model with a variety of heat sinks and sources;

c) sensitivity and parametric analyses of b);

d) documentation and distribution of computer program;

e) incorporation of density variations and free convection.

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PROJECT SUMMARY

ORGANIZATION: Oak Ridge National Laboratory

ADDRESS: P. O. Box X, Oak Ridge, TN 37830

PROJECT TITLE: Thermophysical Properties and Behavioral Characteristics of Phase-Change Materials*

PRINCIPAL INVESTIGATOR: Stanley Cantor TELEPHONE NO.: (615)483-8611
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PROJECT GOALS: (1) Producing a compilation of compounds and mixtures suitable for isothermal heat storage within the range, 90-250°C; listings in the compilation will be based on laboratory evaluation as well as on published data.
(2) Developing the differential scanning calorimeter (DSC) and other laboratory tools for rapidly evaluating chemical behavior and thermal performance of phase-change materials; these tools will be used not only for the laboratory phases of the compilation but also to support other in-house technical activities.

PROJECT STATUS: Organic compounds have been screened according to bulk price, thermal stability, and safety. Compounds were selected for further consideration if they cost less than $1.10/kg and if encyclopedia articles or handbooks indicated that they were reasonably stable chemically and were not toxic or otherwise hazardous. Of seven compounds thus selected, four (urea, phthalimide, adipic acid, phthalic anhydride) have been examined by DSC and other methods. Urea, the compound with the most favorable heat of fusion per unit cost, decreased both in melting point and in heat of fusion when thermally cycled; it also was found to supercool. Phthalimide did not decompose when thermally cycled through its melting point, nor did it exhibit much supercooling in test-tube experiments. Phthalic anhydride and adipic acid are presently being evaluated.

The differential scanning calorimeter was used with two fairly well-characterized PCM's to test its applicability for rapidly evaluating thermal decomposition and supercooling. With $Na_2SO_4 \cdot 10H_2O$, DSC data indicated (a) decrease in heat of transition with thermal cycling, and (b) considerable supercooling; with 3-6% borax added, supercooling was greatly lessened but not entirely eliminated. Measurements with paraffin wax showed that this material does not supercool nor does it degrade in thermal performance with cycling. The DSC results with these two materials confirmed (and extended) thermal performance characteristics obtained by other means. However, studies of supercooling in urea and in phthalimide suggested that DSC techniques may magnify the extent of supercooling at elevated temperatures.

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*Research sponsored by the Energy Research and Development Administration under contract with Union Carbide Corporation.

I. PURPOSE

The primary and near-term objective of this project is to compile a handbook of compounds and mixtures that melt in the range of 90 to 250°C and which are suitable for isothermal heat storage.

A secondary, longer-range — but, nonetheless important — objective of this project is to apply, adapt, and develop laboratory tools to obtain thermophysical properties and behavior characteristics of thermal-energy-storage media. Such tools are needed to estimate the performance, reliability and safety of systems that utilize materials other than air, water, and rocks.

II. BACKGROUND INFORMATION

In selecting and developing thermal storage media that store energy by melting or by undergoing solid-state transformations, several important factors can be readily identified. The transition should occur at a temperature relevant to the storage application. The heat of transition per unit cost should be high. The thermal energy which, for the most part, is charged isothermally should be discharged or extracted reversibly; kinetic impediments such as supercooling or low diffusion rates should be negligible or at least tolerable. The thermal-storage medium should not undergo thermal decomposition nor should it react with its containment or with materials added to catalyze precipitation (nucleating agents) or to increase thermal conductance (metallic fillers); such chemical reactions are likely to degrade the energy-storing potential of the medium and to shift the temperature at which the energy is stored. Of course, the material should not be hazardous. These then are the criteria that are generally considered in screening phase change materials.

The criteria thus stated can really be summarized in terms of three factors: cost, reliability, and safety. The latter two — reliability and safety — are, of course, related to the overall economics of the system. Since it is so pivotal to thermal energy storage, the cost of the medium was introduced in the first stage of the screening of phase change materials for the range, 90 to 250°C.

For evaluating selected materials, the differential scanning calorimeter (DSC) is a very important tool. With data from this instrument one can: (i) relate the storage and discharge of heat to the transition enthalpies derived from thermal spectra, (ii) obtain useful information on the extent of supercooling and other non-equilibrium phenomena that impede thermal performance, (iii) diagnose chemical changes of the phase change material (PCM) from observed changes in thermal spectra.

III. PROJECT DESCRIPTION

Since much of this report deals with DSC and also with supercooling, some details of the equipment and procedures used for these two subjects are given here.

All DSC data were obtained with a Perkin-Elmer Model DSC-2. Samples as well as indium calibration standards were encapsulated in "volatile-sample" containers in order to accommodate volume changes that accompany phase transitions. Areas under DSC curve peaks were measured with high precision by electronic planimetry: the diagram is placed on a flat bed of sensors called an Elograph (Elographics Co., Oak Ridge, TN); the area to be evaluated is selected by pressing a stylus at successive points along the curve, each press causing the sensors to produce a pair of digital coordinates; the digital information is transmitted to a PDP-8/i computer which processes the coordinates by successive application of the trapezoidal rule; the calculated area is printed by a teletype unit.

For determining supercooling in samples weighing several grams, the materials were contained in test tubes, each fitted with a metal-sheathed chromel-alumel thermocouple passing through a glass stopper fashioned from capillary tubing and polyglass tape. The thermocouple was connected to a digital temperature indicator, Doric Model DS-350. Samples were melted by placing the test tube in a water, oil, or air bath set about 10 degrees above the melting point. After melting, samples were cooled at about 1° per minute by reducing power to the bath, or at 10° per minute by removing the test tube from the bath. Crystallization was observed both directly and by noting temperatures on the digital indicator. After runs were completed with urea and phthalimide, small amounts of sample were removed for subsequent DSC measurement of supercooling. For these, cooling rates were selected to match those used in the test tube experiments.

IV. RESULTS

DSC Study of $Na_2SO_4 \cdot 10H_2O$ and Paraffin Wax

Measurements were carried out on five samples of $Na_2SO_4 \cdot 10H_2O$; three samples also containing 3-6 wt % borax ($Na_2B_4O_7 \cdot 10H_2O$), the nucleating agent for this hydrate. Samples were alternately heated and cooled up to ten times with the heat of transition derived from each recorded endotherm and exotherm. In the initial heating scan, 53-57 cal/g were absorbed at 32°C; this value is less than the 58.6 cal/g determined from adiabatic calorimetry[1] The discrepancy is mostly due to inevitable evaporation losses during weighing and crimping. Subsequent endotherms showed absorption of 22-55 cal/g, the highest values occurring when the sample was maintained overnight at 25°C. All exotherms showed that the heat released varied between 25 and 34 cal/g, crystallization occurring at 22-25°C for the samples with borax and between -10° and -13°C for samples without borax. Neither the energy released nor the extent of supercooling seemed to depend on the cooling rate which varied between 0.31 and 10°/min.

Supercooling can generally be seen in a DSC experiment in two ways: (a) by the oblong shape of the exothermic peak, and (b) by the temperature at which crystallization first begins, usually considerably less than the melting temperature obtained from the preceding endotherm (see Figure 1). Our DSC results on supercooling showed that borax markedly reduces, but does not eliminate, supercooling of $Na_2SO_4 \cdot 10H_2O$. Supercooling obtained by DSC methods ($\sim$7°) are somewhat greater than that observed by Telkes[2] for much larger samples in glass tubes. She reported that crystallization always occurred on cooling when the temperature reached 30.0 to 30.5°C, a supercooling of less than 2°.

The apparent loss in the enthalpy of transition is almost certainly due to the slow rates of recombination. When $Na_2SO_4 \cdot 10H_2O$ is heated at or above 32.4°C the "phase transition" that occurs is actually the formation of a saturated solution of anhydrous $NaSO_4$; this process proceeds rapidly. The reverse process, i.e. the recombination of anhydrous salt with aqueous solution, proceeds far less readily. In large containers, it is difficult to totally recombine the dense anhydrous salt at the bottom of the vessel with much of the solution several centimeters distant. In our DSC experiments, the height of liquid never exceeded 0.8 mm, i.e., the diffusion distances through the solution were negligible. Thus, some other factor inhibited the recombination reaction. The recent suggestion by Biswas[3] that recombination will be limited by the diffusion rate of water through the solid $Na_2SO_4 \cdot 10H_2O$ that forms around the anhydrous sulfate is a plausible explanation for the diminished heat of transition observed by DSC methods.

The paraffin wax reported here was refined from "Pennsylvania-Grade" crude oil and is designated "112/118 White Scale Wax." Its thermal behavior (heat of fusion and solid transition, melting range, low thermal conductivity) is similar to that of other refined paraffin waxes examined in our laboratory. This specific wax was selected for study because it has two solid transitions in addition to the melting transition. These transitions not only add to the thermal storage potential, but also serve as additional thermoanalytic "fingerprints" by which chemical changes in the wax can be detected.

A typical DSC spectrum for the 112/118 White Scale Wax is presented in Fig. 2 in which endotherm and exotherm were both obtained at 5°/min. In the endothermic branch, the temperature difference between the leading edge of the melting peak and the melting peak itself is about the same as the melting range (42°-48°C) for this wax observed in other devices — hot-stage apparatus and visual observation of test-tube samples immersed in a water bath. Perhaps the most interesting feature of the spectrum is that endotherm and exotherm have nearly symmetrical profiles as might be expected of a material that does not supercool. An especially noteworthy feature is that the slope of the leading edge of the crystallization peak is almost parallel to the slope of the trailing edge of the melting peak (see Fig. 2). For a substance that supercools (e.g., $Na_2SO_4 \cdot 10H_2O$, see Fig. 1) the leading edge of the crystallization peak is more nearly perpendicular to the base line that is the trailing edge of the melting peak.

Another purpose of the DSC investigation of paraffin wax was to confirm its thermal stability. Two types of experiments were run. In the first, several samples were repeatedly cycled between 10 and 70°C at 20°/min; one sample was cycled 1743 times. Thermal spectra were recorded intermittently to monitor chemical changes in the wax. No changes were observed in transition temperatures or in the profile of the transitions. The second experiment to test thermal stability also considered the problem of the poor heat-transfer properties of the wax; a simple way of improving heat-transfer is to add a good thermal conductor, such as aluminum, to the wax. However, the aluminum oxide film on the metal might catalyze isomerization reactions, which would probably lower the melting point and heat of fusion. To test these ideas, two glass cylinders of liquid wax were kept at 49°C in a water bath for some 1202 hours. One cylinder contained a piece of corrugated aluminum immersed in the wax; the other cylinder contained only the wax control sample. Thermal spectra taken at the end of the test period showed identical thermal behavior between the two heated samples and these were also identical with the spectrum obtained with the starting material. The two types of experiments indicate the excellent thermal stability of paraffin wax.

Screening and Evaluating Heat Storage Materials Melting Between 90 and 250°C

The initial step in identifying potential candidates involved searching the literature for cost, properties, and effects on safety and health. After the leading candidates are identified, the next steps involve measurement of thermal properties and thermal decomposition by DSC. The literature sources used and the procedures applied are summarized here for organic compounds — the only class of materials surveyed thus far.

First, organic chemicals available in bulk — those listed in each issue of *Chemical Marketing Reporter* — were selected if they cost 50¢/lb or less and melted in the required range. Of the 12 found, five (lactose, sucrose, benzoic acid, oxalic acid, and pentachlorophenol) were immediately eliminated from consideration due to decomposition on melting or hazardous or toxic properties; the description of the compound in *The Merck Index* (9th ed., 1976) was usually sufficient to retain or reject a candidate at this stage. The remaining seven organic compounds were ordered on the basis of storage capacity per unit cost; the compounds are listed in Table 1.

The figure of merit, given in the last column of Table 1, is highest for urea by a considerable margin. Urea also compares favorably in this regard with $Na_2SO_4 \cdot 10H_2O$ (2000 kcal/$) and with paraffin wax, 200 kcal/$. Thus, urea has thus far been accorded the most indepth evaluation.

Starting material for all DSC measurements was reagent-grade urea (Fisher Scientific Co., Fairlawn, N.J.). Initial DSC runs indicated supercooling of approximately 50° and a gradual lengthening of the leading edge of the melting peak with each successive endotherm. The longest run consisted of 29 cycles in which each heating scan was carried out at 5°/minute. The first endotherm yielded a heat of fusion of 55.2 cal/g, somewhat less than the literature value of 57.8 cal/g, the latter derived from solubility measurements; our lesser value is probably due to partial decomposition in the first heating through the melting point. Subsequent endotherms revealed decreases in the heat of fusion and these are plotted in Fig. 3. Also plotted on Fig. 3 are the temperatures of the endothermic peaks; these also tend to decrease with thermal cycle and similarly reflect the gradual decomposition of urea at its melting temperature. This DSC evaluation of urea as a thermal storage medium is pessimistic, but it does not

Table 1. Initial Selection of Latent-Heat Thermal-Storage Materials between 90 and 250°C: Organic Compounds

Compound	Formula	Melting point (°C)	Cost[a] (¢/lb)	Heat of fusion[b] per unit cost (kcal/$)
Urea	NH_2CONH_2	133	7	374
Adipic acid	$HOOC(CH_2)_4COOH$	152	36	75.2[c]
Phthalic anhydride	$C_6H_4(CO)_2O$	130	25.5	66.6
Acetanilide	$C_6H_5NHCOCH_3$	114	30	65[d]
Phthalimide	$C_6H_4(CO)_2NH$	234	40	54.4[c]
Anthracene	$C_{14}H_{10}$	218	42.5	41.2
o-Chlorobenzoic acid	$ClC1_6H_4COOH$	140	50	39.2

[a] *Chemical Marketing Reporter*, Feb. 28, 1977.

[b] Unless otherwise indicated, heat of fusion from W. Auer in *Landolt-Börnstein Tabellen*, Band 2, Teil 4, pp. 261-288 (1961).

[c] Value of heat of fusion obtained in this investigation by DSC.

[d] Heat of fusion based on cryoscopic constant given in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., vol. 1, p. 148.

rule out this compound entirely. Supercooling is about 1/2 as much for larger samples. More important is the possibility that urea might present a tolerable degree of thermal stability as the predominant component of a eutectic mixture with a lower melting temperature. However, for any thermal storage application, urea would have to be kept dry so as to prevent its hydrolysis.

Commercially available Phthalimide ("Baker Grade, melting point, 235-237°C," J. T. Baker Co., Phillipsburg, N.J.) was found by DSC measurement to have a melting point of 234°C. Solid-phase transitions in the range -63 to 234°C were searched for, but none were observed. A sample that was alternately heated and cooled 26 times between 200 and 240°C showed minor, random variations in melting point and in heat of fusion; the favorable thermal stability is most likely associated with the fused-ring structure of the compound. During cooling scans, phthalimide was observed to supercool approximately 28° but test-tube studies indicated practically no supercooling. From areas under endothermic curve peaks, the heat of fusion was found to be 48.1 ± 0.5 cal/g.

For Phthalic Anhydride, DSC measurements agree with the published[4] heat of fusion, 37.5 cal/g. No solid state transitions were observed between -65°C and the melting point (130°C). In the four thermal cycles studied thus far, there have been no changes in either melting point or heat of fusion. For Adipic Acid, our DSC value for the heat of fusion is 59.7 cal/g, more than twice the value given in an encyclopedia article[5]. Only slight supercooling, 2-4°C, has been observed in DSC exotherms. No solid-state transitions were observed from -65°C to the melting point, 152°C.

V. FUTURE ACTIVITIES

Within the next six weeks, supercooling studies and DSC evaluations of adipic acid, acetanilide, and phthalic anhydride will be completed. These results plus those given here will form the basis of an interim report on organic compounds segment of the handbook of isothermal heat-storage materials.

Organic mixtures, inorganic compounds and mixtures will then be examined using procedures similar to those applied to organic compounds. A completed handbook will be in draft form by the end of FY 1978.

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4. D. A. Crooks and F. M. Feltham, *J. Chem. Soc.*, 899 (1946).
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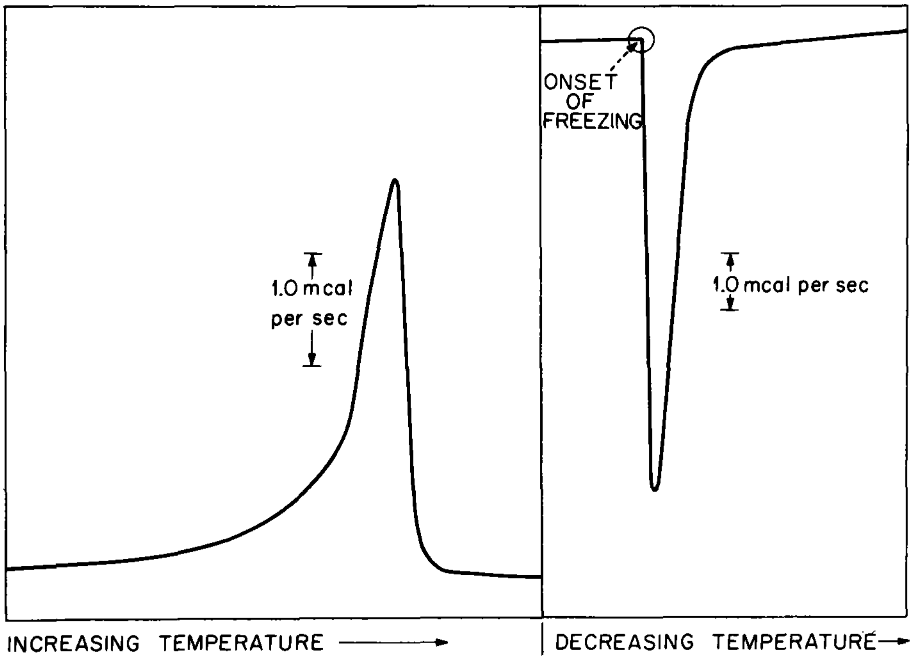

FIG. 1. DSC ENDOTHERM AND EXOTHERM OF $Na_2SO_4 \cdot 10H_2O$ WITH 4% BORAX TAKEN CONSECUTIVELY AT THE SAME SCAN RATE AND CHART SPEED. ASYMMETRY BETWEEN PEAKS INDICATES SUPERCOOLING.

ORNL-DWG 77-16193

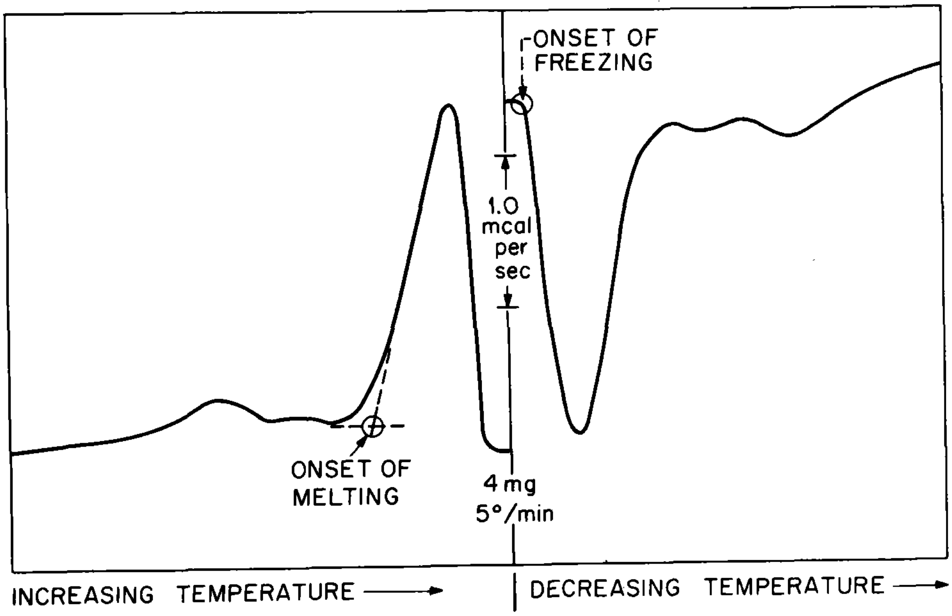

FIG. 2. THERMAL SPECTRUM OF A PARAFFIN WAX (112/118 WHITE SCALE WAX). ENDOTHERM AND EXOTHERM TAKEN AT THE SAME SCAN RATE AND CHART SPEED.

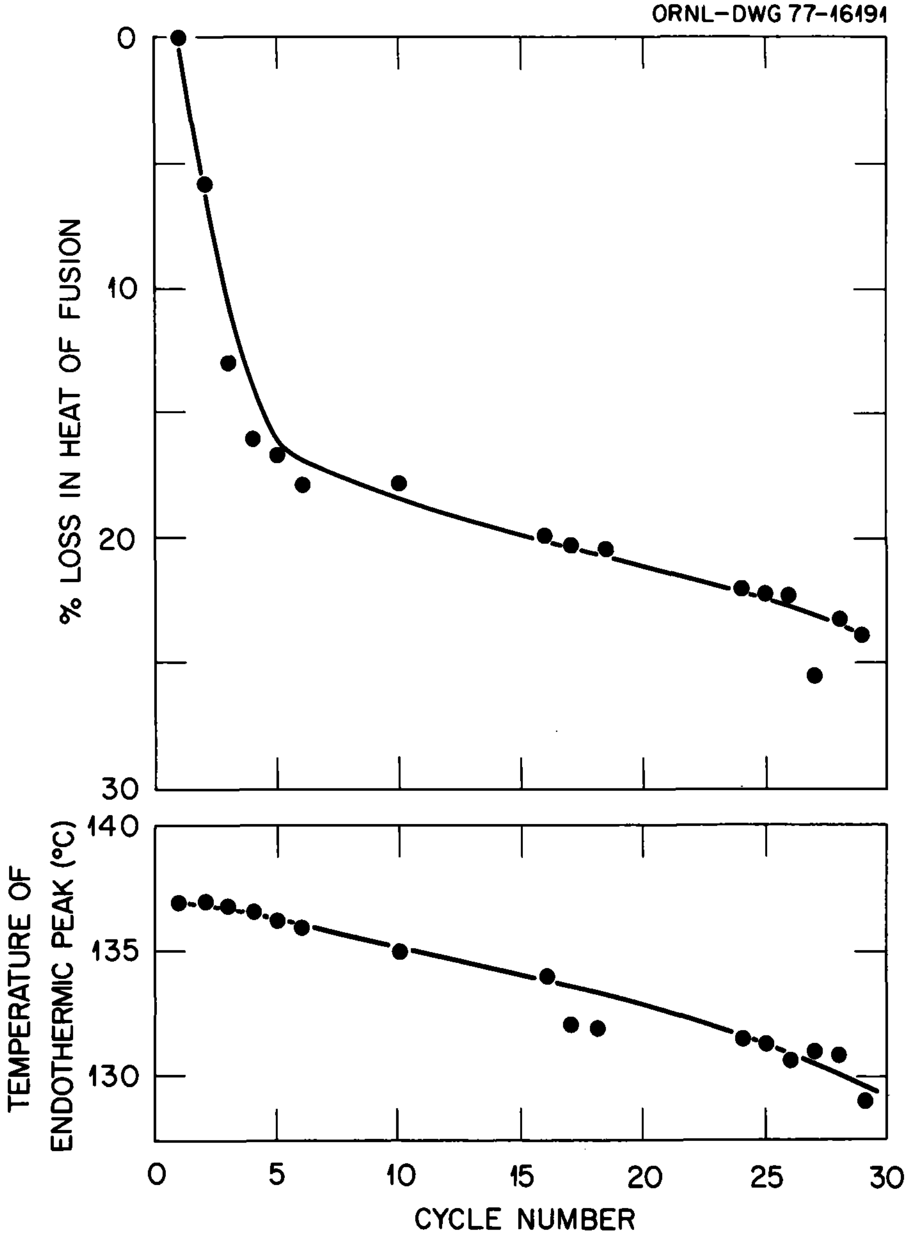

FIG. 3. DECREASES IN HEAT OF FUSION AND MELTING PEAK TEMP. FOR A SAMPLE OF UREA CYCLED IN A DSC. DATA FROM ENDOTHERMS TAKEN AT 5°/MIN.

PROJECT SUMMARY

ORGANIZATION: The Pennsylvania State University

ADDRESS: Mechanical Engineering Department
The Pennsylvania State University
University Park, PA 16802

PROJECT TITLE: Prediction of the Performance of Solid Sensible Heat Thermal Storage Units

PRINCIPAL INVESTIGATOR: F.W. Schmidt

TELEPHONE NO.: (814) 865-2072
(814) 865-2519

CONTRACT NO.: AER-75-16216

CONTRACT PERIOD: July 1, 1975-
Dec. 31, 1977

CONTRACT AMOUNT: $114,000

PROJECT GOALS: Prediction, Optimization and Experimental Verification of the Performance of Solid Sensible Heat Thermal Storage Units

PROJECT STATUS: The computer programs have been developed and are currently being documented to enable the program to be made available to interested parties. The optimization of a "single blow" flat slab storage unit has been completed. Experimental results have been obtained and are currently being analyzed.

I. PURPOSE

The objectives of this grant are:

1) The determination of the parameters which characterize the transient behavior of a sensible heat thermal storage unit;

2) The determination of the transient response of single and two fluid units;

3) The development of a procedure for the optimization of the design of these units to provide either maximum utilization of the heat storage capability of the material or to maximize the storage of the available thermal energy in the fluid entering the unit. Economic considerations may be used in the selection of the final design;

4) To conduct an experimental program to assist in the evaluation of the accuracy of the predicted results and to develop techniques for the on-site fabrication of such units.

II. BACKGROUND INFORMATION

The current emphasis on energy conservation and the utilization of alternative energy sources has encouraged many industrial and commercial establishments to institute energy management studies. The objectives of these studies are to identify all sources and demands for energy placed upon the company and to match these quantities whenever possible in order to reduce the total amount of energy which must be purchased. The matching of the energy supplies and demands may impose difficulties because, frequently, they do not coincide timewise and more efficient utilization of the available energy sources can be achieved if thermal storage capabilities are installed.

Although there are many ways of storing thermal energy, the most common units currently in use are those involving sensible heat storage. There are basically two types of sensible heat storage units, one being those units in which the storage material also acts as the energy transporting fluid. The second group contains those units in which the storage material is stationary and the energy transporting fluid flows over or through the storage material. This study is concerned with stationary storage units whose geometrical configuration is such that discrete fluid passages and continuous elements of storage material can be identified. Packed bed storage units will not be studied. Some applications of sensible heat storage units are of such a nature that they operate with definite time cycles, thus obtaining a periodic operating mode. The majority of the application, however, involves time varying flow rates and fluid inlet temperatures. It thus becomes necessary to be able to predict the transient response of these units if they are to be used effectively.

III. PROGRAM DESCRIPTION AND RESULTS

The transient response of heat storage units with two basic geometrical configurations is to be determined. These involve both one and two fluid solid sensible heat storage units with rectangular and hollow cylindrical storage material cross sections.

Single Blow Units

If the one fluid heat storage unit is considered to be initially at a uniform temperature and the incoming fluid experiences a step change in temperature, the unit is referred to as being in a "single blow" operating mode. The transient response of both the slab and the hollow cylindrical cross section units was obtained using finite difference technique. The mathematical model used considered the thermal storage material to have a finite thermal conductivity, thus both axial and transverse conduction effects were accounted for. The results for the flat slab configuration have been published [1] while those for the hollow cylindrical cross section will be made available in the near future. An interpolation program has been written which, utilizing the results of the parametric studies, enables one to readily determine the nondimensional outlet fluid temperature and heat storage for any specific operating conditions. These results, in conjunction with superposition techniques, can be used to predict the behavior of the storage unit under arbitrary time-varying inlet fluid conditions. The response of these units to time-varying inlet fluid and mass flow rates can also be determined using the complete finite difference program. This program is currently being documented and will be made available in January of 1978.

Design Optimization

The optimization of the design of a solid sensible heat storage unit initially at a uniform temperature has been completed. The storage unit is composed of a number of rectangular cross sectional channels for the flowing fluid connected in parallel and separated by the heat storage material. The Complex method for constrained nonlinear optimization as presented by M.J. Box is utilized with some modification. The design optimization is based upon achieving maximum utilization of the heat storage or removal capabilities of the material for a given set of operating conditions. This is achieved by varying the storage units' geometry while placing restraints on the maximum and minimum length of the unit, fluid channel size, storage material thickness, maximum and minimum outlet fluid temperature, and the minimum amount of heat to be stored. The results of this work have recently been published [2].

Heat Storage Exchangers

As noted previously, the supply and demand for energy placed upon a system do not usually coincide timewise. On many occasions, it is necessary to work with several fluid streams which may, on an intermittent basis, result in heat being added and withdrawn from storage at a given instant of time. System requirements can be easily satisfied if the fluid streams have the same physical properties and the fluid itself is used as the storage material. If the fluids are different and cannot be mixed nor serve as the storage material, the design of the storage system becomes more complex. An example of such a system would be the use of the energy contained in the exhaust gases from an industrial process, waste heat recover, to provide domestic hot water and space heating. There are several ways in which the system could be designed. One approach would involve the use of a secondary storage fluid and the heat is transferred to the storage fluid from the different fluid streams using heat exchangers. A second method would involve the passing of the fluids through channels separated by the solid storage material. Such units can be termed thermal storage exchangers. The flow rate and inlet temperatures of the fluids could vary in an arbitrary manner so that at a given time, a fraction of the energy loss by one fluid would be stored while the remaining energy was transferred to the other fluid. Other combinations for the distribution of the energy between the fluids and the storage material would be possible and depend upon the operating conditions of the unit.

The transient response characteristics of a solid sensible heat storage exchanger which interacts with two energy transporting fluids has been determined. The storage unit is composed of a series of large aspect ratio rectangular channels for the fluids, separated by slabs of the heat storage material, as shown in figure 1. The hot and cold fluids flow in counter current fashion, in alternate channels so that each slab of storage material is in contact with both fluids. The entire system is considered to be initially in equilibrium at a uniform temperature and a step change in the inlet temperature of one of the fluids is imposed. The transient response of the unit is predicted. These results may also be used with a superposition method to determine the transient response of a storage exchanger to an arbitrary time variation of one of the fluid's inlet temperature.

The following assumptions were made in formulating the mathematical model;

a) constant fluid and material properties
b) uniform convective film coefficients
c) two dimensional conduction within the storage material
d) constant fluid mean velocities
e) the initial temperature distribution in the storage material is uniform
f) the process is initiated by a step change in the inlet temperature of the hot fluid.

The differential equations relating the temperature in the solid and the fluids are the two dimensional transient heat conduction equations for the solid material coupled to the two one-dimensional conservation of energy equations for the fluids.

These equations are nondimensionalized using the following nondimensional groups:

Biot numbers: $Bi_h \equiv \frac{h_h w}{k}$, $Bi_c \equiv \frac{h_c w}{k}$;

Fourier number: $Fo \equiv \frac{\alpha\theta}{w^2}$;

dimensionless temperature: $T \equiv \frac{t - t_{ci}}{t_{hi} - t_{ci}}$;

dimensionless flow length: $X \equiv \frac{x}{w}$;

dimensionless transverse coordinate: $Y \equiv \frac{y}{w}$;

thickness/length ratio: $V^+ \equiv \frac{w}{L}$;

capacity rate ratio for fluids: $C^+ \equiv \frac{\dot{m}_c C_c}{\dot{m}_h C_h} = \frac{E_c}{E_h}$;

convective resistance ratio: $R^+ \equiv \frac{Bi_h}{Bi_c}$;

and $G_c^+ \equiv \frac{P_c k}{E_c}$, $G_h^+ = \frac{P_h k}{E_h}$

The resulting set of nondimensional equations and the appropriate initial and boundary conditions are solved mathematically using a procedure described in [3].

In order to present the data in a reasonably compact practical form, a further set of assumptions were made. Both energy transporting fluids were assumed to have identical physical properties and both channels had identical dimensions. The NTU was also introduced as a new variable. The following relationships between variables were obtained assuming both flows to be turbulent;

$$Bi_h = \frac{Bi_c}{C^{+0.8}}, \qquad NTU = \frac{SU}{E_{min}} = \left(\frac{G^+}{V^+}\right)_{max}\left[\frac{1}{Bi_c} + \frac{1}{Bi_h} + 1\right]^{-1}$$

and $$\frac{Fo}{(G^+/V^+)_{max}} = \frac{E_{min}}{(\rho CV)_m}\,\theta.$$

The fraction of the steady state heat stored at time θ is defined as

$$Q^+ = \frac{[\text{amount of heat stored at time } \theta]}{[\text{amount of heat stored at steady state}]} = \frac{Q}{Q^{ss}} = \frac{\overline{T}_m}{\overline{T}_m^{ss}} .$$

where

$$\overline{T}_m^{ss} = \frac{1}{2} \frac{[e^M(\frac{N}{M} - 2) - \frac{N}{M}]}{C^+ - e^M} \quad \text{for } C^+ \neq 1 ;$$

$$\overline{T}_m^{ss} = \frac{1}{2}[1 + \frac{N^*}{NTU + 1}] \quad \text{for } C^+ = 1 \quad \text{where } M = NTU\ (1 - C^+) \quad \text{for } C^+ < 1,$$

$$M = NTU\ (\frac{1 - C^+}{C^+}) \quad \text{for} \quad C^+ > 1$$

$$N = (C^+ + 1) + (C^+ - 1)N^* \qquad N^* = \frac{\frac{1}{Bi_c} - \frac{1}{Bi_h}}{\frac{1}{Bi_c} + \frac{1}{Bi_h} + 1} .$$

The transient response for $C^+ = 1.0$ is shown in figure 2. It should be noted that as the NTU increases, the curves shift to the left. For a given NTU, an increase in the Biot number will also shift the curves to the left. The reader is requested to consult [3] for additional results and a more complete discussion of their significance.

EXPERIMENTAL PROGRAMS

The transient response of a thermal storage unit to step changes in inlet fluid temperature and flow rates was determined experimentally. The unit consists of five rectangular flow channels separated by the storage material as shown in figure 3. The storage material used was Feolite, a material composed of enriched iron ores (93% ($Fe_2O_3 + Fe_3O_4$)). The fluid used in this study was air. A complete description of the experimental unit is given in [4].

The experimental results were compared to those obtained using the finite conductivity model previously discussed. They were also compared with an earlier model which assumed that the thermal conductivity in the storage material was infinite in the direction perpendicular to the flow and zero in the direction of flow. This model is referred to as the simplified model. Typical results obtained for a step change in the inlet fluid temperature are shown in figure 4. The temperature of the inlet fluid entering the unit was 83.5°C, the initial temperature of the storage unit, 31.0°C, the mass rate of flow of the air, 0.112 kg/s and the Biot number, 0.59. The agreement between the experimental results and those predicted by the finite conductivity model was excellent. The simplified model tended to overpredict the heat storage. Further results are presented in [4].

IV. FUTURE ACTIVITIES

The finite difference programs are being documented and will be available for distribution in January, 1978. A draft of the final report is presently being prepared.

NOMENCLATURE - Heat Storage Exchanger

C - specific heat at constant pressure
E - fluid heat capacity
h - convective film coefficient
k - thermal conductivity of storage material
L - length of unit
$\dot{m}$ - mass rate of flow

P - heated perimeter of flow channel
Q - amount of heat stored
t - temperature
T - dimensionless temperature
$\bar{T}_m$ - mean storage material dimensionless temperature averaged over its volume
V - volume of storage material
w - thickness of storage material
x - axial coordinate
y - transverse coordinate
ρ - density
θ - time
α - thermal diffusivity of storage material

Subscripts

c - cold fluid
ci - cold fluid entering
h - hot fluid
hi - hot fluid entering
m - storage material

Superscript

ss - steady state condition

NOMENCLATURE - Experimental Study

c - specific heat of storage material, kJ/m^{3} ^{o}C
Bi - Biot number, hw/k
h - convective heat transfer coefficient, w/m^{2} ^{o}C
k - thermal conductivity of storage material, w/m^{o}C
$\dot{m}$ - mass flow rate, kg/s
M - mass of heat storage material, kg
Q - heat stored or removed, kJ
Q^{+} - nondimensional heat storage, $Q/Mc(t_{fi} - t_o)$
T_{fo} - nondimensional fluid outlet temperature, $(t_{fo} - t_o)/(t_{fi} - t_o)$
t - temperature, ^{o}C
w - thickness of storage material slab, m
ρ - density of heat storage material, kg/m^{3}

Subscripts

fi - fluid inlet
fo - fluid outlet
o - initial

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1. F.W. Schmidt and J. Szego, "Transient Response of Solid Sensible Heat Thermal Storage Units-Single Fluid," J. Heat Transfer, Trans. ASME, Vol. 98, No. 3, p. 471-477 (1976).

2. F.W. Schmidt, R.R. Somers, II, J. Szego and D.H. Laananen, "Design Optimization of a Single Fluid, Solid Sensible Heat Storage Unit," J. Heat Transfer, Trans. ASME, Vol. 99, No. 2, p. 174-179 (1977).

3. J. Szego and F.W. Schmidt, "Transient Behavior of a Solid Sensible Heat Thermal Storage Exchanger," ASME paper 77-HT-37.

4. J. Szego and F.W. Schmidt, "Experimental Investigation of a Solid Sensible Heat Thermal Storage Unit," submitted for publication, 6th International Heat Transfer Conference.

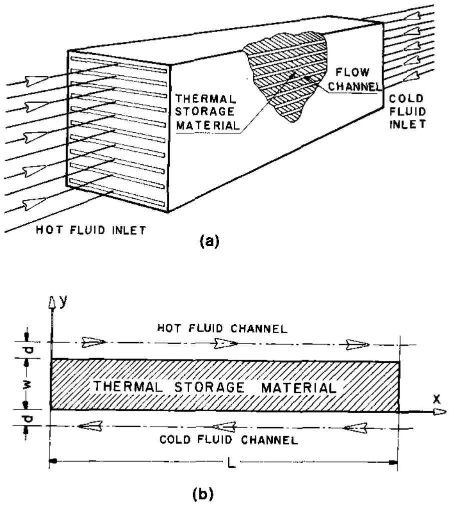

FIGURE 1

HEAT STORAGE EXCHANGER

a) Schematic of typical unit
b) Cross section considered in analysis

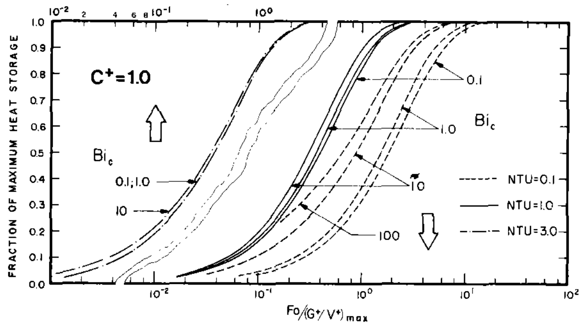

FIGURE 2

FRACTION OF STEADY STATE
HEAT STORED

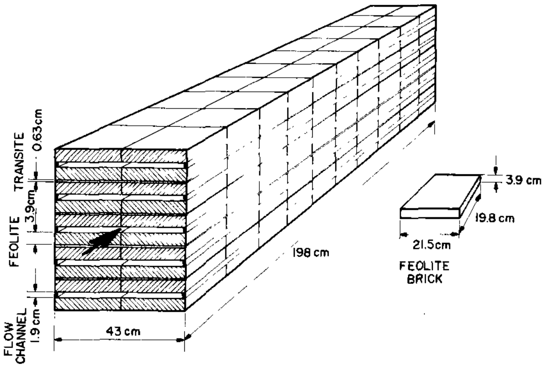

FIGURE 3

THERMAL STORAGE UNIT

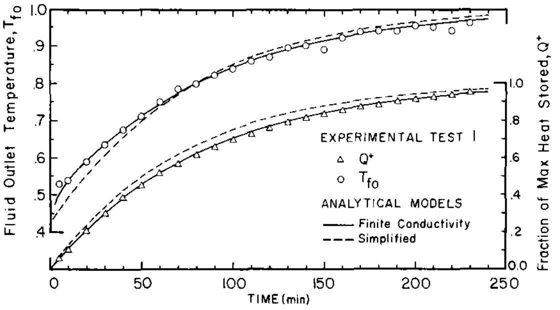

FIGURE 4

COMPARISONS OF PREDICTIONS
WITH EXPERIMENTAL DATA

PROJECT SUMMARY

ORGANIZATION: Rocket Research Company
(Intalco Aluminum Corporation & Bonneville Power Administration)

ADDRESS: York Center
Redmond, Washington 98052

PROJECT TITLE: Applications of Thermal Energy Storage to Process Heat and Waste Heat Recovery in the Aluminum Industry

PRINCIPAL INVESTIGATOR: L. B. Katter

TELEPHONE NO.: (206) 885-5000

CONTRACT NO.: EC-77-C-01-5080

CONTRACT PERIOD: 8/30/77 – 5/30/78

CONTRACT AMOUNT: ERDA $89,428
OTHER

PROJECT GOALS:

The goal of this project is to investigate improved methods of waste heat utilization in the primary aluminum industry through thermal storage.

PROJECT STATUS:

The project is currently in its first month. The team is composed of Rocket Research Company (contractor to ERDA), Intalco Aluminum Corporation (aluminum manufacturer), and Bonneville Power Administration (energy supplier). A survey of waste heat streams at Intalco shows that the gasses drawn from the aluminum reduction cells represent an attractive energy source at approximately 200°F and 4.6 x 10^8 Btu/hr. A ready use for this heat exists in the space heating requirements from the cities of Ferndale and Bellingham, 5 and 20 miles distant respectively. Energy storage, in the form of hot water, will serve to allow greater use of the constant source by the variable demand.

I. Purpose

This project is designed to show how existing energy storage techniques can enhance the utility of low temperature waste heat streams. The system will be designed, costs estimated, and an optimum storage size defined.

II. Background

The electrolytic reduction of aluminum oxide to aluminum is a 24 hr/day, 365 day/year operation. Energy source is primarily electrical, with minor use of fossil fuels for anode production and holding furnace operation. The major heat losses from the operation are found in low-temperature gas streams from the surface of the reduction cells. Pollution control requires the filtration of these gasses, where particulate matter is recovered and returned to the process as raw material.

This very large, low-temperature energy stream can be applied as an energy source for a district heating system for surrounding communities. As the requirement for space heating is notably cyclical, especially on a daily basis, thermal energy storage will allow a greater number of users the benefit of this low-cost energy, or a decreased use of "topping power" during cold snaps.

III. Project Description

Seven tasks are planned for the project. These are described in the following paragraphs.

The first task is a literature search and a survey of aluminum producers. The purpose of this task is to assure that the overall concept will be applicable to as large a fraction of the industry as possible. In the second task, these data are compiled and the storage material chosen.

During the third task, the accuracy of temperature and flow data will be increased. Whereas, much process data exists, this is generally broadly averaged over different seasons, order patterns, etc. The fourth task is included to assure that all site and process restrictions upon the interface between the heat recovery system and ongoing operations are delineated.

The major effort of this project falls in the fifth task, sizing and performance analysis. Analysis will be performed through the development of a computer model of the overall system. Optimum dimensions for the system can be found from multiple runs of this model, differing in the specification of dimensions in question. It is expected that the most critical tradeoffs will involve storage capacity and transmission system size versus energy delivered to customers and system overall cost.

The final two tasks involve the preparation of preliminary system design drawings and an implementation plan.

IV. Results

The project is currently in its first month. Literature search has located district heating system design criteria from both domestic and foreign service. Historical data on the heating and cooling demand for the Bellingham area is on order.

All major producers of aluminum have been contacted by telephone, and have agreed to complete a short questionaire regarding their specific processes. Plants have been visited which use each of the four major variations of the Hall-Heroult process for aluminum production. Considerable enthusiasm for the project has been manifested by the aluminum association, the mayors of Ferndale and Bellingham, Western Washington College (a large potential district heating system customer), as well as nearly every aluminum manufacturer. While all the survey responses are not yet received, it appears that the concept could be applicable to at least 50 percent, perhaps 75 percent, of the aluminum manufacturing sites, with only minor variations.

V. Future Activities

Instrumentation planning is in process, with data flow to commence in mid-October. Other tasks, as described in Section III and shown in Figure 1, the Project Schedule, are anticipated on schedule.

PROCESS HEAT RECOVERY PROGRAM SCHEDULE

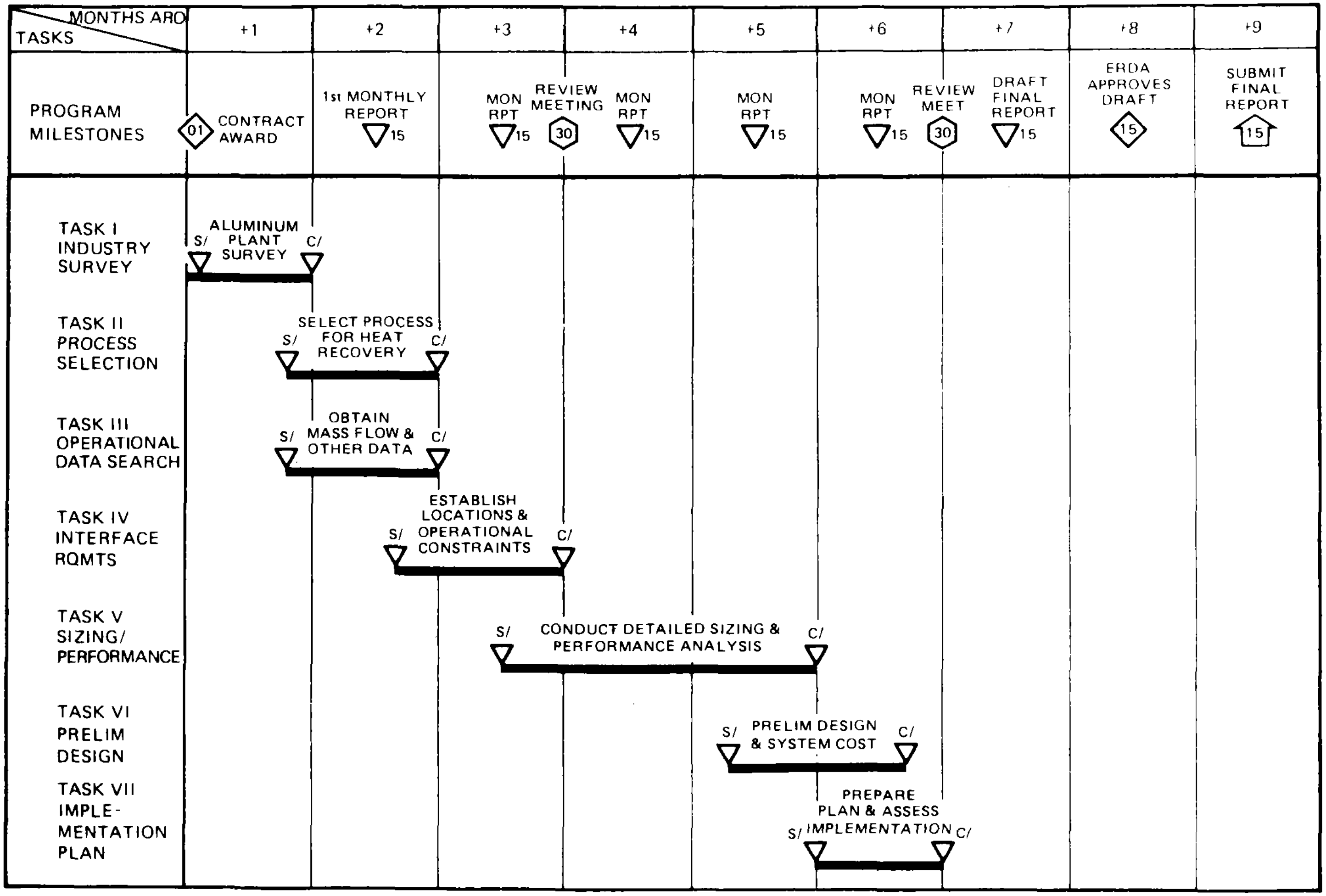

Figure 1

Suntek Research Associates
500 Tamal Vista Blvd. #506
Corte Madera, CA 94925
(415) 924-6887

THERMOCRETE & THERMOTILE

BUILDING COMPONENTS WITH ISOTHERMAL HEAT STORAGE

Principal Investigator: Day Chahroudi

Contract No: EY-76-C-05-5177
Contract Amount: $134,871
October 30, 1976 to October 30, 1976

Project Goals

The primary goal of this project was to take Thermocrete from laboratory curiosity status to a material with predictable and reproducible behavior. Another goal was to determine approximately what performance specifications represent realistic expectations for the material and a useful, marketable product. A measured heat of fusion was sought which represents close to theoretical values of 100% pure materials. This heat of fusion was expected to remain essentially undiminished after 1000 freeze-thaw cycles. The thermal conductivity was expected to be high enough to permit easy access for storing and removing heat. The compressive strength was expected to be adequate for structural applications (1000 psi) in one case and adequate for easy handling and packaging in another case (300 psi). The sealant was expected to remain leak proof throughout the 1000 cycles. The matrix, sealant and PCM were expected to be compatible in that the matrix and sealant should not be chemically corroded by the PCM or physically damaged by the freeze-thaw cycles. The cost of materials was expected to be below five cents per pound. The fabrication methods should be capable of being scaled up to mass production.

Project Status

All of the above goals have been met with PCM's in three temperature ranges - 19-25°C for distributed storage, 25-28°C for passive solar, and 44-46°C for active solar. A suitable PCM in the 75-90°C range for fossil fuel heat storage was not identified.

I. Purpose

The primary purpose of this contract was to demonstrate the feasibility of developing building components with isothermal heat storage through the use of a phase change material (PCM) suspended in a concrete matrix. Depending on the degree of porosity and therefore the strength of the matrix, the building components are structural or non-structural. A typical structural element consists of a 4"x8"x16" block with 50% porosity and 1000 psi compressive strength. This strength is sufficient to pass building codes for load bearing walls. Non-structural elements typically use a matrix with 80% porosity and have a compressive strength of 300 psi.

The areas requiring investigation included:

1. PCM's for each of the application temperatures
2. Nucleating agents appropriate for each PCM.
3. Matrices with the requisite structural and fabrication properties
4. Sealants to contain the PCM in the matrix.

The above material components must work together in a compatible system with no destructive interactions.

Besides screening material components and assembling them into systems, it was necessary to define the end uses where Thermocrete would find cost effective application. The material systems and end uses were then tentatively integrated into completed packages. A final selection of material-end use packages must wait for a definitive study of production methods and economics.

II. Background Information

Members of the Suntek team have a long history in developing PCM thermal storage systems. In 1970 a suspension medium was developed for Glaubers salt consisting of wood pulp fibers, which are inexpensive, readily availible, and are used as only a small (3%) proportion of the total mix. The material was packaged in 3 inch diameter plastic film tubes which we call "sausages". These sausages were hung inside a solar collector to give an integrated collection-storage unit. It was found that after 300 cycles 20% of the initial heat of fusion was lost. This was attributed to lack of rigidity of the suspension medium and the search for a more satisfactory matrix was renewed.

This led, in 1973, to experiments with cement. At first it was hoped to mix the PCM in with the cement so that the aggregate material could be poured into moulds on the building site to form walls, floors, and ceilings. However, it was found that the only PCM's which did not inhibit the cure of the cement were waxes, which were unsatisfactory because of low thermal conductivity, high cost, and flammability. Thus the present more complex Thermocrete material and fabrication system was arrived at.

This consists of foaming concrete and allowing it to cure, permeating the concrete with a nucleating agent, coating the concrete with a sealant and then filling the sealed block or tile with molten PCM by a vacuum technique. This technique consists of drilling a hole in the sealant, applying a vacuum to this hole, and then supplying molten PCM to the hole, so that the block fills with PCM. This filling takes a few minutes, after which the hole is sealed.

III. Project Description

In order to ascertain that Thermocrete is indeed a valid concept that will find acceptance in the marketplace and thereby impact national energy consumption, the following steps were necessary.

1. Satisfactory performance specifications, including cost, were developed for each end use identified.
2. Laboratory techniques were developed which allowed measurement of sample performance, including thermal, physical, and accelerated aging performance.
3. Fabrication methods were developed which gave reproducible results and which, hopefully, lend themselves easily to mass production scale-up.

4. Component materials were selected for each end use, including PCM, nucleating agent, matrix, and sealant. These components must be compatible with each other.

Initially it was expected that the literature would reveal satisfactory PCM's. However, it was found that the literature was inadequate and sometimes inaccurate, so some research was done in this area.
The following were among the PCM's examined:

	Melting Pt.	Cost	Comments
$2CaCl_2 \cdot MgCl_2 \cdot 20H_2O$	25°C	6¢/lb	Corrodes Cement
$FeCl_3 \cdot 5H_2O$	56°C	7¢	Corrodes Cement
$Zn(NO_3)_2 \cdot 2H_2O$	55°C	18¢	Filling Problems
$Zn(NO_3)_2 \cdot 6H_2O$	36°C	13¢	Filling Problems
$CaCl_2 \cdot 6H_2O$	29°C	4¢	O.K.
Palmitic Acid	63°C	25¢	Corrodes Cement
Dichlorobenzene	53°C	15¢	Destroys sealant
$CaCl_2 \cdot 4H_2O$	45°C	6¢	O.K.
$Ca(NO_3)_2 \cdot 3H_2O$	51°C	12¢	Nucleation Problems
$NaSO_4 \cdot 10H_2O$	32°C	2¢	Filling Problems
$5Na_2CO_3K_2CO_3\ 9H_2)$	25°C	5¢	Nucleation Problems
Paraffin		20¢	Low Thermal Conductivity
$CaCl_2 \cdot 6H_2O+NaCl$	23°C	6¢	O.K.

The following classes of concrete matrices were examined:

	Typical Porosity	Typical Strength	Comments
Foamed	75-85%	100-300psi	Good low density
Vermiculite	70%	300 psi	Attacked by PCM's
Pumice	55%	1100 psi	Good high density
Foamed plaster	70%	700 psi	Attacked by PCM's
Poured in place	60%	1000 psi	Good for wax only
Calcium Silicate foam	85%	600 psi	Very expensive
Perlite	65%	800 psi	Inaccessible pores

The following sealants were examined:

Epoxy - too expensive and brittle

Rubberized epoxy and sand - satisfactory

Sodium silicate - too brittle and thin

Polyester - too brittle

Saran emulsion - poor film forming

Neoprene - poor film forming, expensive

Urethane coal tar - satisfactory

Polyester and glass fiber - hard to apply

Polyester cloth - too weak

Polyethylene/Aluminum foil/Polypropylene laminate - foil was corroded

Polyethylene/scrim/aluminum foil laminate - foil was corroded
Polyethylene/saran/mylar - satisfactory
16 mil vinyl - loss of plasticizer

IV. Results

Satisfactory combination of the above PCM's, matrices, sealants, and nucleating agents were found which satisfied the specifications developed for Thermocrete structural blocks for passive solar and Thermotiles for distributed and active solar.

Specifications for Thermocrete blocks for passive solar:
Size: 4x16x8 inches
Weight: 13 pounds or 11.6 Kilograms
Compressive Strength: 1000 psi
Heat of fusion: 670 BTU or 169,000 calories
Melting range: 77-8.5°F or 25-27°C
Thermal Conductivity:
  Liquid PCM: 4.6 BTU/ft^2 in °F hr or 15.8×10^{-4} cal/cm°C sec
  Solid PCM: 2.8BTU/ft^2 in°F hr or 9.6×10^{-4} cal/cm°C sec
Cost of Materials 2.7¢/pound or 90¢/therm
PCM: 97% pure $CaCl_2\cdot 6H_2O$
Matrix: Pumice Cement
Sealant: Urethane Coal Tar
Nucleating Agent: $BaCl_2\cdot 6H_2O$

Specifications for Thermotiles for distributed Storage:
Heat of fusion: 30 cal/gm
Melting range: 19-25°C
Thermal Conductivity:
  liquid PCM: 28×10^{-4} cal/cm°C sec
  solid PCM 17×10^{-4} cal/cm°C sec
Compressive strength: 300 psi
Density: 1.60 gm/cm^3
Cost of materials: 4.8¢/pound, 110¢/therm
PCM: 97% pure $CaCl_2\cdot 6H_2O$ + 3% saturated NaCl solution
Matrix: foamed cement
Sealant: polyester and fiber glass
Nucleating agent: $BaCl_2\cdot 6H_2O$

Specifications for Thermotiles for active solar storage:
Heat of fusion: 27 cal/gm
Melting range: 44-46°C

Thermal Conductivity

Liquid PCM: approx 28×10^{-4} cal/cm°C sec

Solid PCM: approx 17×10^{-4} cal/cm°C sec

Compressive Strength: 300 psi

Density: 1.68 gm/cm^3

Cost of materials: 5.1¢/pound, 127¢/therm

PCM: 96% pure $CaCl_2 \cdot 4H_2O$

Matrix: foamed cement

Sealant: Polyester and fiber glass

Nucleating Agent: $BaCl_2 \cdot 6H_2O$

V. Future Activities

Further work will be in the following areas:

1. Applications Analysis
   Market research
   Distribution analysis
   Installation procedures
   Packaging specifications
   Cost effectiveness
2. Production Simulation
   Sealing methods and materials
   Filling methods and materials
   Testing
   Production cost analysis
3. Field Testing
   Los Alamos passive test cells, Trombe wall type
   MIT test structure, beam daylighting
   California State office buildings, passive solar gain, night air "cool" storage.

PROJECT SUMMARY

ORGANIZATION: Texas A&M Research Foundation

ADDRESS: FE Box H, College Station, Texas 77843

PROJECT TITLE: Storage of Cold Water in Groundwater Aquifers for Cooling Purposes - Phase I

PRINCIPAL INVESTIGATOR: Donald L. Reddell TELEPHONE NO.: (713) 845-3931

CONTRACT NO.: 7836 CONTRACT PERIOD: September 1, 1977 to December 31, 1977

CONTRACT AMOUNT: ERDA - $30,830.00

PROJECT GOALS:

A field study and evaluation of a cold water storage system is proposed in the flood-plain alluvium aquifer along the Brazos River near Bryan-College Station, Texas. A cooling pond will be designed and constructed to chill water from 70°F to less than 50°F. Two production-injection wells of approximately 200 gpm capacity and 60 feet deep will be drilled on the Plantation Farm owned by Texas A&M University. Water will be pumped from one of the wells, chilled in the cooling pond and injected back into the aquifer via the second well. During summer periods, the cold water will be pumped back to the surface, used for air conditioning, and the warmed water injected back into the first well. The resulting water movement and temperature profiles will be monitored using a system of observation wells. The results will be used to verify available numerical models, and evaluate the concept of storing cold water in groundwater aquifers.

PROJECT STATUS:

The project is only one month old. Detailed design of the cooling pond is nearing completion. Two sites on the Plantation Farm have been selected for test hole drilling. Results from the test holes will determine the exact site and location of the wells.

PURPOSE

Roughly one-third of the energy consumed in the United States is employed at temperatures below 200°F. Space heating alone requires about 20 percent of our total energy budget. Air conditioning of homes and commercial businesses in the United States requires only about 3 to 4 percent of our total energy needs. However, the air conditioning load in the southern states is much greater than the national average. In Texas, about one-third of the residential energy load is used for air conditioning.

The mean annual temperature in Texas has varied from 63.1°F in 1976 to 67.4°F in 1933. During the winter (December-February), the mean Texas temperature has varied from 44°F in 1963-64 to 52.8°F in 1951-52. In the Bryan-College Station, Texas area, the temperature is below 50°F approximately fifty percent of the time from November through March. If the "cold" during this winter period could be collected and stored, it could be used for air conditioning purposes during the summer. Because it is clean, renewable, and safe, the use of the winter's cold to air condition homes and businesses is a glamorous alternative energy source which should be explored.

Since cold water cannot be generated during the summer, it must be generated during the winter. For the system to work, storage of large quantities of cold water for periods of several months must be achieved. Long-term storage of cold water also provides a statistical averaging of weather conditions, so that short periods of hot weather with large air conditioning demands can easily be handled.

The long-term storage of winter cold is essentially a problem of storing cold water efficiently for long periods of time. A natural water storage system exists below ground level in virtually every part of the world. This water storage system consists of the many groundwater aquifers located throughout the world. Conservative estimates indicate that 80 percent of the land area in Texas is underlain by either a major or minor groundwater aquifer. Much of the remaining area is probably underlain by small quantities of groundwater.

To test the concept of storing cold water in groundwater aquifers, a field study is proposed in a flood-plain alluvium aquifer along the Brazos River near Bryan-College Station, Texas. The site is on the Plantation Farm owned by Texas A&M University in Burleson County, Texas, about 10 miles west of the main campus of Texas A&M.

Several design problems and environmental problems must be evaluated before the aquifer cold water storage system can be widely adopted. Potential thermal losses from the aquifer and well must be evaluated. In addition, the general public will want any environmental problems to be adequately documented. The specific research objectives of this project are:

(1) Design, construct, and operate a cooling pond to chill water from 70°F to less than 50°F and evaluate the operation of the cooling pond when interfaced with an injection well,

(2) Evaluate in detail the transmissivity, storativity, heat transfer coefficients, and heat storage properties of a groundwater aquifer located near Texas A&M University in Burleson County, Texas,

(3) Perform a field test in which cold water produced by the cooling pond is injected into the aquifer, stored in the aquifer for several months, and then pumped out of the aquifer for air conditioning purposes, and

(4) Monitor the resulting water movement and temperature profiles in a system of observation wells, use the results to verify available numerical models, and evaluate the concept of storing cold water in groundwater aquifers during the wintertime for use in air conditioning buildings during the summertime.

BACKGROUND INFORMATION

Groundwater has been pumped from wells for centuries. Only during the past century, however, has the hydrology and hydraulics of groundwater movement been fully understood. For instance, it is now known that groundwater under natural conditions moves at a very slow rate. For most sand, sandstone, and gravel aquifers, this movement is probably less than 125 feet per year. Recognizing this slow rate of movement, artificial recharge of aquifers with excess surface water has been practiced for many years in California, Texas, and other states. An artificial recharge experiment near Amarillo, Texas, indicated that over 80 percent of the injected water was recovered by pumping 6 months later.

The storage of cold water in groundwater aquifers appears to be technically feasible. At this time, a better understanding of heat losses from the cold water injection system and how the various system components interact is needed. Physical requirements, such as optimum temperature regimes, size of wells, size of cooling pond, and operation modes, are not generally understood.

To efficiently operate systems of cold water storage in aquifers over long periods of time, groundwater models will be needed to predict the movement of water in aquifers and the resulting temperature profiles. Several numerical models have been developed (California, Kansas, Texas, and the U.S. Geological Survey) for analyzing heat and mass transfer in aquifer systems. Very little field information is available with which to verify these models. This study will supply the needed field data.

PROJECT DESCRIPTION

In this study, a concept for utilizing the winter's cold for air conditioning during the summer is proposed. Groundwater from a shallow aquifer (water temperature = 70°F) will be pumped from a well (Well A) to a cooling pond during the winter. When the wet bulb temperature drops below 50°F, the water will be pumped through a spray system and chilled to the wet bulb temperature. After chilling the water will be pumped to a nearby injection well (Well B), injected into the shallow aquifer, and stored until the summertime. During the summer, the cold water will be pumped from Well B and used in a heat exchange process to air condition buildings. After the heat exchange process, the water (warmed from the heat exchange process) will be returned to Well A and injected back into the aquifer.

The flood-plain alluvium is a shallow groundwater unit which exists extensively along the Brazos River in Texas. The alluvium is composed of fine to coarse sand, gravel, silt and clay. Gravel ranges from pea size or less to cobbles about 5 inches in diameter. The alluvium reaches depths of about 85 feet and averages 50 to 60 feet deep. Well yields range from 250 to 1000 gpm. About 50 percent of the wells yield between 250 and 500 gpm. The depth of the water level varies from less than 10 to more than 30 feet. Most water levels are about 15 to 25 feet deep.

The cooling pond will be approximately 5000 ft^2 in area and produces an average of 100 gpm of water at a temperature of 40 to 50°F over a period of approximately 5 months. This facility is expected to produce about 10 million gallons of chilled water during an average winter at Bryan-College Station, Texas.

Two wells will be drilled and equipped to operate the cooling systems, one a water supply well and the second a cold water storage well. Both wells must be capable of being pumped or having water injected into them. Approximately 11 observation wells will be drilled around the two wells. These observation wells will be used to monitor water levels and temperature profiles in the aquifer. A record of the volume and temperature of water injected and pumped from both the cold and warm wells will be maintained to evaluate the heat recovery efficiency of the system.

RESULTS

The project is only one month old. Detailed design of the cooling pond is nearing completion. Two sites on the Plantation Farm have been selected for test hole drilling. Results from the test holes will determine the exact sites and locations of the wells.

FUTURE ACTIVITIES

The cooling pond will be excavated and lined. The production and injection wells will be drilled and equipped. Four observation wells will be constructed. Aquifer hydraulic properties and thermal properties will be evaluated. The system will be constructed and made ready to operate during Phase I of the study.

Phase II of the study will involve the performance of field tests in which cold water is produced and injected into the aquifer. This will continue for a period of 3 years. Water movement and temperature profiles will be monitored during Phase II. These data will be used to evaluate the efficiency of storing cold water in aquifers and to verify existing numerical models.

PROJECT SUMMARY

ORGANIZATION: TRW Energy System Planning Division

ADDRESS: 7600 Colshire Drive, McLean, Virginia 22101

PROJECT TITLE: Evaluation of Heat Recovery Methods

PRINCIPAL INVESTIGATOR: David Goldenberg TELEPHONE: (213) 536-4485

CONTRACT NO.: ORNL 7286 CONTRACT PERIOD: 4-77 to 10-77

CONTRACT AMOUNT: ERDA = $15,000 (Part of Larger Effort)

PROJECT GOALS:

- Establish the relationship between heat recovery rate and installed costs for temperature differences (ΔT) appropriate to plate and fin, shell and tube, heat pipe and heat wheel exchangers.
- Calculate cost correction factors for the above relationships covering situations where an exchanger is operated at a ΔT different from the baseline value.
- Establish the relationship between heat recovery rate and installed costs for electrostatic, centrifugal and filter type (bag house) air cleaning devices.
- Develop a methodology for evaluating the thermodynamic and economic feasibility of various systems to recover, store, and utilize waste heat.

PURPOSE

The main purpose of this project is to develop cost/performance relationships on commercially available gas to gas heat exchangers and air cleaning devices used to recover low-temperature (<500°F) waste heat. Additionally, the purpose was to develop a methodology for evaluating the thermodynamic and economic feasibility of various systems to recover and store waste heat.

BACKGROUND INFORMATION

Low-temperature waste heat uses include space heating/cooling, process heating, combustion air preheating and power generation. These uses plus hot water account for about one-fourth of the energy consumed in the United States. Accordingly, the market potential for low-temperature waste heat is enormous.

A major source of waste heat is combustion gases. These gases, however, often contain CO and SO_x; therefore, indirect heat recovery with exchangers is required. Other sources of waste heat are discharges from foundry, annealing and electroplating operations. But these discharges cannot be recycled directly for heat recovery because of their dust and oil fume content. Therefore, air cleaning devices are needed. Accordingly, the cost/performance relationships of gas to gas heat exchangers and air cleaning devices were studied in the project.

PROJECT DESCRIPTION

Thirty-two manufacturers of the type of equipment identified above were contracted to obtain characteristics and performance/cost data. Equipment characteristics are summarized in Tables 1 and 2, while certain key cost/performance relationships are exhibited in Figure 1.

Several types of heat recovery and storage systems are defined and some typical applications identified. In most cases, the applications are in the commercial or industrial sectors because:

- The quantity of heat is greater relative to sources in the residential sector.
- The quality of heat (temperature, source concentration) is greater relative to the residential sector.
- Larger scale, more economical equipment can be used in the commercial and industrial sector than in residences.

In addition, information is presented which can be used to determine the thermodynamic feasibility of various heat recovery systems. Also, an economic evaluation methodology is developed and the logic flow of the methodology presented. The logic flow of the methodology is illustrated by a hypothetical example. Finally, the cost/performance data developed and the economic methodology proposed are combined into two sample calculations.

RESULTS

The main results of the project are shown in Tables 1 and 2 and Figure 1. Certain conclusions reached were:

- Suitable heat exchangers and air cleaning devices are presently available on an off-the-shelf basis.
- Plate fin heat exchangers are most economical for gas to gas heat transfer in the temperature and capacity range investigated.

TABLE 1 SALIENT FEATURES OF LOW TEMPERATURE HX

	HEAT EXCHANGE TYPES			
Features	Plate-and-Fin	Heat Pipe	Shell-and-Tube	Heat Wheel
Applications	Gas-to-Gas	Gas-to-Gas	Gas-to-Gas Gas-to-Liquid	Gas-to-Gas
Temperature Range	100F - 500F	100F - 300F - 500F	100F - 500F	100F - 500F
HX Material	Aluminum - Carbon Steel - Stainless Steel	Aluminum - Copper - Carbon Steel - Stainless Steel	Carbon Steel Stainless Steel	Standard Materials, Stainless Steel
Size	Compact	Compact	Large	Compact
Corrosion Resistance	Low - Low*	Low - Low*	Low	Low
Durability and Maintainability	Fair	Good	Good	Fair
Life Time	15 year**	15-20 years***	15-20 years**	15 years**
Parasite Pressure Drop	≤ 5 inches W.G.	∿ 1 inch W.G.	Gas Side ∿ 5 inches W.G. Liquid Side is Higher	∿ 1 inch W.G.
Efficiency	62 - 72%	∿ 60%	∿ 62%	85 - 93%

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* Can be improved by protective coating

** Estimates

*** One manufacturer guaranteed for 15 years.

TABLE 2 SALIENT FEATURES OF AIR CLEANERS

	AIR CLEANER		
Feature	TRION	ELTRON	ALCAR
Type	Single-stage electrostatic	Two-stage electrostatic	Cyclonic and filtering combined
Application	dust	oil fume	dust
Particulate loading	medium	light to medium	heavy
Durability and maintainability	good	good	good
Operating temperature	100F	140F	up to 500F
Parasite pressure drop	very low	very low	∿ 1.5 in. W.G.
Effectiveness	effective for dust in micron range	effective for oil-fume in micron and sub-micron ranges.	effective for dust down to micron range

- Heat transport costs are peculiar to each installation and vary widely.

FUTURE ACTIVITIES

Waste heat recovery is economically feasible for various applications, but specific identification of these applications requires a total systems analysis including cost optimization. Therefore, to determine the value of using a system consisting of low temperature TES, heat exchangers, and distribution network for a specific application, a systems approach is required. The methodology developed in this project represents the skelton for achieving such systems analyses.

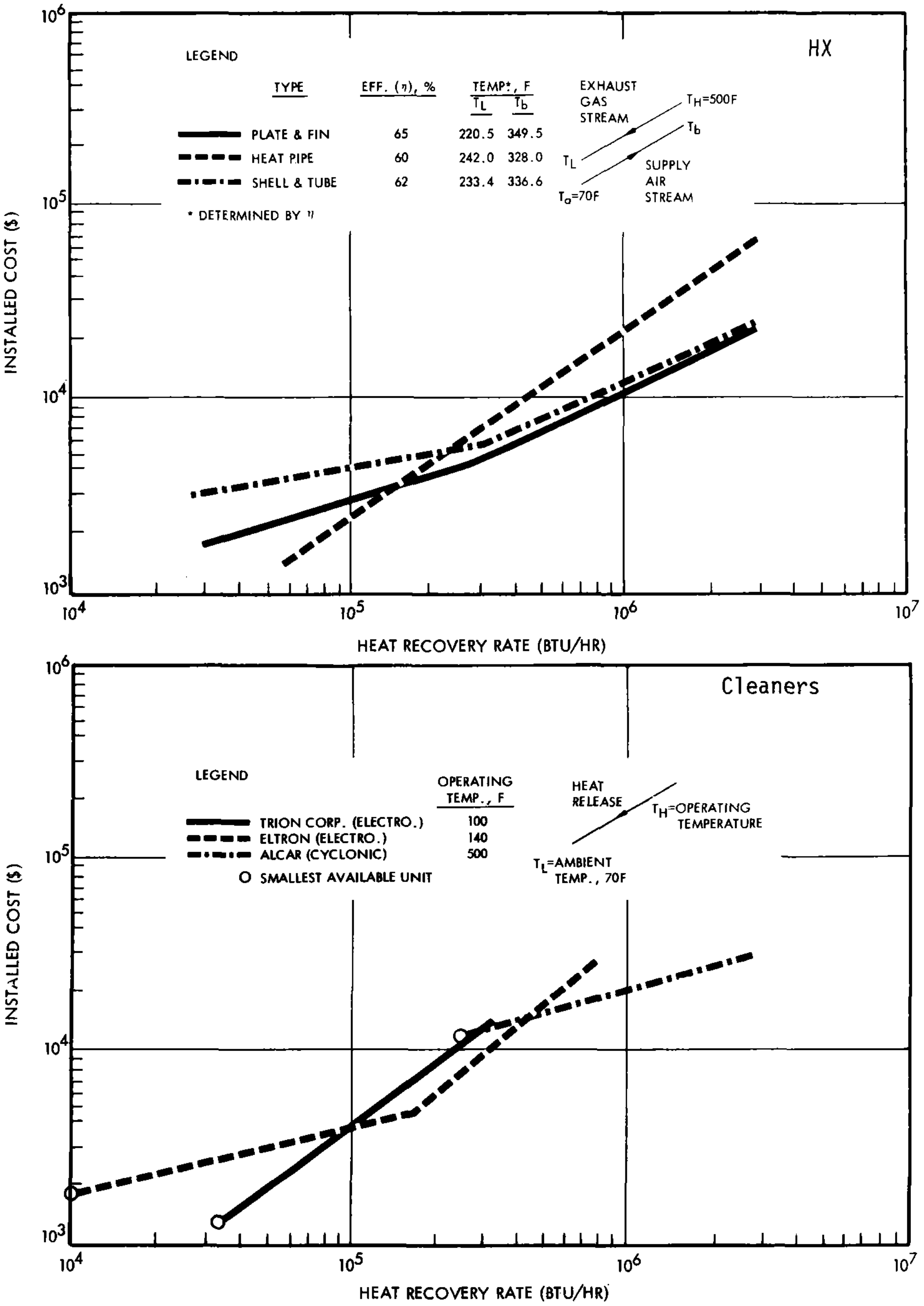


Figure 1. Heat Recovery Equipment Cost Versus Performance

PROJECT SUMMARY

ORGANIZATION: TRW Energy System Planning Division

ADDRESS: 7600 Colshire Drive, McLean, Virginia 22101

PROJECT TITLE: Fossil Energy Home Heating Furnace Efficiency Improvement Using Thermal Energy Storage

PRINCIPAL INVESTIGATOR: Richard Gorman (703) 893-2000 Ext. 2338

CONTRACT NO.: ORNL #7286 CONTRACT PERIOD: 4/77- 10/77

CONTRACT AMOUNT: ERDA = $7200 (Part of Larger Effort)

PROJECT GOALS:

The goal of this project is to develop a method of recovering waste heat and to use it efficiently through the mechanism of Low Temperature Thermal Energy Storage (LTTES).

PURPOSE

The purpose of this project is to study the concept of using thermal energy storage to cost-effectively improve the efficiency of home hot-air furnaces by using a thermal energy storage-recovery system to recover sensible and latent heat lost through the flue of a home hot-air furnace.

BACKGROUND INFORMATION

The majority of home gas and oil furnaces are hot air furnaces which heat the air by passing hot combustion gases through a heat exchanger that has the house air on the other side. Due to the low cost of energy in the past and the historical use of dirty manufactured gas, the systems are designed to be no more than 75 percent efficient on a steady state basis. The stack gas from gas furnaces can exceed 300°F and that from oil furnaces 700°F. Due to the historical use of thermal convection-driven flues, often as much as three to four times the air necessary for combustion is drawn through the combustion chamber or the flue bypass. All the excess air escaped through the flue and was replaced by cold outside air through infiltration with an efficiency loss as high as 10 percent.

A recent study by Oak Ridge National Laboratory (ORNL) (Ref.1) has shown that the normal thermal cycling, pilot light, output oversizing, and excess air thermal losses reduce the seasonal average efficiency of a gas furnace to about 55 percent (national average).

PROJECT DESCRIPTION

The results of the initial investigation into the pebble heat recovery and storage unit as a method of increasing home hot-air furnace efficiency are presented in this report. The heat transfer and energy storage of the pebble bed was computed with recently published methodology originally devised for solar energy rock bed heat storage. The effort was aimed at estimating the increase in efficiency and the cost to the consumer of the system. The national energy implications in terms of energy and money saved versus cost was also estimated.

Figure 1 shows the energy storage and recovery device installed on an existing gas furnace. This is a small furnace with a gas input of 60,000 Btu/hr or 1 ft^3/min of natural gas. The heat recovery device cycles alternately with the furnace burner. Table 1 shows the complete cycle.

Table 1. Cycle Timing

Function	Minutes	Furnace Fan	Flue Fan 1	Furnace Gas Burner	Recovery Fan 2	Stack Flow	BTU/Hr to House
Storage Charge	0-10	On	On	On	Off	15Cfm exhaust Gas @ 68°F.	45,000
Storage Rinse	10-11	On	On	Off	Off	15Cfm Rinse Air @ 68°F.	45,000-10,000
Sensible Heat Discharge	11-13 or 14	On	Off	Off	On	0	45,000
Latent Heat Discharge	13-14 to 18 to 20	On	Off	Off	On	0	10,000-0

Next Cycle ... if thermostat still calls for heat.

Storage Charge: During the first ten minutes of the cycle the storage charge is taking place. The temperature distribution in the pebbles is shown in Figure 2. The heat transfer in the pebbles is very effective. The surface area of 1 ft^3 of 1/2-inch diameter pebbles is about 110 ft^2; due to the tortuous path in the pebble interstices the heat transfer per unit area is good. When the heat transfer correlation of Löf (ref. 2) and the resultant volumetric heat transfer coefficient are used for a single blow regenerator (ref. 3), the temperature profile for the first 1/2 ft^3 for the pebbles versus cubic feet of bed is derived as shown in Figure 2. The heat transfer is almost reversible. The temperature distribution for the next 2 ft^3 is derived for the latent heat of vaporization of the water vapor assuming negligible temperature difference between the rocks and the saturated moist air. For stoichiometric combustion of methane 10 percent of the heat of combustion is contained in the latent heat of vaporization of water vapor in the exhaust gas. The flue temperature at which the water vapor begins to condense is 137^oF.

In the 50 percent excess air combustion case, the water vapor begins to condense at 123^oF. As the pebbles cool the exhaust air to 68^oF, 81.4 percent (for 50 percent excess air) of the latent heat of vaporization is recaptured as well as 100 percent of the sensible heat. However, as the stack outlet air at 68^oF must be compared to the temperature of the outdoor air at 40^oF (assumed for this calculation) which will infiltrate through the house gaps to replace the combustion air, the total thermal efficiency should be considered to be 96.7 percent. The thermal efficiency is about 97.6 percent for the stoichiometric air case (which may not be realizable for current gas and oil furnaces).

Rinse Phase and System Safety: During the rinse phase, clean air is drawn through the storage bed for one minute. The void fraction of pebbles is about one-third. The air volume in the pebbles is about 1 ft^3. During that minute the 15 cfm combustion air fan draws 15 air changes through the pebbles. With perfect mixing this would dilute the CO_2 in the exhaust by three million times.

The one-way butterfly valves (similar to the barometric damper used on oil furnace flues) in the stack and the two fresh air ducts to the warm air supply duct prevent leakage of flow in the wrong direction. If the pressure across the valves produces leakage, the system will allow only fresh air to dilute the exhaust gas. No leakage from the exhaust to the "house" air can occur because the house air supply plenum is at a higher pressure than the exhaust system.

The rinse phase provides a flow of 68^oF air into the pebble bed. The 68^oF air is heated to 400^oF in the first 1/2 ft^3 of the bed, passes through the cooler pebbles, and is cooled to 68^oF. The rinse air has the effect of moving the temperature profile about 1/4 ft^3 downstream in the pebble bed. No energy is lost from the pebbles. The clean rinse air exhausted up the stack is at 68^oF so that the only loss is 68^oF air from the house. The furnace fan continues to remove heat from the hot heat exchanger in the furnace so the heat to the house comes from the heat stored in the thermal mass of the heat exchanger. In normal furnaces this stored heat slowly convects up the stack after the furnace fan turns off.

Recovery Phase: During the recovery phase, the recovery fan pressurizes the pebble bed in the opposite direction. The cool house air is drawn from the house air plenum to the cool end of the bed and heated to $400\text{-}600^oF$ at the warm end of the bed. The recovery fan is only 30 cfm so the heat it recovers from the pebbles is equal to the heat normally released from the burner. The limited amount of hot air ($400\text{-}600^oF$) is mixed with the cooler 68^oF house air to produce a 160^oF house air supply similar to that which accompanies normal burner operation. The air flow continues until the 1600 Btu in the high temperature sensible heat section of the pebbles is discharged. The 130^oF section of the pebbles is then discharged. The

800 Btu contained in the pebbles from the latent heat of vaporization are discharged more slowly and only raise the plenum temperature to 85°F. The discharge continues until the temperature of the rocks is 68°F. Thus, all the heat recovered from the stack gas is delivered to the house.

If the house needs more heat, the furnace-recovery system cycles again. The control system always runs a full cycle so the rock bed does not sit half full of heat. Figure 3 shows the temperature of the duct air during the cycle and the resultant derating of the furnace.

RESULTS

System Performance: Assuming a 55 percent average national seasonal performance, this system with 50 percent excess air will perform at 96 percent efficiency or reduce fuel consumption by 43 percent and work on gas or oil furnaces.

System Cost: Preliminary cost estimates including ducting, bed container, pebbles, insulation, two blowers, relays, timer, valves, installation labor, and profit result in an installed cost of $244 to an existing house as a retrofit. Because the exhaust gas is 68°F, the exhaust stack need only be a 2-3" plastic tube similar to the ducting used for dryer vents. This could provide a substantial savings for a new house if a high-temperature flue can be eliminated. Based on average gas consumption, the cost of the system will be repayed in less than two years.

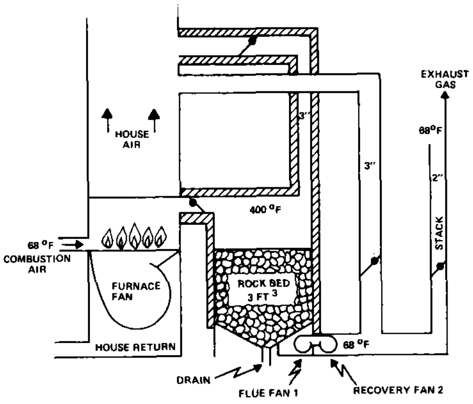
Overall National Energy Saving: The cost of converting all of the nation's gas and oil furnaces at government expense will be less than $10 billion and will save 2.5 quads/year (425 X 10^6 BOE). By contrast, the Alaskan oil pipeline and the proposed Canadian gas pipeline will cost three times as much and only transport (for as long as the resource lasts) 1.5 quads/year. The government tax write-off (also an expenditure) on the pipelines will be greater than the cost of retrofitting every furnace in the country. The consumer savings will accrue to the nation as a whole and reduce oil and gas imports proportionately.

Not surprisingly, energy conservation is more cost-effective than energy supply.

FUTURE ACTIVITIES

For the immediate future, the calculations will be refined using a more recent heat transfer methodology derived by Dunkel (ref. 4). In addition, a preliminary design for testing will be evolved and a lower cost control system investigated. Better cost estimates will be devised.

ERDA funding will be solicited for testing a number of prototype systems on commercial oil and gas furnaces at the TRW Environmental Laboratories in Vienna, Virginia. The systems will be tested for cyclical performance and pollution. Also, performance characteristics will be established. As each year's delay to full implementation costs the nation $7 billion, it is prudent to proceed toward full system development as quickly as possible.



SAMPLE 60,000 BTU/HR 1 FT³/MIN GAS } STOICHIOMETRIC
9 FT³ AIR

1 FT³/MIN GAS } 50% EXCESS AIR
14 FT³/MIN AIR

2 FOOT HIGH CYLINDER 28 INCHES IN DIAMETER (WITH INSULATION)

Figure 1. Home Furnace With Energy Storage Heat Recovery Unit

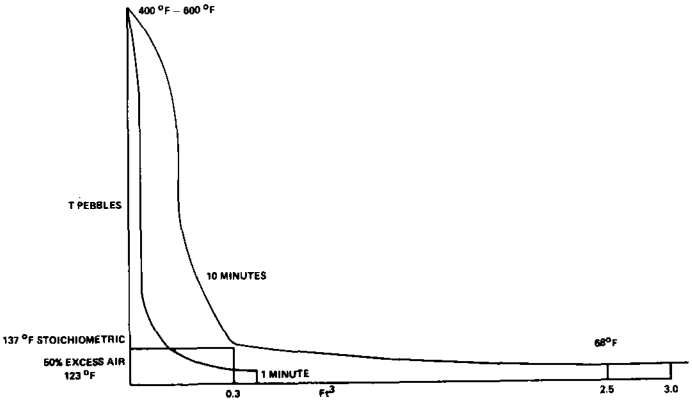
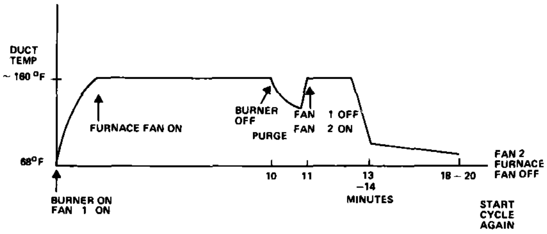


Figure 2. Pebble Bed Temperature



$$\text{FURNACE FULL ON OUTPUT} = 60{,}000\ \frac{\text{BTU}}{\text{HR}} \times 75\% \times \frac{10\ \text{MIN}}{10\ \text{MIN}} = 45\text{K BTUH}$$

$$\text{FURNACE WITH RECOVERY OUTPUT} = 96\% \times 60{,}000 \times \frac{10\ \text{MIN}}{20\ \text{MIN}} = 29\text{K BTUH}$$

HOWEVER AVERAGE FURNACE IS 100% OVERSIZED

Figure 3. Furnace Cycle

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3. "Handbook of Heat Transfer," Warren M. Rohsenow and James P. Harnett, Eds. McGraw-Hill Book Company, 1973.

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SODIUM SULFATE DEKAHYDRATE ($Na_2SO_4 \cdot 10\ H_2O$ - GLAUBER'S SALT) AS A LOW TO MEDIUM TEMPERATURE PHASE CHANGE THERMAL STORAGE MATERIAL

Contract E(11-1)-4042

July 1, 1976 - October 31, 1977

Maria Telkes and Paul F. Kando

Institute of Energy Conversion
University of Delaware
Newark, Delaware 19711

SUMMARY

This research constitutes the low temperature part of a two segment contract (the high temperature portion is presented separately) covered by the work statement.

1. Report in detail prior research on this material as a TES medium.
2. Describe the preparation procedure for the mixture
3. Document the successful 1000 cycle performance experiment
4. Perform necessary measurements to amplify the above; reproduce cycling.

Accordingly, a survey of the significant literature was made and a bibliography assembled which forms a part of the Final Report.

The $Na_2SO_4 \cdot 10\ H_2O$ based phase change storage material, including any additives, has been described and characterized.

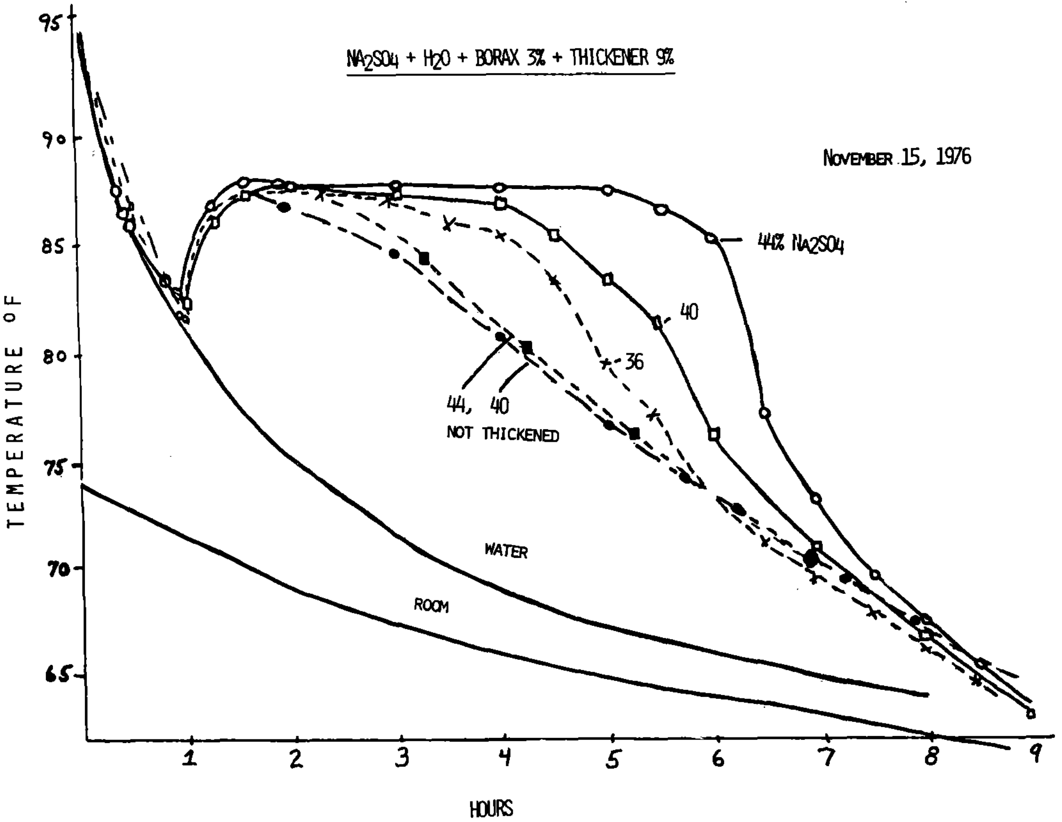
The results of a successful 1000 cycle performance test are presented, along with test results of subsequent cycling experiments which corroborates the original conclusions.

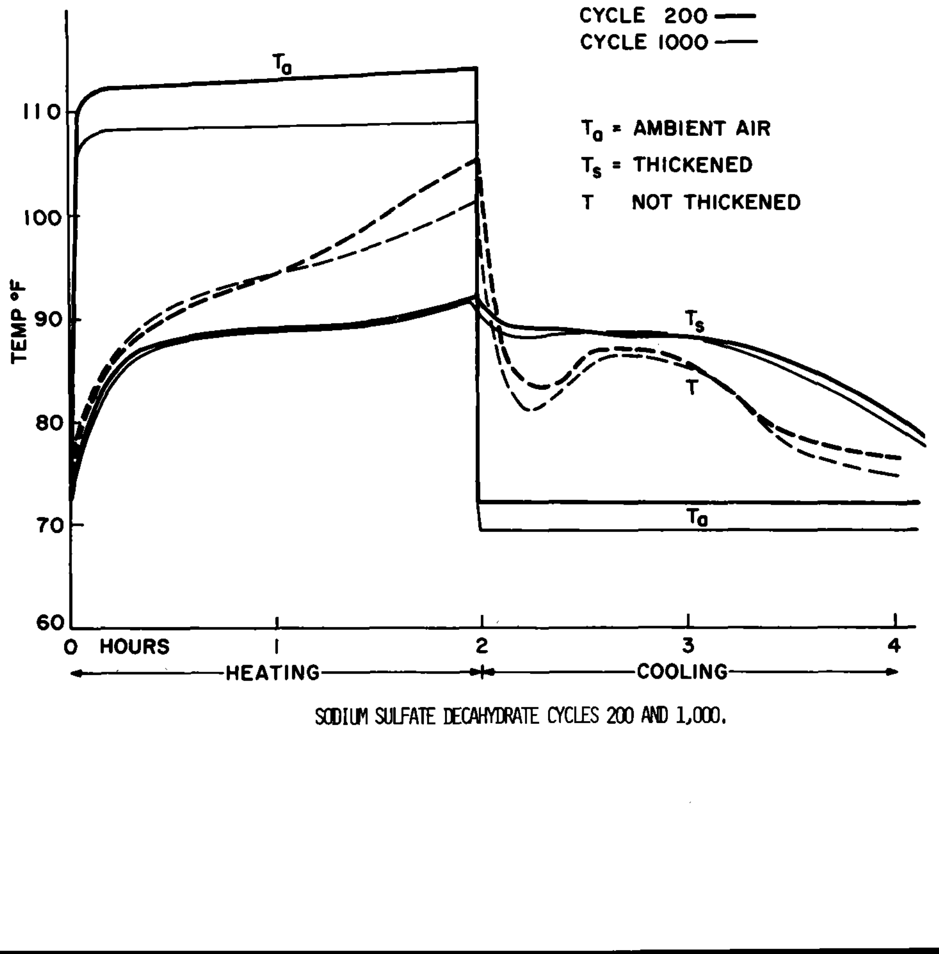
Preliminary results of large scale calorimetric experiments are presented.

The material discussed at this briefing is substantially identical to that presented to a review panel at ERDA/Washington on September 1, 1977.

THERMOPHYSICAL PROPERTIES OF $Na_2SO_4 \cdot 10\ H_2O$ WITH SODIUM TETRABORATE (BORAX) NUCLEATOR

	SI UNITS	ENGLISH UNITS
MELTING POINT	32°C	89°F
DENSITY	1.46 g/cm^3	91 LBS/CU. FT.
SPECIFIC HEAT		
SOLID	.42	.42
LIQUID	.79	.79
HEAT OF FUSION	60 CAL/G	108 BTU/LB.
VOLUMETRIC HEAT OF FUSION	88 cal/cm^3	9800 BTU/CU. FT.
THERMAL CONDUCTIVITY (K) OF SOLID (AT 30°C)	2.25 W/M-°K	1.25-1.32 BTU/FT-HR-°F
FOR COMPARISON:		
THERMAL CONDUCTIVITY (K) OF		
WATER	.61 W/M-°K	.36 BTU/FT-HR-°F
ICE	2.25 W/M-°K	1.30 BTU/FT-HR-°F





SODIUM SULFATE DECAHYDRATE CYCLES 200 AND 1,000.

The Use of Solid State Phase Transitions for Thermal Energy Storage

Energy Research and Development Administration & Union Carbide
No. 7299

Villanova University
Villanova, Pa. 19085

Principle Investigator Dr. Amos Leffler

I. Purpose The purpose of this project is to find new substances capable of undergoing solid state phase transitions for use in thermal energy storage.

II. Background A possible method of storing thermal energy is in solid state phase transitions exhibited by many compounds. The phase transitions of interest are those that occur between ambient temperature and 250°C with an energy of transition greater than 100 J/g. In addition to these properties other factors such as toxicity, stability in cycling, and cost are important factors.

III. Project Description The purpose of this project is to carry out both a literature and laboratory search for compounds with the properties listed above. In addition consideration will be given to the problems that would be encountered in the construction of heat exchangers using materials with solid state phase transitions.

IV. Results Up to the present time the major effort in the project has been a literature search to identify possible candidates for testing. During the course of the search the theoretical literature on solid state phase transitions has been studied and new developments have been noted. The most important theoretical development has been the realization that solid state phase transitions are similar to critical phenomena and thus all "mean field" theories are inadequate. It has also been shown that transitions only occur when there are potential wells of varying energy depth for adjacent positions of neighboring molecules thus explaining why for example benzene does not show a solid state transition. Finally it has been shown that there is an empirical relation between the entropy of transitions and the difference in molecular dimensions (length - width) for families of compounds.

During the course of the literature search the following classes of molecules have been searched for possible candidates for solid state transitions.

1. Benzene derivatives
2. Naphthalene derivatives
3. Anthracene derivatives
4. Heterocyclic compounds including benzthiazoles
5. Cyclohexane derivatives
6. Phosphazenes
7. Triazines
8. Tropones
9. Adamantanes and diamantanes
10. Oxa, Aza, and Thia adamantanes
11. Twistanes
12. Para cyclophanes
13. Tricyclo and hetero tricyclo cage compounds
14. Camphor derivatives
15. Donor acceptor complexes

V Future Activities We are in the process of obtaining some of the more promising candidate compounds for testing. In all cases the compounds are impure as received and must be purified by crystallization or sublimation. All compounds will be checked by differential scanning calorimetry to determine whether there are solid state transitions. For those having transitions of the desired magnitude in the temperature range of interest, related compounds will be tested and more detailed studies of their properties will be undertaken.

PROJECT SUMMARY

ORGANIZATION: Westinghouse Electric Corporation

ADDRESS: Advanced Energy Systems Division
P. O. Box 10864
Pittsburgh, Pennsylvania 15236

PROJECT TITLE: Applications of Thermal Energy Storage to Waste Heat Recovery in the Food Processing Industry

PRINCIPAL INVESTIGATOR: Wayne L. Lundberg TELEPHONE NO.: (412)892-5600

CONTRACT NO.: EC-77-C-01-5002 CONTRACT PERIOD: 8/31/77-5/31/78

CONTRACT AMOUNT: ERDA - $96, 195

PROJECT GOAL:

To identify practical waste heat recovery systems applying thermal energy storage which could produce significant fuel and energy savings in the food processing industry.

PROJECT STATUS:

Work on the first phase of the project was begun early in September, 1977 and will require two months to complete. That phase involves the collection of operating data from H. J. Heinz manufacturing facilities which will be used to establish current energy usage and waste heat production patterns.

APPLICATIONS OF THERMAL ENERGY STORAGE TO WASTE HEAT RECOVERY IN THE FOOD PROCESSING INDUSTRY

Purpose

Westinghouse Electric Corporation (Advanced Energy Systems Division), in cooperation with the H. J. Heinz Company (USA Division), has begun a project to identify practical waste heat recovery systems for application in the food processing industry. The systems will employ thermal energy storage and their purpose is to achieve more efficient fuel utilization when applied in that industry. In this paper, the goals and status of the project are described as well as the results of a preliminary Westinghouse survey of waste heat recovery possibilities at the Heinz Pittsburgh factory.

Background Information

The food processing industry is a major user of low temperature (250°F or less) process heat. It is estimated that 85 percent of the fuel consumed by the industry is used to produce process steam and hot water having temperatures in the low temperature range. The energy contained by the process steam and water is employed in a variety of applications. Among them, the principal ones are cooking, package sterilization, handling equipment washing and sanitizing and work area cleanup. Unfortunately, a considerable quantity of energy leaves the processes as waste heat. This heat is present in steam and vapors that are vented to the atmosphere and in water that is sent to clear water sewers or to waste treatment facilities. Waste heat also results from product cooling and freezing processes. It is believed that significant fuel and energy savings can be realized in the food processing industry through recovery and further use of this waste heat.

Westinghouse recently completed a preliminary survey of energy usage patterns at the H. J. Heinz Company, Pittsburgh factory. The Pittsburgh factory produces canned and bottled foods and energy for the various food handling processes is initially contained in steam produced by an on-site power plant (see Figure 1). Seven coal, oil or gas fired boilers have a combined steam generating capacity of 340,000 lb/hr at 750°F and 600 psig. The steam is routed to two 3000 kw turbine-generator sets which satisfy 40 to 85 percent of the Pittsburgh factory electrical needs; the remaining electrical demand is met by a utility supplier. The turbines are back-pressure units and the still superheated exhaust steam (450°F at 115 psig) is expended further in the food handling processes. In fact, the production of electricity by the Pittsburgh factory is strictly a by-product operation. The main function of the factory power plant is to supply steam for use in processing food and the on-site generation of electricity varies directly with the demand for process steam.

The preliminary survey of energy usage and waste heat production patterns at the Heinz Pittsburgh factory provided evidence that waste heat recovery could be performed profitably at the factory when combined with thermal energy storage. An obvious energy storage application involves the handling equipment and work area cleanup operations which are performed daily during third shift. Those operations require nearly 25,000 gallons of water per day at 180°F. Currently, the hot water is produced by mixing steam and cold well water. However, instead of using steam as the energy source, the water intended for cleanup operations could be heated by waste heat from the first and second shift operations and held in storage until needed during the third shift. The Westinghouse survey indicated that in this single waste heat application, the annual savings in steam generation costs would be $17,000. At this rate, the total cost of installing the required waste heat recovery and thermal energy storage system would be regained in approximately 2.5 years. This investment return rate is favorable and it adds to the attractiveness of installing waste heat recovery systems.

Other potential applications of waste heat at the Heinz Pittsburgh factory have been identified. Examples are the batch sterilization and the continuous pasteurization processes. During those processes, the packaged food product is held in contact with hot water (200 - 250°F) for a specified period of time. Presently, the hot water leaving the processes is discharged from the factory in volumes that could approach 500,000 gallons per day. Methods for extracting heat from the used water and for making it available for further in-plant use via heat exchanger, heat pump and thermal energy storage systems are to be evaluated.

Project Description

The project is being conducted by Westinghouse Electric Corporation (Advanced Energy Systems Division) with the full cooperation of the H. J. Heinz Company (USA Division). The purpose of the project is to identify practical waste heat recovery systems, utilizing thermal energy storage, which could significantly reduce the energy consumption rate in the food processing industry. Plant operating data supplied by Heinz will be used to size waste heat recovery equipment for application at a particular Heinz installation. Assuming the operations at that installation are typical of those of other producers in the industry, the potential fuel and energy savings to be realized by Heinz through waste heat recovery will then be extrapolated to the industry on a nationwide basis. Upon selecting an appropriate Heinz facility, the project will be structured as follows:

Phase 1: Identify current energy consumption and waste heat production patterns.

Phase 2: Specify the conceptual design of waste heat recovery systems utilizing thermal energy storage.

Phase 3: Predict fuel and energy savings in the food processing industry due to the implementation of the waste heat recovery systems.

Phase 4: Develop a demonstration and commercialization plan for promising waste heat recovery systems.

The Phase 1 effort will require two months to complete and will determine the energy usage rate vs time for the major plant processes. It will also identify the waste heat production rate as a function of time. The data from the Phase 1 work will be used in the design of appropriate waste heat recovery systems. Phases 2 and 3 will be conducted in parallel and will require three months for completion. During those phases, potential waste heat recovery systems will be evaluated based upon cost and effectiveness considerations. Phase 4 will also proceed in parallel with Phases 2 and 3 and will require approximately two and one-half months for completion. That phase will involve the selection of a system design(s) for demonstration purposes and the development of a commercialization plan which would alert prospective customers, assess the market size, identify potential hardware manufacturers, etc. The entire project is scheduled for completion by March 1, 1978 and a final report will be issued prior to May 31, 1978.

At the time of this writing, the project has been underway for approximately three weeks. Meetings have been held with Heinz personnel at their Pittsburgh factory and the Phase 1 effort has begun to identify energy usage and waste heat production patterns. Flow rate and temperature information is being assembled for the processes that occur at the Pittsburgh factory and instrumentation is being specified where data are needed but are currently unavailable.

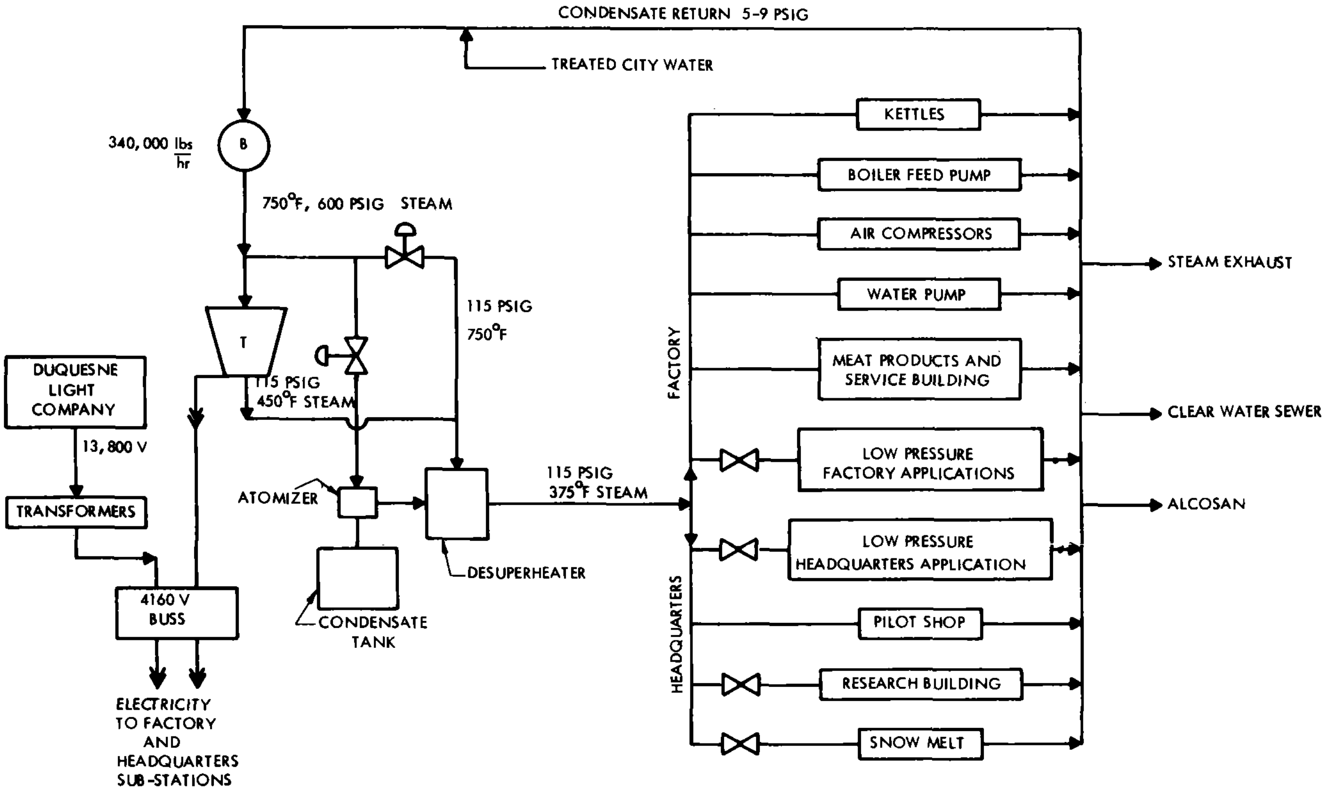


Figure 1. Heinz Pittsburgh Plant Power Supply Network

II. HIGH-TEMPERATURE THERMAL ENERGY STORAGE

HIGH TEMPERATURE THERMAL ENERGY STORAGE
PROJECT OVERVIEW

William J. Masica
Head, Thermal and Mechanical Energy Storage Section
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 is being systematically 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 was given the primary responsibility for the development of high temperature sensible and latent heat storage technology. Project management 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 Project's activities are conducted principally under contracts within the private sector. Procurements are awarded and managed by NASA Lewis using DOE reimbursed funding wherever feasible and in the best interests of the government. The management of the Project involves extensive interaction with the DOE end-use Divisions and coordination of related activities with the National Laboratories, NSF, NRL, and NBS.

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 commercial users or for demonstration by a DOE end-use Division. The Project's activities are currently being directed toward four application sectors and are concentrated in six major areas. These are:

1. Conventional Electric Utility Power Generation
    - Select and develop near-term sensible heat storage options
    - Explore advanced storage and power system applications

2. Industrial Process and Waste Heat
    - Identify, develop, and validate thermal energy storage systems for near-term application in the iron and steel, paper and pulp, and cement industries.

3. Transportation
    - Assess, develop, and validate thermal energy storage systems for highway vehicle propulsion

4. Solar Thermal Power Generation

   - Develop and validate latent heat storage for Solar Total Energy System applications
   - Develop advanced thermal energy storage systems for Alternative Solar Central Power System applications.

The Project has been structured into four major elements to provide a framework for the management of specific activities or tasks relating to the areas of concentration. The elements are System Studies, Concept Development, Technology Validation, and Supporting Research and Technology. The System Studies element is application oriented and includes concept identification, techno-economic feasibility, assessment, and conceptual design studies. The Concept Development element is technology oriented and consists of laboratory scale technology studies, component development, and engineering evaluations of specific candidate storage concepts. The results from these elements will be used to select the more promising concepts and applications for Technology Validation. Within this element, proof-of-concept development and testing will be conducted on a systems scale sufficient to validate the technology and provide reliable projections of costs for the selected systems. The Supporting Research and Technology element consists of generic, exploratory research and technology studies such as materials research and fundamental heat transfer analyses.

A list of the Project's System Studies is given in Figure 1. The conceptual design study for near-term utility applications is being coordinated with the DOE Division of Electric Energy Systems and the Electric Power Research Institute. If thermal energy storage continues to be a contender for utility applications, required development for selected systems will be initiated in FY 78-79, leading toward the initiation of a large-scale field test in FY 85. The response to DOE's Industrial Application PRDA has produced three industries where thermal energy storage appears attractive. These industries are iron and steel, paper and pulp, and cement. Together they account for 25% of the total national industrial energy usage. Potential energy savings of about 0.5 quad is achievable by nationwide implementation of near-term thermal energy storage systems throughout these three industries. Assessment studies for these industries have begun and will supply detailed benefits and an application base for development activities planned for FY 78. The Argonne National Laboratory is defining and managing an activity to develop thermal energy storage for application with a heat engine for a highway urban vehicle. In FY 78 competitive awards will be made to perform engineering and economic analyses and conceptual designs of candidate storage systems. These studies will supply the rationale and preferred system concepts. If the concepts are feasible, component development will be initiated in FY 79. Summary description of each of the System Studies are in the Proceedings.

A list of the Project's Concept Development activities is given in Figure 2. Thus far, the majority of the development efforts have been directed toward latent heat systems selected on the basis of potential applications, economics, material considerations, and engineering performance. The current development tasks are described in the Proceedings. The advanced system concept employing an active heat exchanger is a planned activity to be competitively awarded in FY 78. One problem inherent to latent heat storage systems which utilize passive heat exchange processes is the accumulation of solid deposits on discharge tube surfaces. This imposes a large heat exchanger surface area requirement which can be the major cost item of the system. To minimize a potentially large capital investment in required heat exchangers, alternate heat exchange concepts have been proposed to enhance energy removal by actively inhibiting or removing the formation of deposits on the discharge tube surfaces. The planned procurement will emphasize operational temperatures in the range from 250-350 C for steam power cycles. Promising concepts will be identified, selected, and tested. The best concepts will be validated in FY 79 for selected utility and solar thermal power generation applications.

No tasks relating to Technology Validation are currently being performed.

Supporting Research and Technology activities are listed in Figure 3. Again, descriptions of these can be found in the Proceedings. A small number of laboratory-scale experiments and engineering evaluations of systems developed under contract are being conducted in-house at NASA Lewis. Depending on available funding and the priority of other activities, competitive procurements for laboratory studies of advanced concepts (such as storage systems using metal foam or fluidized bed heat exchangers) may also be awarded.

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

HIGH TEMPERATURE THERMAL ENERGY STORAGE PROJECT ACTIVITIES

SYSTEM STUDIES

APPLICATION ORIENTED - CONCEPT IDENTIFICATION, TECHNOECONOMIC FEASIBILITY, CONCEPTUAL DESIGN STUDIES

1. EVALUATION AND CONCEPTUAL DESIGN OF SYSTEMS FOR NEAR-TERM UTILITY APPLICATIONS (GENERAL ELECTRIC)
2. APPLICATIONS STUDIES OF STORAGE TO INDUSTRIAL PROCESS AND WASTE HEAT RECOVERY IN
    - STEEL AND IRON INDUSTRY (ROCKET RESEARCH CORPORATION)
    - PAPER AND PULP INDUSTRY (BOEING ENGINEERING)
    - CEMENT INDUSTRY (MARTIN MARIETTA)
3. ASSESSMENT OF STORAGE FOR ROAD VEHICLE PROPULSION SYSTEMS (TBD)
4. ASSESSMENT OF SOLID SENSIBLE HEAT CONCEPTS (JET PROPULSION LABORATORY)
5. ASSESSMENT OF STORAGE IN PRESTRESSED CAST IRON VESSELS (GILLI)
6. ASSESSMENT OF LATENT HEAT STORAGE FOR UTILITY APPLICATIONS (GRUMMAN)
7. IDENTIFICATION AND CONCEPTUAL DESIGN OF SYSTEMS FOR SOLAR THERMAL POWER SYSTEMS (XEROX)
8. FEASIBILITY STUDY OF ROCK BED HEAT ACCUMULATORS (UNIVERSITY OF MINNESOTA)
9. FEASIBILITY STUDY OF UNDERGROUND STORAGE OF SOLAR ENERGY (ENERGY FOUNDATION OF TEXAS)
10. CONCEPTUAL DESIGN STUDY OF THERMAL / COMPRESSED AIR ENERGY STORAGE (M. I. T.)

FIGURE 2

HIGH TEMPERATURE THERMAL ENERGY STORAGE PROJECT ACTIVITIES

CONCEPT DEVELOPMENT

TECHNOLOGY ORIENTED - LABORATORY SCALE STUDIES AND ENGINEERING EVALUATIONS OF SPECIFIC TECHNOLOGIES, COMPONENT DEVELOPMENT, PRELIMINARY SYSTEM DESIGN

- SENSIBLE HEAT STORAGE DEVELOPMENT (TBD)
- LATENT HEAT STORAGE DEVELOPMENT
    1. DESIGN AND FABRICATION OF SODIUM SULFATE PEBBLE BED UNIT (200-260 C) (CALMAC)
    2. LABORATORY STUDIES OF SODIUM HYDROXIDE STORAGE SYSTEM (260-310 C) (COMSTOCK & WESCOTT)
    3. FABRICATION OF NRL ENERGY STORAGE BOILER TANK (300-450 C) (NRL)
    4. LABORATORY STUDIES OF CARBONATE SYSTEMS (450-540 C) (IGT)
    5. ADVANCED SYSTEM CONCEPTS: ACTIVE HEAT EXCHANGER (250-350 C) (TBD)

FIGURE 3

HIGH TEMPERATURE THERMAL ENERGY STORAGE PROJECT

SUPPORTING RESEARCH AND TECHNOLOGY

GENERIC ADVANCED TECHNOLOGY AND EXPLORATORY RESEARCH STUDIES

1. ASSESSMENT OF METAL FLUORIDES FOR STORAGE (PENNWALT)
2. THERMOPHYSICAL PROPERTY MEASUREMENTS OF METAL ALLOY STORAGE MEDIA (UNIV. OF DELAWARE)
3. HEAT TRANSFER ASPECTS OF MOLTEN SALT SYSTEMS (ENERGY FOUNDATION OF TEXAS)
4. LABORATORY STUDIES OF ADVANCED CONCEPTS (TBD)
5. NASA-LeRC IN-HOUSE EXPERIMENTS AND ANALYTICAL SUPPORT

PROJECT SUMMARY

Organization: Argonne National Laboratory
9700 S. Cass Avenue
Argonne, Illinois 60439

Project Title: Thermal Storage for Highway Vehicle Propulsion

Principal Investigator: A. A. Chilenskas (312)739-7711 x3676

Contract No: NASA/ANL Contract No. C-2325

Project Goals:

The objective of the thermal energy storage for highway vehicle propulsion activity is to develop effective thermal energy storage for mating with a heat engine to provide a vehicle propulsion system. Applications for off-highway vehicle and special purpose power systems will be assessed when they are identified. Technologies include sensible and latent heat, and reversible chemical reaction at temperatures in the order of 500 to 750 C. Prior experimental work points to sensible and latent heat concepts as most applicable.

Project Status:

Experimental work completed by industry has shown that sensible and latent heat storage can provide energy to operate a heat engine, viz.Stirling Cycle heat engine, for automobile propulsion. Mechanical Technology Incorporated, under contract to ERDA/TEC, has computed the total energy storage to achieve a 160 kilometer range with a compact urban vehicle of 1680 kg gross weight. The objective of this element is to complete a techno-economic assessment of thermal energy storage for application to this same vehicle, and the description of TES subsystem conceptual designs.

This element will be accomplished under contract with an estimated period of performance equal to eight (8) months. The request-for-proposal was issued by the Argonne National Laboratory on August 8, and proposals are due September 19. The statement of work provides flexibility for the bidders to propose mating a Brayton, Rankine, or Stirling Cycle heat engine to TES. It is anticipated that ANL will award two contracts to complete competitive conceptual designs. Bidders responding to this RFP are requested to describe their capability to fabricate and test the TES unit in the subsequent Concept Development element.

Background Information:

The thermal energy storage concept for vehicle propulsion uses a storage unit, a heat engine, and a power transmission/differential to drive the wheels. The storage unit has inherent compatibility with heat sources that provide the required temperature, e.g., electric resistance heating, intermittent energy from solar heating, and combustion of a fuel. Once charged, the thermal energy storage/heat engine propulsion system operates with zero exhaust emissions. The actual performance of the TES unit will be influenced by the thermal insulation. The fully charged TES unit will continuously lose heat and must be used swiftly and completely to maximize energy utilization.

The ERDA Division of Energy Storage Systems and Transportation Energy Conservation both recognize that the TES/heat engine concept has potential of being a viable alternate propulsion system for vehicle propulsion. ERDA/STOR is responsible for formulating and managing the research and development of necessary technology. The technology development is coordinated with ERDA/TEC, the end-use division. ERDA/TEC will provide identification of the total energy storage required to adequately support the experimental phases of the technology development. Their participation and support of the activity will provide timely transition to ERDA/TES support for demonstration of the concept by road test in a suitable vehicle.

As part of ERDA/STOR's Thermal Energy Storage Program, the NASA Lewis Research Center was given project management for the High Temperature Thermal Energy Storage Project under Interagency Agreement EC-77-A31-1034. Thermal energy storage for highway vehicle propulsion is a major activity in this project.

The Argonne National Laboratory will define and manage the activity to develop thermal energy storage for application with a heat engine to provide a propulsion system for a concept urban vehicle. Under other ERDA-funded work, ANL is developing technologies that are complementary to TESV activity. Among these are methods of coal combustion in an environmentally acceptable way and high temperature insulating systems for battery powered vehicles. It is anticipated that the ANL will initiate limited in-house support effort that will enhance their management capability, and contribute to the concept development.

This element will be performed under amendment to the ANL prime contract number 31-109-EN6-38 administered by the ERDA Chicago Operations Office as defined in NASA Purchase Order C2325.

PROJECT SUMMARY

ORGANIZATION: Boeing Engineering and Construction

ADDRESS: P.O. Box 3707, Seattle, Washington, 98124

PROJECT TITLE: Applications of Thermal Energy Storage to Process Heat Storage and Recovery in the Paper and Pulp Industry

PRINCIPLE INVESTIGATOR: William W. Engle TELEPHONE: (206) 773-2441

CONTRACT NO: EC-77-C-01-5082 CONTRACT PERIOD: 9 months

CONTRACT AMOUNT: ERDA $140K
OTHER $ 45K

PROJECT GOALS:

The objectives of the study are as follows:

1) Identify and quantify the fossil fuel consumption in the paper and pulp industry that could be impacted by application of TES to hog fuel boiler load leveling.
2) Conceptualize the most promising TES device and system application alternative for the selected industrial site. The selected industrial site is the Weyerhaeuser paper and pulp mill in Longview, Washington. Feedwater heating and steam generating application alternatives will be considered. Sensible heat and phase change TES device technology will be assessed.
3) Assess the impact (energy resource, environmental, and other) of TES on the paper and pulp industry.
4) Assess the actions required to assure commercialization.

PROJECT STATUS:

The project was initiated September 1, 1977. A kickoff meeting has been held, detailed project planning is complete, manning is on schedule, and all project tasks have been initiated on schedule.

I. Purpose

The purpose of this project is to perform a preliminary assessment of the application of process heat storage and recovery in the Paper and Pulp Industry.

II. Background Information

A typical process steam generation and storage concept for this application study is shown in Figure 1. The concept features a recovery boiler, a fossil fuel boiler, a hog fuel boiler, an in-plant electrical power generation system, a process heat storage system, and the process steam load of a large multi-component paper and pulp process plant. During periods of low process steam demand, excess steam is extracted from the turbine and used to charge storage. During periods of high process steam demand, boiler feedwater is fed to the storage system where steam is generated to supplement the capacity of the boilers. In this role, the storage system provides load-following capability and can consequently eliminate or greatly reduce the use of fossil fuel in mills where the steam demand is near the combined capacity of hog fuel and recovery boilers.

A specific industrial site has been selected for the purpose of this study and the potential subsequent research, development, and proof-of-concept demonstration program. The site selected is a major paper and pulp process plant located in Longview, Washington. This plant is owned by the Weyerhaeuser Company which has joined Boeing as an industrial participant to provide the point of application for the proposed study and to further support the study through the acquisition and evaluation of industry wide energy use data.

The forest products industry as a whole is one of the largest users of fossil fuels for in-plant process steam generation. Weyerhaeuser's Longview plant has a warm weather steam demand of approximately 1,100,000 lb/hr. Steam supply from the various energy sources is typically: chemical recovery - 50%, hydrogen - 5%, hog fuel - 20%, oil or gas - 25%. The plant also has an in-plant electrical generating capacity of 72 MW_e. A storage system capacity of 100,000 lb/hr integrated into the plant is expected to output more than 100,000 tons of steam a year for direct consumption by the process system. This steam, which would normally be generated from oil or gas and would now be generated by waste products in the form of hog fuel, is equivalent to 77,000 barrels of oil a year.

Weyerhaeuser produces approximately 5% of the nations paper and pulp. Projecting Weyerhaeuser's application potential across the industry, the thermal energy storage system may reduce fossil fuel consumption in the Paper and Pulp Industry by as much as 17% in 5-10 years.

Boeing views this application of thermal energy principally in terms of the potential substitution of hog fuel for oil, and the substantial economic advantage of such a change. We also recognize the potential operational flexibility, potential reduction in stack emissions, expanded in-plant steam and power generating capacity, and improved operating efficiency of all boilers in a plant employing the proposed storage system.

III. Project Description

The project is composed of four tasks:

1.0 Process Analysis
2.0 Storage System Design
3.0 Energy Resource Impact Analysis
4.0 Commercialization Plan

Task 1.0 involves the acquisition and interpretation of representative demand data and other process data characteristics of the Longview mill. An industry survey will also be included in this task and a process system thermodynamic model will be developed. The most economically promising TES system for the Longview mill will be conceptualized in Task 2.0. Industry wide energy resource impact will be evaluated in Task 3.0 and a commercialization plan will be developed in Task 4.0.

The project has a duration of nine months and involves six months of technical work. Tasks 1.0 and 2.0 have been initiated and process system data from the Longview mill is currently being evaluated.

IV. Results

Project initiated September 1, 1977

V. Future Activities

See Project Description

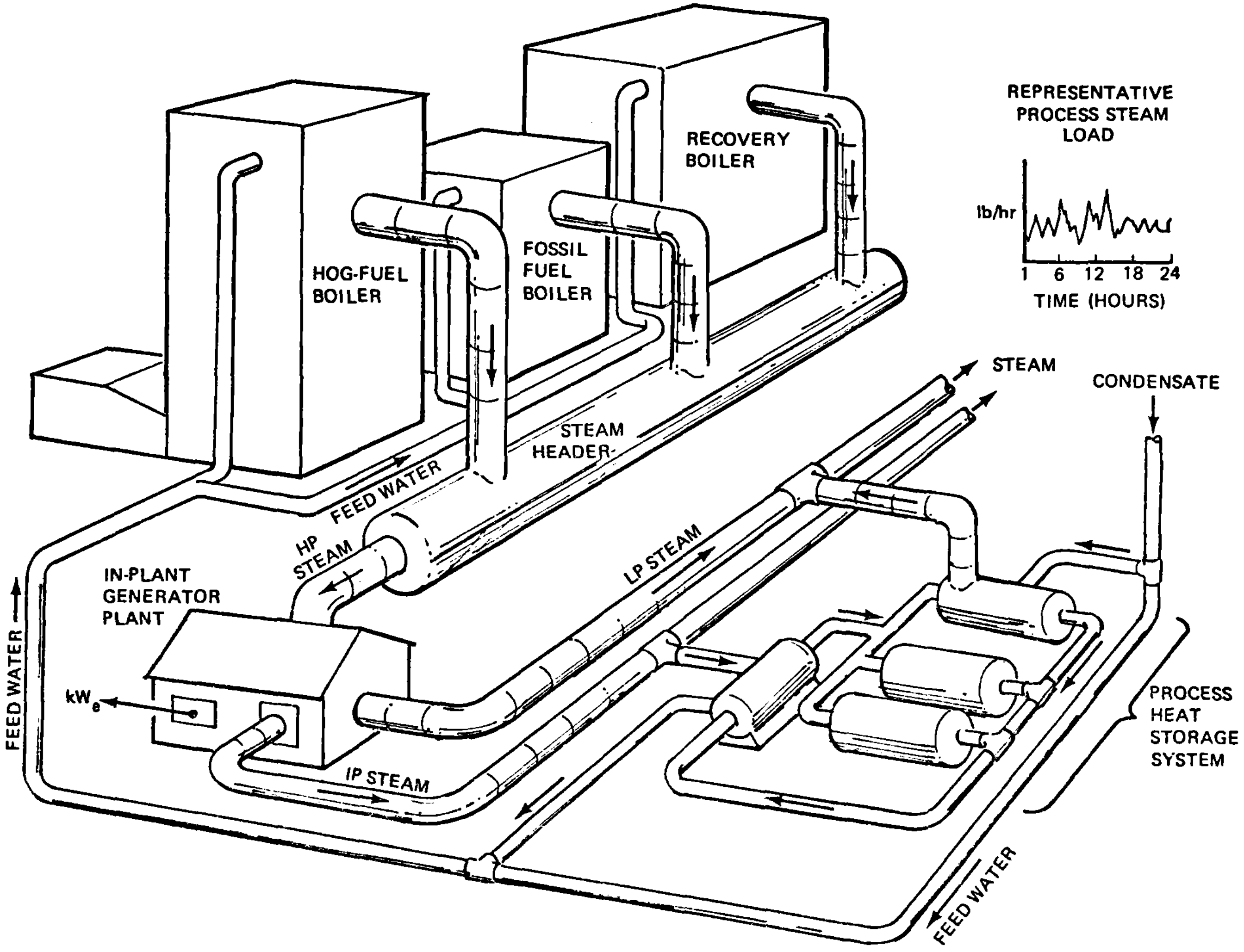


Figure 1. Paper and Pulp Process Heat/Storage Facility

PROJECT SUMMARY

ORGANIZATION: Comstock & Wescott, Inc.

ADDRESS: 765 Concord Ave., Cambridge, MA 02138

PROJECT TITLE: Development of a Phase Change Thermal Energy Storage Unit Utilizing Modified Anhydrous Sodium Hydroxide

PRINCIPAL INVESTIGATOR: Barry M. Cohen TELEPHONE NO.: (617)547-2580

CONTRACT NO.: NAS3-20615 CONTRACT PERIOD: April 1977 to January 1978

CONTRACT AMOUNT: $98,500

PROJECT GOALS:

The goal of this project is to develop a preliminary design of a phase change regenerative thermal energy storage (TES) unit for an intermittent heat source power generation system. The unit will utilize for its storage medium a modified form of anhydrous caustic soda known as Thermkeep which undergoes a fusion phase change in the range 516 K to 584 K. The tasks to be performed under this contract will lead to the preliminary design of a TES unit for the Sandia Laboratories Solar Total Energy Test Facility (STETF) in Albuquerque, New Mexico.

The program includes the following tasks:

1) Measurement of the relevant thermophysical properties of the TES medium.

2) A reference design of the TES unit utilizing an analytical model developed in part in a previous program.

3) The design, construction, testing, and analysis of a 1/10 scale model of the TES.

4) A preliminary design of a full scale TES unit of 3.1×10^6 kilojoules capacity for the Sandia Laboratories STETF at Albuquerque, New Mexico.

PROJECT STATUS:

1) The measurement of properties has been done; 2) the reference analytical design as well as the model analytical design have been completed; 3) the mechanical design of the model and the design and selection of components for a test facility have been completed; and 4) fabrication of the model TES unit and the test facility is nearly completed.

I. Purpose

Preliminary study of TES units employing phase change (heat-of-fusion) thermal storage media for solar central power generation facilities has suggested that this method may provide a compact, cost-effective means of storing heat to be utilized during periods when solar energy is unavailable. Although the experience of Comstock & Wescott in the use of heat-of-fusion TES media based upon anhydrous sodium hydroxide spans many years, the only prior applications have been in the areas of space heating and facility water heating. In applications such as these, thermodynamic efficiency is not important. Therefore, while the previous work advanced the state-of-the-art in materials, structural, and containment problems, units had never been designed which must provide the high thermodynamic efficiency demanded by a power conversion system.

Consequently, a research and development project is underway whereby a suitable detailed performance analysis will be composed, an engineering scale model of such a unit will be tested, and better measurements of the properties of the storage medium under consideration will be generated. The storage medium is known as Thermkeep^R and is primarily anhydrous sodium hydroxide with about 8% sodium nitrate.

Subjecting a well instrumented model to performance testing simulating real operating modes will demonstrate first whether such a unit can be operated in the efficient manner required or will indicate directions in which to move to more efficient operation. Second, it will provide test data needed to validate the analytical model (or improve it) so that it can be used with confidence for design of larger TES systems.

The final product of this project will be a preliminary design of a full scale, 3.1 x 10^6 kilojoule Thermkeep^R TES unit for the Sandia Laboratories Solar Total Energy Test Facility (STETF) in Albuquerque, New Mexico. If the design proves to be cost-effective and efficient when compared to alternatives, it is expected that the detailed design and construction of this unit would be authorized in a subsequent contract.

II. Background Information

The use of modified anhydrous sodium hydroxide as a high temperature phase change heat storage medium has been under development by Comstock & Wescott, Inc. since 1958. The initial proposed use for TES units was for domestic space heating in conjunction with heat pumps. Off-peak electric energy was to be used to charge the TES units which would assist the heat pumps during periods of high heating requirement. The development, sponsored by the Edison Electric Institute and the Philadelphia Electric Company was carried through a successful field test from 1962-1964, but was then discontinued because the anticipated large scale use of heat pumps did not materialize.

Beginning in 1964, in cooperation with the Hooker Chemicals and Plastics Corp., Comstock & Wescott undertook further development of heat storage materials (now called Thermkeep^R) and equipment.

Registered Trademark Hooker Chemicals and Plastics Corp.

Extensive studies were carried out on chemical formulations and the compatibility of Thermkeep with containment materials, which has resulted in nearly complete elimination of corrosion of containers and heat exchangers fabricated from ordinary mild steel.

A result of the cooperative effort between Comstock & Wescott and Hooker Chemicals and Plastics Corp. has been the development of the Thermbank Electric Water Heater, which was designed to provide hot water for all-electric buildings. Five Thermbanks were successfully carried through a one-year field test in a cooperative program with the Hydro Electric Power Commission of Ontario. A Thermbank Electric Water Heater of this type has recently been supplied to the NASA Lewis Research Center under Contract No. NAS3-20240 for installation in the Wind Turbine Generator demonstration at Plum Brook Station.

With the proven ability of a Thermkeep TES system to provide either heated air or water for domestic use, extension of this technology to power generation is the next desired step. When the stored thermal energy is to be used for power generation rather than space heating or water heating, a drop in temperature of the heat supplied to the heat engine reduces the efficiency of the power generating cycle. This requirement for delivery of stored heat at a nearly uniform temperature imposes a new and stringent set of conditions on the unit design.

III. Project Description

This project will provide information for cost and performance projections for designs of heat-of-fusion TES units employing Thermkeep in a regenerative heat exchange mode. The reference system for the design is the Sandia Laboratories Solar Total Energy Test Facility (STETF) in Albuquerque, New Mexico, but the results will be applicable to larger systems.

At the STETF, concentrating solar collectors provide Therminol-66 (T-66), a Monsanto heat transfer oil, at a nominal temperature of 584 K for operation of a power conversion system. The T-66 passes through a boiler producing superheated toluene vapor for the turbine of a Rankine cycle power generation system. The cooled T-66 then returns to the solar collectors at about 516 K for reheating. The collectors are sized to provide at least the full daily energy requirement of the Rankine Cycle boiler. Storage is employed to allow collection of excess heat during the day for use during the night.

The regenerative storage unit being studied consists of an insulated vessel containing Thermkeep in which a tubular heat exchanger is immersed. The T-66 passes through the heat exchanger and alternately heats and cools the Thermkeep, these processes constituting the storage and retrieval of energy. Figure 1 describes the unit schematically and, in principle, the change in temperature distribution from the beginning to the end of the discharge cycle.

During heating, T-66 enters at the top and exits from the bottom, and vice versa during cooling. Therefore, the top is always the hottest and the bottom always the coldest portion. When the Thermkeep is in the liquid phase, thermal stratification would also stabilize this sort of gradient.

As in all regenerative devices, the discharge temperature of the heat transfer fluid varies in time as a function both of state of charge and of heat exchange effectiveness. The critical temperature variation in terms of the efficiency of the power conversion system is that of the fluid delivered to the boiler, i.e., the temperature variation, ΔT, indicated on Figure 1. This ΔT may be minimized in general by providing a large thermal capacity or a highly efficient heat exchanger, both of which influence the cost of the unit.

The analytical model and computer program utilized predicts the temperature in the storage medium and the heat transfer oil as a function of time and vertical distance. Horizontal planes in the storage medium are assumed isothermal. Also computed are cyclic heat balances, pressure drops, costs, and geometric factors. The ability to change the mode of operation is built into the analysis so that solar cycles, utility cycles or others may be modeled.

The computer analysis was used to develop the reference design of the storage device for the Sandia Laboratories STETF. The sizing of this unit was based on optimization of unit storage cost (e.g., $/kilojoule) at an acceptable thermal efficiency. The efficiency will be defined in the next section. The 1/10 scale model of the unit was also designed with the aid of the computer program.

A test bed is being constructed for the model testing. It will provide heated T-66 to the storage device in the direction and at the flow rate consistent with the cycle to be modeled. External heating and cooling means are provided to simulate the effect of solar heat addition or boiler heat extraction on the heat transfer oil. Through the use of an automatic program controller and an appropriate feedback control circuit, nearly any mode of operation may be simulated. The modes are limited to those in which flow rate is variable but delivery temperature is constant at either of two temperatures (collector outlet or boiler outlet temperature).

The model unit will be subjected to various types of tests. Controlled tests will be run to determine where the analysis is deficient and the analysis will be modified to be consistent with the test data. Following testing and data correlation, a preliminary design will be made for a full scale unit, utilizing the updated computer analysis. A full scale unit for the Sandia Laboratories' system may then be built in the next phase of the program.

In addition to the design and testing described above, accurate measurements of the thermophysical properties of Thermkeep have been made. Measurements were to be taken in both the solid and liquid regions. Densities, viscosities, thermal conductivities, and specific heats were to be determined. Compatibility of T-66 and Thermkeep in the event of failure of a heat exchanger was to be investigated.

IV. Results

At the present time, the test bed and the 1/10 scale TES unit are being fabricated and assembled so that no test data have yet been obtained. Consequently, the major results to date relate to the analytical work and the TES unit and test bed design.

The first analytical task was to compose a full scale reference design. All designs were evaluated by being subjected to the same duty cycle. This was a solar daily cycle as provided by Sandia Laboratories. Boiler demand is constant at 250 kw for 12 hours a day and is zero for the remaining 12 hours which include the night. Solar collector output peaks at 500 kw (thermal). Therefore, peak input rate to storage is 250 kw (thermal) as is peak output rate from storage. Total storage requirement in the numerically approximated cycle is 3.4 x 10^6 kilojoules. During charging, the inlet temperature of the T-66 to storage is 584 K and during discharging, the inlet temperature to storage is 516 K.

For evaluation purposes, two factors were considered. The first is cost per unit of stored heat (e.g., $ per thousand kilojoules). It is on this basis that an optimum design was formulated. The amount of stored heat is considered to be the amount supplied to the heat transfer oil integrated over a daily cycle. The amount of heat put into storage is higher, the difference representing losses to the environment.

The second factor is an efficiency which characterizes the performance. This factor is more difficult to define and, depending upon what is desired, efficiencies are defined differently by different people. It is understood that it is actually preferable to consider the effect of the performance of the TES unit on the components to which it is linked if adequate information were available. For example, a drop in temperature of T-66 to the boiler can be related to an increased T-66 flow requirement to produce the desired output from the Rankine cycle system.

The definition of efficiency based upon heat flows around the TES unit only is

$$\eta = \frac{Q_o}{Q_o + Q_L + Q_A}$$

where

η = TES efficiency

Q_o = storage output (capacity)

Q_L = heat loss to the environment

Q_A = additional heating to supply T-66 at 584 K

This definition is felt to be meaningful if all designs are compared when subjected to the identical duty cycle.

Figure 2 describes the results of trading off surface area against amount of storage medium. Each design is characterized by amount of medium and efficiency. Different efficiencies occur only because of variation in amount of heat exchange tubing. In all cases tube size, insulation thickness, and all other parameters considered were fixed. Each curve plotted represents a constant overall efficiency as defined above.

Clearly the definition of efficiency does not discriminate between surface loss and make-up heating to the fluid. In reality, these factors would be weighted differently. Large units would have a higher component of losses to the environment due to size, but a lower make-up heating requirement due to improved heat exchange effectiveness than small units.

At any efficiency there appears to be a minimum specific cost. The first-cut reference design selected uses 15000 kg of Thermkeep, has a 91% efficiency and costs $8.60 per thousand kilojoules. Following this selection, other factors were considered and a design was selected which would appear to be optimal in terms of other less important parameters. The minor parameters are items such as thickness of insulation, tube series-parallel configuration at fixed surface area, ratio of vessel height to diameter, etc.

The final reference design selected uses 15000 kg of Thermkeep, has a 92% efficiency, costs \$8.76 per thousand kilojoules, has a capacity of 3.24 x 10^6 kilojoules and measures 3.47 m diameter by 3.5 m tall overall, including insulation which is 0.61 m thick. In larger size units, the specific cost would drop. For example, the 1/10 scale model was estimated at \$17.90 per thousand kilojoules while the full scale unit was estimated at \$8.76 per thousand kilojoules. Since the full scale unit is relatively small, utility size units are expected to have significantly lower specific costs.

Figure 3 describes the computed daily dynamic thermal response of the full scale reference design. The temperature profile is described by four key times in the daily cycle. T6 represents the fully charged condition and occurs in late afternoon. T5 is the fully discharged stage. From T5 to T6 the collector field puts out excess heating and the TES unit is recharged.

Figure 4 describes the T-66 outlet temperature vs. time during discharge when heat from storage powers the boiler. The times indicated on this plot correspond to the ones discussed above. Note the 12-hour standby period which is indicated only by a discontinuity in T-66 outlet temperature. As with any regenerative heat storage device, the outlet temperature progressively drops during discharge of the unit, except for the effect of varying flow rate.

The scaling guidelines were examined to produce the model design. It was determined that the most dependable method of scaling would be to simply utilize essentially a full height section of the full scale unit. Thus, to produce a one-tenth scale version, the amount of Thermkeep and the number of parallel heat exchanger tubes were reduced to one-tenth. Consequently, T-66 flow rates and heating and cooling rates are reduced to one-tenth.

Since the model has a higher surface-to-volume ratio than the full scale unit, provision must be made to reduce the surface loss. It was determined that adding insulation would not adequately accomplish this, and a heated shroud was finally selected. The model performance turns out analytically to be substantially the same as the full scale performance in both gradients, outlet temperature characteristics, efficiencies, etc. The model size, including insulation outside and within the heated shroud, will be 1.93 m diameter by 3.47 m tall. The model will contain 1500 kg of Thermkeep and will have a capacity of 3.24 x 10^5 kilojoules.

V. Future Activities

In the coming months, the model TES unit will be tested both in simplified duty cycles, e.g., constant T-66 flow rate tests, and the solar daily cycle. The simpler tests are included to allow refinement of the analysis without the difficulty imposed by a complex duty cycle.

A full scale preliminary design will be produced for application to the STETF at Albuquerque, New Mexico. This will not be a complete engineering design but will indicate the size, performance, and economics that can be expected.

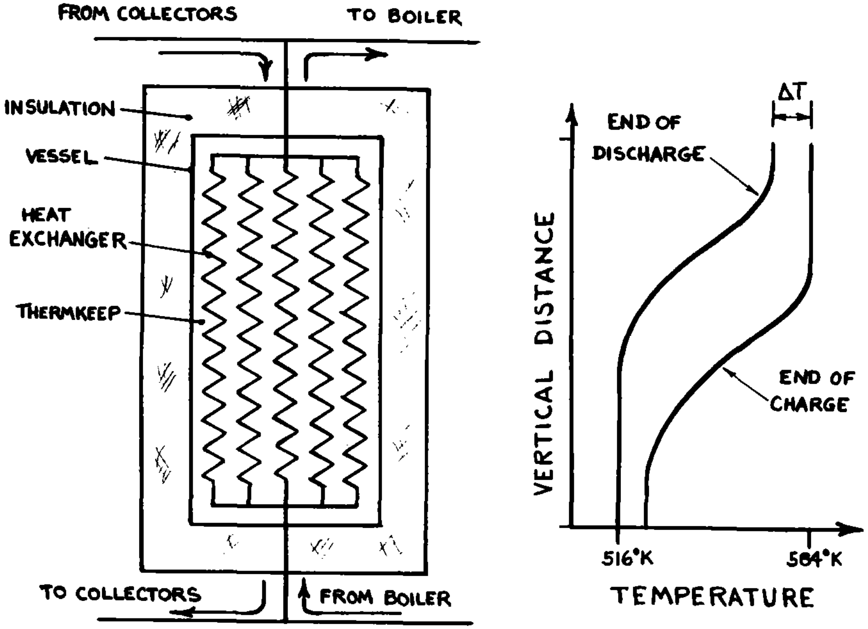


Figure 1. Schematic Diagram of TES Unit and Movement of Thermal Gradient.

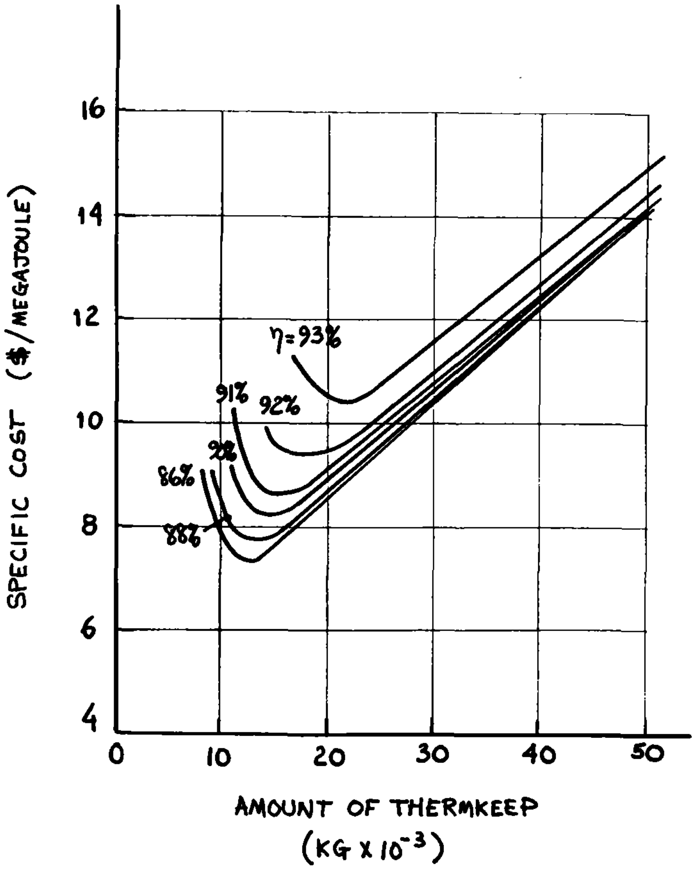


Figure 2. Specific Cost of Thermkeep TES units for 3.2 x 10^6 Kilojoule Capacity

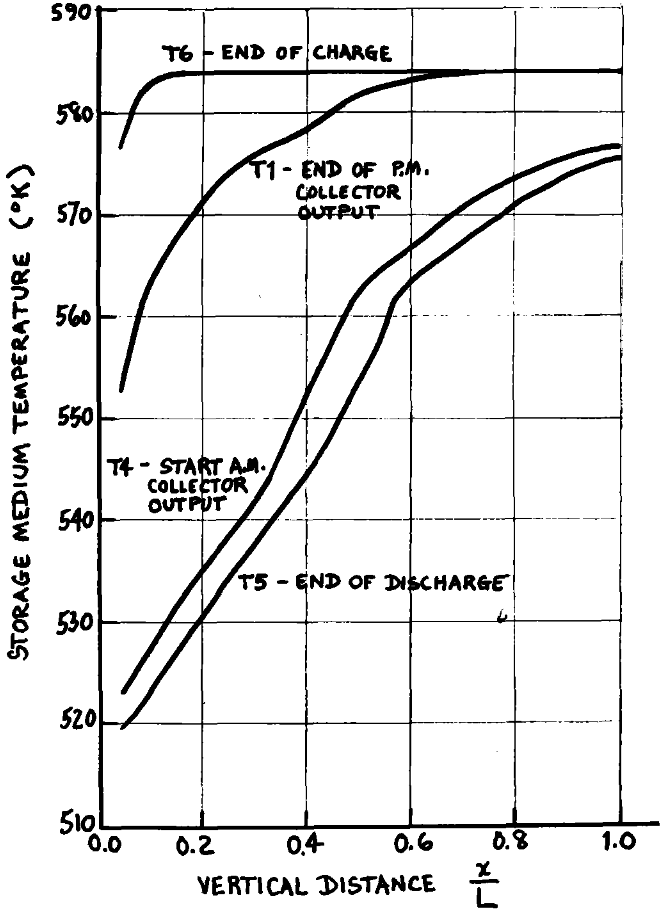


Figure 3. Dynamic Thermal Response of Thermkeep TES Unit.

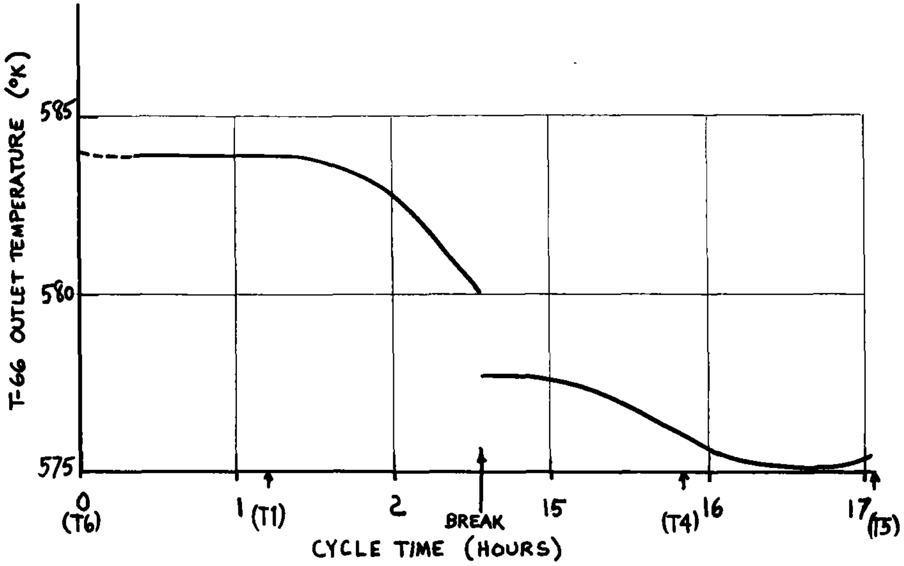


Figure 4. Temperature vs. Cycle Time of T-66 Delivered to Toluene Boiler.

PROJECT SUMMARY

ORGANIZATION: ENERGY TECHNOLOGY OPERATION / GENERAL ELECTRIC COMPANY

ADDRESS: 1 RIVER ROAD, SCHENECTADY, NEW YORK 12345

PROJECT TITLE: CONCEPTUAL DESIGN OF THERMAL ENERGY STORAGE SYSTEMS FOR NEAR-TERM ELECTRIC UTILITY APPLICATIONS.

PRINCIPAL INVESTIGATOR: ELDON W. HALL TELEPHONE NO. (518) 385-9090

CONTRACT NO: PENDING CONTRACT PERIOD: OCTOBER'77-JUNE'78

CONTRACT AMOUNT: BEING NEGOTIATED

PROJECT GOALS:

To determine the most attractive near-term thermal energy storage systems by analysis and conceptual design, and recommend development and demonstration programs that will lead to early commercialization in new plants. Storage systems that are near-term will more quickly improve the utilities' capability to generate peaking and intermediate power at lower costs and save scarce fuels.

PROJECT STATUS:

NOT YET BEGUN.

I. Purpose

To determine the attractiveness of thermal energy storage (TES) systems for utilizing off-peak base load generating capacity to meet peak load electric power demands in near-term utility applications. TES systems will be selected from an evaluation made on a consistent basis; conceptual designs and technical and economic evaluations will be made, benefit and market potential analyses will be performed, and recommendations made for development and field test and evaluation programs.

II. Background Information

The availability of off-peak, base load generating capacity is providing an incentive to develop practical electric utility energy storage systems. Energy storage can result in cost savings through better utilization of assets, such as capital intensive and spinning reserve equipment. Conservation as well as economic benefits can result if petroleum distillate and natural gas peaking and intermediate power generation systems are replaced by energy storage systems integrated with base load power plants. Recent assessment of energy storage systems suitable for use by electric utilities have shown that thermal energy storage is a contender because of its technical and economic features and potential for early commercialization. The objective of this program is to confirm the apparent attractiveness of thermal energy storage and if the attractiveness is confirmed, to select and conceptually design the most promising systems for near-term utility applications. The results of this study will be used by ERDA and EPRI to aid in their selection of utility energy storage systems for further test and evaluation.

This program is concerned only with applications involving conventional electric utility power plants using steam turbine-generator power conversion systems.

The program consists of the selection, conceptual design, and evaluation of the most feasible thermal energy storage systems, and program recommendations for further test and evaluation. The program will concentrate on the selection and conceptual design tasks.

III. Project Description

The project will be accomplished in the following four steps:

1. System Selection - This step is concerned with selection of three or less preferred systems for applying thermal energy storage to electric utilities.

2. Conceptual Systems Design - A detailed conceptual design will be produced for the three or less preferred systems, taking into consideration significant design options and operating variables.

3. Techno-economic Evaluations - This step will provide a preliminary assessment of the technical and economic aspects of each of the systems conceptually designed in Step 2 to determine their technical, economic, and operational characteristics and potential value to the electric utility industry.

4. Recommendations - Recommendations for development and further test and evaluation programs which are necessary to achieve TES system near-term commercialization will be provided.

The project will be performed by a team of General Electric Company participants led by Energy Technology Operation and including TEMPO, Corporate Research and Development, Energy Systems Programs Department, Installation and Service Engineering Business Division, Electric Utility Systems Engineering Department, and Turbine Operations. Consultants and proponents will also be utilized such as Public Service Electric and Gas Company of New Jersey and Niagara Mohawk Power Corporation.

IV. Results and Future Activities

Project is expected to be started in October 1977.

PROJECT SUMMARY

ORGANIZATION: Graz University of Technology

ADDRESS: Obere Teichstrasse 21/i
A - 8010 Graz, Austria

PROJECT TITLE: Thermal Energy Storage using Prestressed Cast Iron Vessels (PCIV)

PRINCIPAL INVESTIGATOR: P.V.Gilli/G.Beckmann TELEPHONE NO.: (0316) 43732

CONTRACT NO.: EY-76-C-02-2886 CONTRACT PERIOD: May 1976-June 1977

CONTRACT AMOUNT: ERDA $ 20,000
OTHER -

PROJECT GOALS:

The aim of the investigation was to assess the feasibility and economics of the Prestressed Cast Iron Vessel (PCIV) - developed as a nuclear reactor pressure vessel by Siempelkamp Giesserei KG of Krefeld, FRG - for thermal energy storage and high-pressure air storage applications in nuclear, solar, and coal-fired thermal power plants. Since no Code applicable to the PCIV exists as yet, the design philosophy and the design base had to be established first. Design principles and design details were to be worked out and a Reference vessel to be developed, designed and stress-analyzed. Consequences of using a PCIV instead of the well-known welded steel vessel regarding unit size, flow schemes for application as peak-load or stand-by plant, steam conditions, and modes of operation were to be investigated. A parametric study was to establish specific cost of PCIV TES and its dependence on flow sheet, pressure, superheat temperature, and size. The general objective of the project was to clarify the possible role of the new PCIV technology for energy storage in thermal power stations from the technical, operational, and economic viewpoints.

PROJECT STATUS:

A progress report on the project had been given in September 1976 /1/. The project was completed in June 1977. The Final Report /2/ has been approved and has been submitted for publication which is due in the autumn of 1977.

I. Purpose

The purpose of the project was to assess the potential economical advantages of the PCIV in its role as a high-pressure energy storage vessel for the following applications: high-pressure air storage for the quick start-up of open cycle gas turbines; pressurized high-temperature sensible heat storage by means of solids with a gaseous heat transfer medium for closed cycle gas turbines of future solar power stations; and - for applications in the near future - pressurized hot water storage for nuclear, solar, and coal-fired steam power plants, employing either separate peak-load turbines or overloadable main turbine sets.

The envisaged economics of the PCIV versus welded steel vessels accrue from the following facts:
- highly stressed redundant tendons taking the load,
- inexpensive cast iron body,
- no expensive welding operations,
- higher optimum working pressure leads to lower mass flow and volumetric flow and therefore to savings in piping, valves, turbine and condenser,
- very large units become feasible,
- possibility of disassembly and reerection if required.

Advantages of the PCIV for TES versus the Prestressed Concrete Pressure Vessel (PCPV) include:
- high compressive strength of cast iron (16 times that of concrete) and high degree of dimensional stability,
- no cooling system required, i.e. potential of hot going vessels avoiding internal insulation,
- hydraulic prestressing (and restressing if required) of cable bundles instead of winding individual tendons becomes possible by the high compressive strength of cast iron,
- potential of avoiding a separate liner.

As opposed to the rock cavern as a TES storage vessel, the PCIV features the following advantages:
- potential of hot going vessel, avoiding internal insulation,
- suitable for all geological conditions, not only for special sites.

II. Background Information

Whereas the PCIV is new technology, TES by pressurized hot water ("steam storage" or feedwater storage) is not. The largest steam storage plant according to the varying pressure (Ruths) principle with internal steam generation has been built in 1929 at Berlin-Charlottenburg with 1.4 MPa (210 psi) pressure, 50 MW electric power, and 67 MW-hours storage capacity. This plant is now - after 48 years - still in day and night stand-by and peak-load operation for the Berlin island network /3/. Several other systems including expansion-type schemes with external steam generation /4/ and feed water storage by means of displacement type (thermocline) schemes /5/ as well as combined schemes /6/ have been proposed since.

The PCIV has been developed by the Siempelkamp Giesserei KG of Krefeld, FRG during the last years as a reactor pressure vessel for HTGR and BWR nuclear power plants. Despite there being no specific Code available for the PCIV (data of the ASME Code, Section III, Div.2 for concrete reactor vessels may be applied to the tendons), a nuclear pressure vessel of 230 bar pressure and 17.5 m^3 internal volume is on order and being built by Siempelkamp to serve as a scram drive pressure vessel for the German Thorium High Temperature Reactor. The application of the PCIV for TES duties in nuclear power plants has first been proposed in 1974 /7/, and for solar power plants in 1976 /6/.

III. Project Description

A high-pressure air PCIV would have no thermal insulation at all; PCIV for solar gas turbine high-temperature sensible heat storage would have efficient thermal insulation at the inside of the vessel and would therefore be a cold going PCIV. Applications of the PCIV to nuclear, solar or coal-fired steam power plants may be either cold going (with inside thermal insulation under water pressure), or hot going with thermal insulation outside the main cast iron body, and the latter one either with cold tendons (necessitating pressurized thermal insulation between shoes and main body) or with hot tendons (of low relaxation or with the possibility of restressing).

As is known from Prestressed Concrete Pressure Vessels under development for water-cooled reactors, an efficient thermal insulation inside a vessel with hot water is difficult and expensive (much more so than for a vessel under gas pressure). Particular attention is therefore given to the hot going PCIV. The hot going vessel with hot going tendons needs wires with low relaxation that are not readily available at present. On the other hand, the problem of the pressurized thermal insulation between shoes and main body is solved by using relatively inexpensive "Klingerit 1000" sheets; the hot going vessel/cold going tendons concept was therefore chosen for the reference design PCIV (8000 m^3 internal volume, 12 m internal diameter, 71 m internal height, 6 MPa = = 900 psi working pressure) shown in Fig. 1. It provides stored energy corresponding to between about 200 and 300 MW-hours of electric energy.

A design base for hot and cold going PCIV is developed and proposed. Its main points are definition of a safety factor 1.5 against gapping and a safety factor 1.5 between tendons failure and gapping. For the hot going vessel with cold going tendons self-stressing is to be considered.

Transient thermal stresses during discharge of the reference PCIV are also to be considered since they may lead to surface gapping and to fatigue. Surface gapping can be tolerated to some extent and it may be minimized by proper design of the internal surface. Fatigue data are only available for large numbers of cycles (10^7). Tests with numbers of cycles applicable to TES (10^4 to 10^5) are being carried out by Siempelkamp and should become available during 1977. With present data (for 10^7 cycles) a temperature shock of about 40 K and a temperature swing for one hour discharge time of 60 K is possible for the reference design, necessitating the use of the cold going concept for displacement-type storage schemes.

Which flow sheet is suitable for steam power plant with integrated TES depends on many considerations. Flow sheets based on a separate peaking turbine are typical for peak load generation, for steam storage, and for large nuclear sets the generator of which is usually of limit size and may not be forced for peaking and where any change in the main plant to accomodate TES (except a few small steam or feed water lines for charging the TES plant and the corresponding return lines) would be difficult. Flow sheets in which the main turbine/generator set may be overloaded for peaking purposes are typical for feed water or combined feed water/steam storage and for coal-fired and solar steam power plants.

Whereas flow sheets with separate peaking turbines have been published before, Fig. 2 shows a new flow sheet for a coal-fired station. It is based on combined steam and feed water storage in an expansion-type arrangement at a storage pressure suitable for PCIV. Charging is carried out by feed water and throttled live steam which are being mixed within the PCIV.

Optimization of the operating pressure of such a plant may be carried out in the usual way. However, choosing the operating pressure somewhat higher than the theoretical optimum may be of interest if a high ratio of peak load to base load is required. Fig. 3 shows the additional peak power in percent of the base load power as a function of storage pressure. As an example: Increasing storage pressure from the theoretical optimum 4 MPa for 2 hours discharge to 8 MPa means an increase of specific cost by 5% but an increase of the possible additional peak power from 14 to 21% of base load, that is by 50%. There is not only the advantage of higher peak power but also the cost degression of PCIV and turbine etc. which may more than compensate the 5% cost increase due to higher pressure.

IV. Results

- The envisaged use of the PCIV opens up new technical and economical possibilities of integrated TES for peaking and reserve duty in thermal power plants. Apart from the application in coal-fired, nuclear, and solar steam plants, use of the PCIV for the quick start-up of peaking gas turbine sets and for sensible heat storage in solar gas turbine plants has been considered.
- Optimum pressures of TES in steam power plants depend strongly on the load duration and annual number of discharges considered and vary widely. Typical pressure should be between 40 bar (600 psi) and 80 bar (1200 psi). L/D ratios will be larger than 4 and in many cases even larger than 6. Specific cost should decrease up to unit internal volumes of about 10 000 m^3 at high pressures, and about 15 000 m^3 at lower pressures.
- Cost of the reference vessel is about $ 10,000.000 or 33 to 50 $ per kWh of electric energy stored. Capital cost of the peak power plant will be about 50 to 80 $ per kWh electric energy stored. Cost of peak power will be from about 30 to 100 mills/kWh, depending on many parameters.

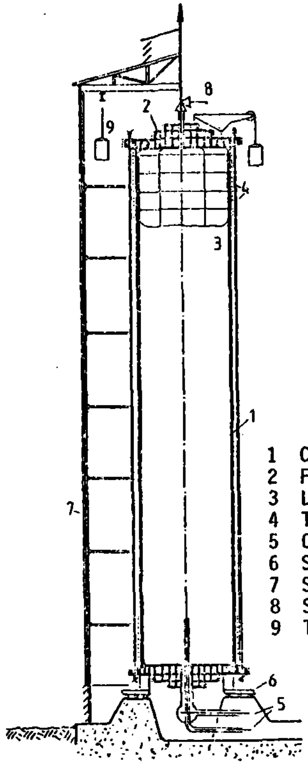
V. Future Activities

Possible further developments of the PCIV for TES applications include:

- more advanced design stress for cast iron, at least up to 40% of compressive strength as is permissible according to the ASME Code for concrete reactor vessels, against 25% of compressive strength used as design base,
- horizontal arrangement of the PCIV with axial tendons between main body and tangential tendons,
- an efficient and inexpensive inside thermal insulation for pressurized hot water applications (cold going PCIV),
- different liner concepts and liner materials including the no-liner concept.

For the introduction of the TES by PCIV concept into the power generation market, the following procedure is recommended:

(a) Detailed design studies on the PCIV for hot water as well as for high pressure air and high temperature gas duties, featuring the vertical as well as the horizontal arrangement, and the hot going vessel with cold going tendons as well as the cold going design with internal thermal insulation (1978/79/80);
(b) Selection of suitable reference plants (conventional, nuclear, solar) and optimization of the lay-out and design with integrated TES plants for specific cases (1979/80);
(c) Continuation of experimental work on cast iron fatigue data and on some design datails; construction and testing of a 60 m^3 test module PCIV (1978/79/80);
(d) Approval of the design base from local Authorities (1979/80);
(e) Design, building and commissioning of a prototype (pilot) plant for steam and for feed water storage of about 1000 m^3 internal volume and about 6 MPa (about 900 psi) working pressure (1980/82);
(f) Extended testing of the prototype plant by operating it for one year (1982/83).



1 Cylindrical wall
2 Flat plate
3 Liner
4 Tendons
5 Charging/discharging pipes
6 Supports
7 Structural steel
8 Safety valve
9 Trolley

Fig. 1 Reference design, general arrangement

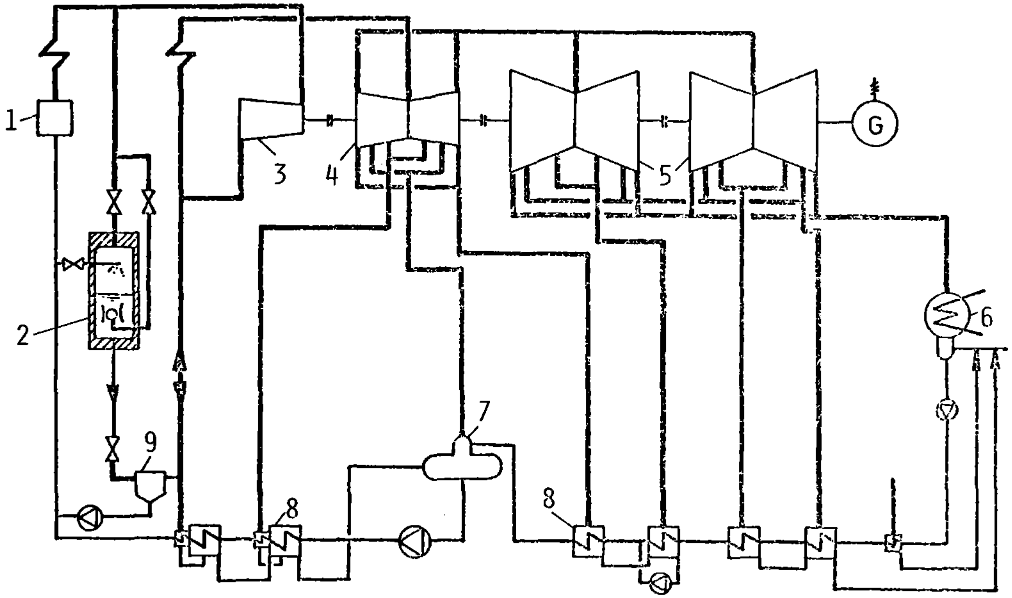


Fig. 2 Expansion-type feed water and steam storage with overloadable main turbine

1 Heat source	6 Main condenser
2 Expansion-type PCIV	7 Feed water tank (cold storage)
3 Main turbine, HP	8 Feed water heater
4 " " IP	9 Flash evaporator
5 " " LP	

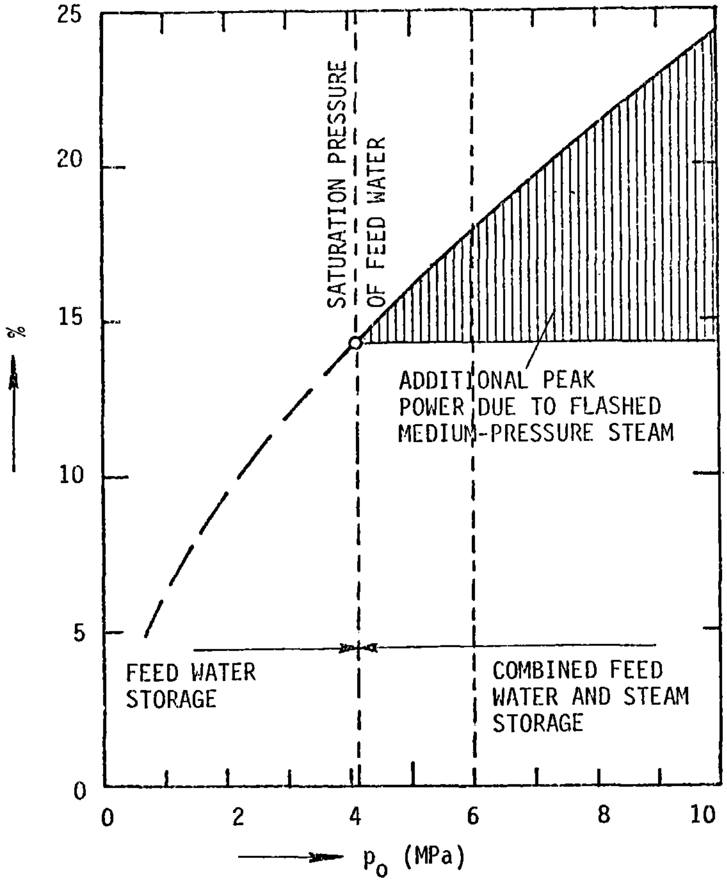


Fig. 3 Peak power in percent of base load power for expansion-type combined feed water and steam storage, as a function of operating pressure p_0

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Project Summary

Organization: Grumman Aerospace Corporation

Address: Bethpage, New York 11714

Project Title: Thermal Energy Storage Heat Exchanger

Principal Investigator: Angelo Ferrara (516) 575-2433

Contract No.: NAS-3-20117 Contract Period: 7/76 - 5/77

Contract Amount: $133,000

Project Goals: Analytical study to determine the technical and economic feasibility of using salts and salt eutectics for latent heat thermal energy storage to provide peaking capability in conventional (coal and nuclear) electric utility plants.

Project Status: Complete, Final and Topical (sizing) Reports to be issued 1 Nov. 1977

In his energy message, President Carter stated that the U.S. dependence on oil must be greatly reduced. In the near term, new electric utility plants will be coal or nuclear fueled and some existing plants will be switched from oil to coal. The current dependence on oil-fired equipment to provide intermediate and peaking loads can be reduced in one of two ways: (1) by cycling coal or nuclear plants to follow the load curve, or (2) by base-loading coal or nuclear plants and storing excess off-peak energy for later use in meeting peak demands. Many methods of energy storage; e.g., batteries, compressed gas, fly wheels, and super-conducting magnets have been suggested. Currently, the only method in use is pumped hydro storage and this relies on suitable site geography. This study was specifically to evaluate the potential for thermal energy storage (TES) to meet peaking power demands. In particular, the use of the latent heat capacity of salts that melt at the high temperatures required for utility energy storage was to be explored and a suitable heat exchanger defined. The heat absorbed in melting a material can be double or triple the sensible heat stored by heating the material to a higher temperature. Latent heat storage thus offers the possibility of designing much smaller TES systems, but also introduces many technical concerns since salts are typically corrosive, have a low thermal conductivity and may be hazardous.

This paper summarizes a ten month study performed for the NASA Lewis Research Center to assess the technical and economic acceptability of a latent heat TES heat exchanger system for application in conventional utilities. The overall goal of our program was to determine whether a coal or nuclear electric generating plant with a TES system is cost effective (considering both investment and operating costs), compared to a similar sized plant cycled to follow the load curve. Since both plants must meet the electrical demand the turbine/generator requirements are the same. The investment cost comparison is thus the cost of the TES system versus the cost of the larger steam capacity (boiler or nuclear island), which is (in 1977 prices) approximately \$450 per KW_e. Based on the latent heat capacity of suitable salts and typical plant load curves which determine the total energy to be stored, we showed that the TES system must cost less than about \$1 per pound of salt for a system providing significant peaking capability (~7% increase in capacity). A typical 1000 megawatt electrical plant requires approximately 14 million pounds of salt to store the required 900 megawatt-hours of thermal energy to provide 6 hours of peaking capability.

Operating costs with the TES system must consider two thermal inefficiencies; one is the heat loss from the storage unit and the second is the thermodynamic necessity that heat must be returned to the power plant cycle at a lower temperature than it is extracted due to the temperature differences required to transfer heat into and out of storage. The latter is not a heat loss but is a loss in energy availability. The alternate approach of cycling a (larger) plant to follow the load curve, however, also introduces an inefficiency (operating the boiler at less than 100% load). Detailed heat balances based on specific energy storage and usage conditions and plant duty cycles are required to determine which system, in fact, has the lower fuel cost.

To maximize the realism of our plant cycle analysis, five (5) existing nuclear and fossil electric utility plants were chosen as representative of present day technology (see Fig. 1). TES concepts can be considered as possible retrofits to these plants or as new plant construction of that generic type. Ten (10) locations for the TES in the plant cycle were identified, which resulted in 35 feasible plant/location combinations. Since the study was to emphasize heat exchanger concepts and not differences between plants, the choices were screened down to one plant; the coal fired Ft. Martin unit in West Virginia and two locations (or uses) of thermal energy storage. Both cycle locations used main steam as the heat source. Usage in one case was for feedwater heating which decreased turbine steam extraction and hence increased turbine output; and the second case used the stored energy to generate steam for a separate turbine/generator (see Fig. 2).

In parallel to the plant cycle analysis we identified candidate salts for use as the storage media. Selection was based on cost, compatibility with steel container materials, thermal performance and safety. The recommended salt eutectics are in the chloride, nitrate/nitrite and hydroxide families. Figure 3 summarizes the 16 salts selected, which cover the temperature range of interest (~300 to 900°F), in about 100°F increments.

The final screening in the program was to select two promising TES systems for detailed performance and economic evaluation. Alternate heat exchanger concepts were assessed, including standard technology such as a tube/shell heat exchanger with the salt on the shell side, and variations using heat pipes or an intermediate loop to transfer heat from the utility fluid to the salt. These are examples of passive systems where the salt phase change material (PCM) is used in bulk and is static. Alternately, macroencapsulated PCM (bricks) can be configured into a checkerboard heat exchanger or microencapsulated PCM can be fluidized and heat transferred to and from the flowing stream. Moving bulk PCM systems can also be devised using molten salt pumps, solid conveyors and scrapers. The motivation for moving or fluidized systems is to eliminate the large thermal resistance resulting from any significant thickness of static salt. All the static systems require a large heat exchanger area to overcome this resistance.

The advantages and disadvantages of these heat exchanger concepts were reviewed and it was decided that macroencapsulated systems did not offer any advantages over the tube/shell unit and that the microencapsulation costs are likely to be extremely high. The heat pipe unit, while exhibiting desirable features, was not feasible at the temperature level of the Ft. Martin plant since no suitable heat pipe working fluid is available. Heat pipe units are reasonable for the lower temperature steam conditions typical of nuclear plants but we felt that the first applications of a new technology (TES) would not be in a nuclear plant. Near term recommendations are therefore the standard tube/shell and the tube/shell with intermediate (liquid metal) fluid loop. The latter offers the advantage of isolating the salt from the utility steam and has certain control advantages, but does add the complexity of a liquid metal loop. For the longer term a moving PCM system has promise. The molten salt is pumped to a rotating drum where it solidifies and is scraped off. The solid is collected in a storage tank. Melting is by heating coils in the bottom of the tank and the liquid is drawn off for transfer to a separate tank. Total storage volume is twice as large as the tube/shell, but the required heat exchanger surface area is much less.

The tube/shell and the intermediate loop tube/shell that were selected as the two concepts for design refinement and cost analysis were applied to both the feedwater heating and separate cycle usage locations in the Ft. Martin plant cycle and plant heat balances computed for comparison with the base plant. The incorporation of the TES in the cycle to supply feedwater heating results in an improvement in net plant heat rate with fuel (coal) saving of $183,000 per year compared to cycling the plant. No change in net plant heat rate results in the separate power cycle case.

We suggest a stayed structural arrangement for the upper and lower domes of the tube and shell unit which greatly reduces the unit weight and cost. Although not optimized, this approach results in a TES capital cost of ~$22.5 million which is about $2 million less than the cost of enlarging the plant to provide a peaking capability of about 7% (see Fig. 4).

A special situation for the application of TES exists when a plant is being converted from oil to coal. This results in a derating of the boiler thus leaving excess turbine capacity. For a 500 megawatt plant the extra 7% peaking capability would require a larger T-G costing about $8.6 million. If this is available "free" in a conversion it considerably improves the TES economics. In addition the installation of TES removes a disincentive to coal conversion; namely, the loss of capacity, which would require the utility to accelerate its new plant construction schedule.

Overall we feel that latent heat TES is a viable means of providing peaking capability, on its own merits, compared to cycling a coal or nuclear plant. This does not mean it is necessarily superior to other TES systems using sensible heat storage. Some of these systems use very inexpensive storage material (water, rock, etc.) and containers (underground caverns, etc.). Although our study has identified salts that are also relatively low in cost, containment costs are high due to the high temperature and pressure. It is suggested, therefore, that a further evaluation of active heat exchanger designs be performed to better evaluate the latent heat TES option. We have identified the signficant peripheral costs (such as interconnect piping, A&E fees, etc.) that must be included in any comparative evaluation of systems.

Complete documentation of this study is contained in the contract Final and Topical reports to be distributed by NASA Lewis Research Center on 1 Nov. 1977. A technical paper "Molten Salt Thermal Energy Storage for Utility Peaking Loads" was presented at the 12th Intersociety Energy Conversion Engineering Conference, 1 Sept. 1977 in Washington, D.C.

GENERIC TYPE	OPERATING STATION CONSIDERED	LOC	GROSS MW OUTPUT	THROTTLE PRESS. PSIG	THROTTLE TEMP °F	REHEAT °F
BOILING WATER REACTOR	COOPER NUCLEAR STA UNIT 1	NEBR (NEPP)	835	970	541	–
PRESSURIZED WATER REACTOR	THREE-MI ISLAND UNIT 1	PA. (GPU)	870	900	565	–
SUPERCRITICAL COAL FIRED BOILER*	FORT MARTIN UNIT 1	W. VA. (ALGPS)	540	3500	1000	1000
HIGH TEMP GAS–COOLED REACTOR	FORT ST. VRAIN UNIT 1	COLO (PSCO)	355	2400	1000	1000
HIGH PRESS. OIL FIRED BOILER*	ROSETON UNIT 1	N. Y. (CEHG)	600	2400	1000	1000

*TYPICAL CYCLES, COULD APPLY TO EITHER OIL OR COAL FIRED PLANTS.

Figure 1 Reference Utility Power Plants

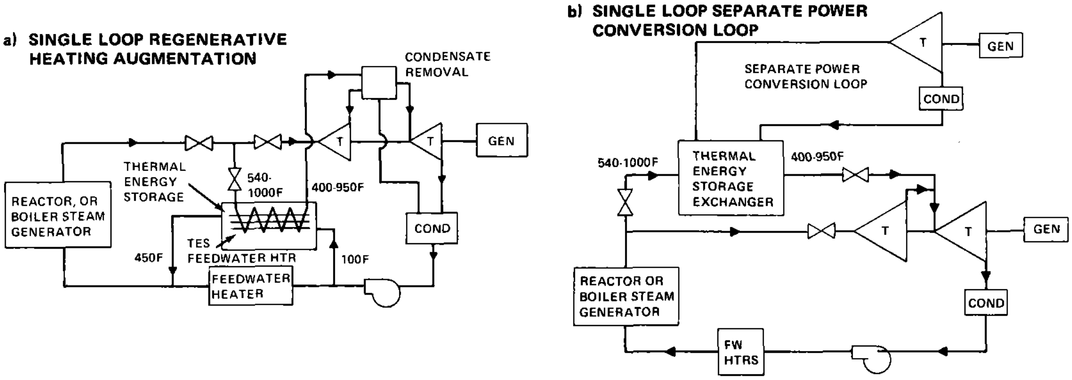

Figure 2 TES Locations in Power Plant Cycles

SALT ELEMENT A·B·C	MELT POINT °C (°F)	COMPOSITION WEIGHT % A	B	C	HEAT OF FUSION, ΔH_{fg} CAL/GM (BTU/LB)	SPECIFIC HEAT CAL/GM °C SOLID (C_{ps})	LIQUID (C_{pl})
$KNO_3 \cdot NaNO_3 \cdot NaNO_2$	142 (287)	53	7	40	18.5 (35)	.29	.32
$KNO_3 \cdot NaNO_3 \cdot NaNO_2$	179 (354)	PARTHERM		350	19.5 (35)	.29	.32
$Ca(NO_3)_2 \cdot NaNO_2$	204 (399)	48.3	51.7	–	31.2 (56)	.33	.36
$NaNO_3 \cdot KNO_3$	220 (428)	45.7	54.3	–	32.8 (58.8)	.36	.36
$NaNO_3 \cdot NaOH$	246 (475)	84.5	15.5	–	42.6 (76.5)	.45	.45
$NaCl \cdot NaNO_3$	297 (567)	4.6	95.4	–	46.8 (84)	.44	.43
$NaNO_3$	307 (585)	100	–	–	43.5 (78.1)	.46	.44
$NaOH$	318 (605)	100	-	–	76 (136)	.48	.50
$KCl \cdot KNO_3$	320 (608)	4.5	95.5	–	26.21 (47)	.28	.29
KOH	360 (680)	100	–	–	32.1 (57.6)	.32	.36
$KCl \cdot NaCl \cdot MgCl_2$	385 (725)	14.5	22.3	63.2	110 (197)	.23	.248
$NaCl \cdot BaCl_2 \cdot MgCl_2$	418 (784)	28.4	31.8	39.8	81.6 (146)	.19	.21
$NaCl \cdot MgCl_2$	460 (842)	60	40	–	111 (199)	.22	.24
$CaCl_2 \cdot KCl \cdot NaCl$	465 (869)	64.5	6.5	29	77.6 (139)	.21	.23
$NaCl \cdot CaCl_2$	500 (928)	33	67	–	67 (121)	.20	.24
$KCl \cdot NaCl \cdot CaCl_2$	504 (939)	5	29	66	67 (120)	.26	.24

Figure 3 Thermophysical Property Data of Selected Salts

	COST
EARTHWORK AND GRADING	$ 8,200
ROADS AND PAVING	1,300
LAND AND LAND RIGHTS	50,000
FOUNDATIONS	93,000
PIPING AND VALVING	1,166,800
INSTRUMENTATION AND CONTROL	50,000
FLASH TANK	36,000
RECUPERATOR	500,000
TES UNITS	7,800,000
TES SALT	1,219,000
SUBTOTAL	$10,924,300
CONTINGENCY & INT DURING CONSTR AT 15%	1,638,650
ENGRG & CONSTR MGMT AT 12%	1,310,920
INCREM T-G (37.36MW) & ELECT COST AT $230/KW$_e$	8,592,000
TOTAL	$22,465,860
SYSTEM BREAKEVEN = (37.36 MW) ($650/KW) =	$24,284,000
NET SAVINGS – NEW PLANT OR PLANT w/o EXCESS T-G	$ 1,818,140
– RETROFIT, PLANT WITH EXCESS T-G	$10,410,140

Figure 4 Total TES System Capital Costs – Ft. Martin, Feedwater Heating Case

PROJECT SUMMARY

ORGANIZATION: Institute of Gas Technology

ADDRESS: 3424 South State Street, Chicago, Illinois 60616

PROJECT TITLE: Molten-Salt Thermal-Energy Storage Systems

PRINCIPAL INVESTIGATORS: John Dullea and Hans C. Maru

TELEPHONE NO: 312-567-3971

CONTRACT NO.: EY-76-02-2888 CONTRACT PERIOD: 6/1/76-5/30/77

CONTRACT AMOUNT: ERDA $181,440

PROJECT GOALS

The goals of this program are to determine the technical feasibility of using inorganic salts as phase-change thermal-storage materials (PCM) for high-temperature (> 300°C) applications, to develop a mathematical model able to predict the behavior of a PCM in a latent-heat thermal-energy storage (TES) system, and to use this information in designing prototype, large-scale (100 to 1000 $kWhr_t$) storage systems for further technical and economic evaluation.

PROJECT STATUS

The first phase of the program, involving selection of a suitable storage material, mathematical modeling, heat-transfer analysis, and operation of small-scale (< 10 $kWhr_t$) TES systems, has been completed. Results have been encouraging, showing good agreement between the mathematical model and the observed performance. Further work on system analysis, performance improvements, and large-scale system design is now in progress.

I. PURPOSE AND BACKGROUND INFORMATION

Storage of thermal energy at temperatures above 300°C is required for a number of applications, including conventional and solar power plants, industrial processes, and vehicular propulsion. Generally, shaft power from a thermal engine and/or thermal energy itself can be produced via heat exchange with a thermal storage medium. Consideration of the temperature of the thermal input, thermal stability, compatibility of the storage medium with its means of containment and of heat exchange, and the useful end product desired (shaft power or thermal energy) set the storage temperature. For example, in the case of storage for power plants, the desired useful temperature range of the storage medium is expected to be 450° to 535°C. The production of shaft power can be considered the highest quality use of stored thermal energy; therefore, maximizing the storage capacity in a narrow temperature band in this range is desirable. Ideally, materials which undergo a phase change in the specified temperature range are desirable because relatively high energy densities are obtainable at a fixed temperature, the melting point.

However, the techno-economic feasibility of this concept cannot be accurately assessed until the thermal behavior of these systems is determined. Therefore, the goal of this program is to generate the technical information (salt stability, containment materials stability, and thermal fluxes) required to determine the feasibility of storing high-quality thermal energy using, primarily, the latent heat of fusion of inorganic salts.

II. PROJECT DESCRIPTION

The technical effort was organized into four tasks. Our efforts in this program were focussed on salts undergoing phase changes in the temperature range of 450° to 550°C. However, the methodology developed is applicable to the behavior of inorganic salts used as phase-change storage materials in general. In the first task, a model storage material was selected from the more than 30 compositions investigated. During the second task, an intensive review of past modeling studies was made, and the information used to develop an appropriate model describing the behavior of a storage material in terms of its thermal properties and conditions of use. Concurrently with the model development, 10 laboratory-scale (0.1 $kWhr_t$) TES units were operated to verify assumptions made in the model development and to study performance improvements by thermal conduction enhancement and volume change control additives. Pertinent thermal and thermophysical properties of the storage material were experimentally verified, and the engineering-scale (8 $kWhr_t$) TES system was designed to generate data for comparison with the modeled behavior and to provide "first cut" engineering data for performance evaluation and large-scale system design. During the third task, three engineering-scale units were operated for periods up to

1400 hours (30 cycles) to verify the mathematical model and to study the performance stability and the performance improvements associated with heat-exchanger design. The data generated was analyzed in the fourth task, and the performance evaluated and compared with the predicted performance.

III. RESULTS

Salt Selection

Numerous salts and mixtures of salts can be considered for storage of thermal energy in the 450° to 540°C temperature range. However, if cost, availability, stability, nontoxicity, and corrosiveness are the first criteria for salt choice, the number dwindles to include only chlorides, bromides, hydroxides, fluorides, and carbonates. We concluded that, because alkali carbonate mixtures show relatively high thermal conductivity, low volumetric expansion on melting, low corrosivity, and good stability as compared with other salts, they are attractive as heat-of-fusion storage materials in this temperature range. An equimolar mixture of Li_2CO_3 and K_2CO_3, which forms an intermediate compound, $LiKCO_3$, having a melting point of 505°C and a heat of fusion of 148 Btu/lb, was selected as the experimental phase-change storage material and model system.

Model Development and System Design

The purpose of developing the model was to establish a relationship among system design factors, heat-transfer characteristics, thermal properties of the storage material, and the rate at which the salt solidifies (governing the energy availability). The resulting equation was derived from past studies[1] with suitable modifications to give the velocity of a liquid-solid interface as it moves away from the center of a cylinder while being cooled internally. The terms[2] in which this is expressed are —

The Fourier number, $N_{Fo} = \dfrac{kt}{C_p \rho a^2} = \dfrac{\alpha\, t}{r_0^2}$

The phase change number, $N_{ph} = \dfrac{\Delta H_f}{C_p\,(T_m - T_a)}$

The Biot number, $N_{B_i} = \dfrac{hr_0}{k}$

The dimensionless radius, $r^* = \dfrac{r}{r_0}$

where r_0 is the heat-exchanger radius and r is the radial location of the interface. Equation 1 was derived using these relationships and gives the time needed to solidify the molten PCM from $r^* = 1$ to $r^* = R$:

$$N_{Fo} = \int_1^R \frac{r^* \ln r^* \, (N_{Bi} \ln r^* + 2)\, dr^*}{\sqrt{(N_{Bi} \ln r^* + 1)^2 + 2 \frac{N_{Bi}}{N_{ph}} \ln r^* \, (N_{Bi} \ln r^* + 2)} - (N_{Bi} \ln r^* + 1)} \qquad (1)$$

This equation can be used to determine critical system design parameters, such as heat-exchanger dimensions and spacing (r_θ), depending on the storage material being used (k, C_p, ρ, ΔH_F, T_m) and the working fluid temperature and flow characteristics (h, T_a).

The engineering-scale units were designed to generate the information needed to verify Equation 1. An annular arrangement was selected, having an internal radius, r_0, of 1 inch and an external radius of 6 inches with an 18-inch length (capacity of ~1 ft^3 of salt). Thermocouples were located at various radial positions and their response with time recorded to determine the time required for the interface to reach those locations. The unit design and a typical discharge trace are shown in Figure 1.

The heat of fusion and melting point of $LiKCO_3$ was verified by DTA and DSC, and no supercooling effects were detected. A 6% volume change on fusion was measured, and, as a result, inert supports were not used in the TES units. However, the behavior of inert supports for controlling the thermal expansion was investigated,* but their use showed a decrease in system performance and raised the problem of sedimentation. Thermal conductivity enhancement was studied by adding 3 to 15 volume percent of metallic fins, screens, wool or honeycomb matrix; stainless steel and aluminum were both found compatible with the salt and improved the output energy flux by 25% to 100%.

Engineering-Scale Performance and Model Comparison

The engineering-scale units were charged electrically, and the power input was recorded. Discharging was accomplished by blowing ambient air through the heat exchanger (single pass) at 350 lb/hr, producing fully turbulent flow. The air temperatures at the heat-exchanger inlet and outlet and the air flow were recorded continuously and used to calculate the energy discharge rates. The performance of units containing a single-tube heat exchanger and a finned single-tube heat exchanger are shown in Figure 2. The average energy discharge rate without fins was found to be 4000 Btu/hr-ft^2 and with fins was 5500 Btu/hr-ft^2 (800 to 1250 Btu/hr-ft^2 if steam at 480°C was used). However discharge rates as high as 40,000 Btu/hr-ft^2 were observed during the first few minutes of discharge before a significant thickness of solid formed, indicating performance that may be attainable with an

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* $LiAlO_2$ was selected due to its proven effectiveness in this application with the model system.

active heat-exchanger design. The storage efficiencies during a 24-hour period were in the range of 50% to 60%. However, larger scale units exhibiting the same rate of heat loss (per unit surface area) would have storage efficiencies above 98%.[3]

The performance of the units was found to be stable and unaffected by under or overcharging to simulate variations in duty cycles. Investigation of the containers showed little internal corrosion, and no containment difficulties were encountered. No significant salt loss by vaporization was detected, indicating that complex container sealing is not necessary as it would be if salts such as chlorides or fluorides were used. Analyses of the salt after 1400 hours of operation revealed no changes in the melting point, heat of fusion, or composition.

A comparison of the mathematical model with the experimental results can be obtained by numerically evaluating the integral in Equation 1, as shown for two cases in Figure 3. The family of curves with $N_{ph} = 0.57$ describes the solid-layer thickness of the model storage material as a function of the time (N_{Fo}) the salt was cooled with room-temperature air. The curves with $N_{ph} = 10$ represent the same material with the coolant at a temperature 25°C below the melting point of the salt. In our experimental system, $N_{Bi} = 0.75$ and $N_{Fo} = 4.133t$. The resulting system behavior is shown in Figure 3 and is in good agreement with the predicted curve ($N_{ph} = 0.57$, $N_{Bi} = 0.75$) when the time is corrected to allow for the cooling of the liquid to the melting point (the model assumes the liquid phase is uniform at the melting point when solidification begins). The observed deviation from the model behavior is a result of heat-transfer effects associated with strong convective mixing in the molten salt, which was not considered in the modeling study. Radial and axial temperature profiles through the salt obtained during discharging are shown in Figure 4. The strong convective mixing in the molten salt is verified by the flat temperature profiles in both directions through the still molten salt. The strong heat-transfer resistance of the solidified salt, which appears to limit the energy discharge rates, can also be seen by the steep radial thermal gradient between the heat-transfer surface and the solid-liquid interface.

IV. FUTURE PLANS

Near-term plans include system analysis to identify specific utilization concepts and temperature ranges, and selection of storage materials for these uses. Engineering and laboratory-scale units will continue to be operated to establish performance and material endurance projections, and to test other promising salt mixtures and conduction enhancement concepts. These results will then be used in the design of prototype large-scale systems for accurate technical and economic feasibility assessment.

NOTES

1. A more detailed treatment of the modeling studies is presented in topical report number COO-2888-2, "Molten Salt Thermal Energy Storage Systems: System Design," February 1977, available from the National Technical Information Service, U.S. Department of Commerce, Springfield, Va. 22161 (Paper copy $6.00, Microfiche $3.00).

2. The nomenclature is described below:

   k = thermal conductivity of the solid phase, mW/m-K
   C_p = heat capacity, J/g
   ρ = density, kg/m^3
   a = characteristic thickness (r_0), m, cm
   α = thermal diffusivity, m^2/s
   t = time, min
   ΔH_F = heat of fusion, kJ/kg
   T_m = PCM melting point, K
   T_a = coolant entering temperature, K
   h = surface heat-transfer coefficient, mW/m^2-K

3. Values calculated based on a TES design conceived by Grumman Aerospace Corporation to meet auxiliary power-generation requirements at Fort Martin, West Virginia (supercritical fossil-fueled boiler).

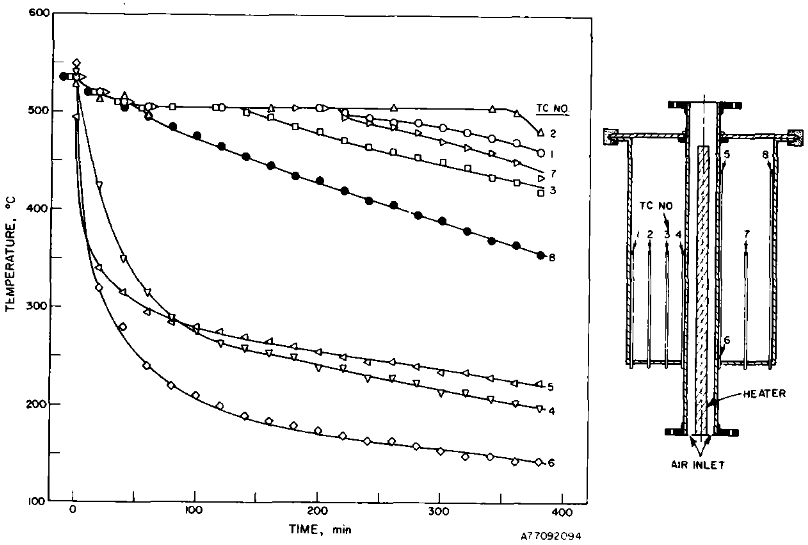


Figure 1. TYPICAL TEMPERATURE RESPONSE AT VARIOUS LOCATIONS IN THE ENGINEERING-SCALE UNITS DURING DISCHARGING

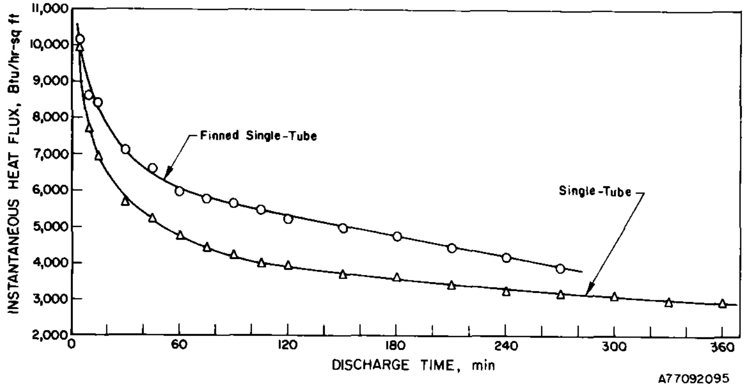


Figure 2. ENERGY DISCHARGE RATES WITH DIFFERENT HEAT EXCHANGER DESIGNS (Engineering Scale)

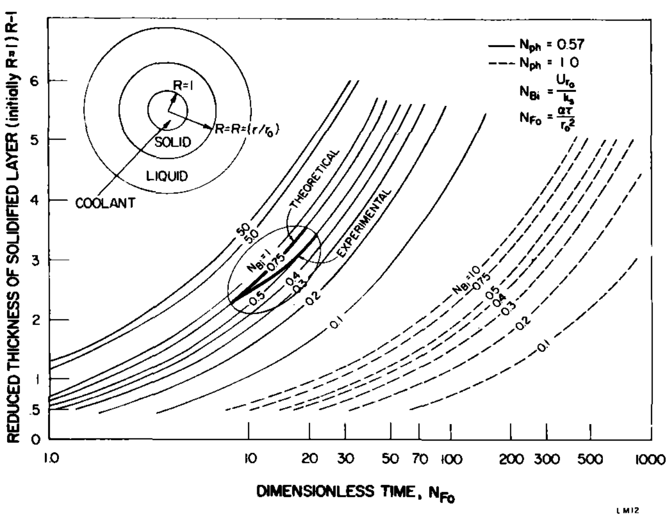


Figure 3. SOLIDIFICATION OF A CYLINDRICAL MELT FROM WITHIN CALCULATED FROM EQUATION 1 USING $LiKCO_3$ AS THE MELT IN AN ENGINEERING-SCALE UNIT COOLED WITH EITHER ROOM-TEMPERATURE AIR (N_{ph} = 0.57) OR A COOLANT RUNNING 25°C BELOW THE $LiKCO_3$ MELTING POINT (N_{ph} = 10.0)

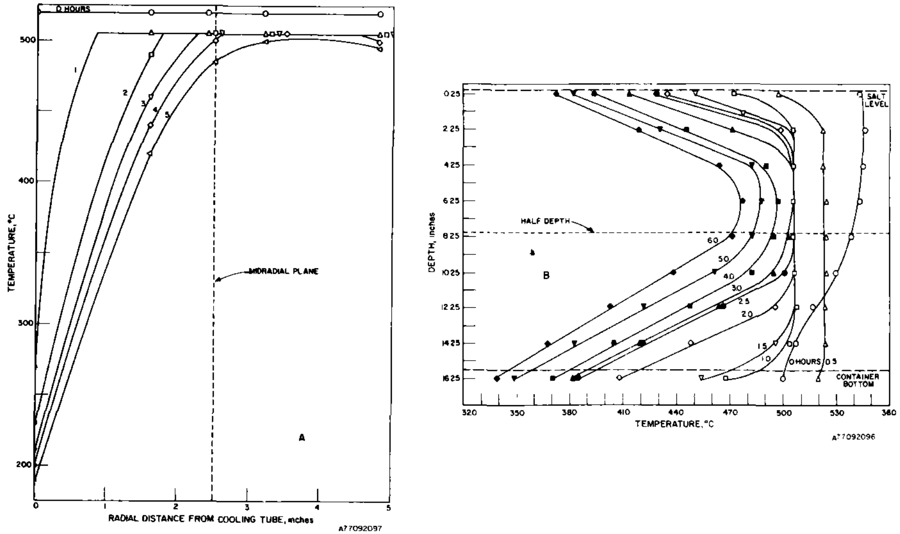


Figure 4. RADIAL (A) AND AXIAL (B) TEMPERATURE PROFILES THROUGH THE $LiKCO_3$ OBTAINED DURING DISCHARGING OF AN ENGINEERING-SCALE UNIT

ORGANIZATION: JET PROPULSION LABORATORY

ADDRESS: 4800 Oak Grove Drive., Pasadena, Calif. 91103

PROJECT TITLE: Thermal Energy Storage in Solids

PRINCIPAL INVESTIGATOR: Robert H. Turner

CONTRACT NO.: L-776-71-43-01-35

CONTRACT AMOUNT: ERDA=$101,167 OTHER=0

TELEPHONE NO.: (213) 354-6333

CONTRACT PERIOD: May 76 to March 77

PROJECT GOALS:

Hollow steel ingots stacked together to form a thermal storage unit offers direct contact between the pressurized working fluid (steam) in a power cycle and and the storage medium. No external containment is necessary and heat exchangers are eliminated. An alternate storage technique is to pour an inexpensive solid around a matrix of closely packed pipes, which pipes can contain pressurized water or steam. Problems and feasibility of both approaches are being assessed, and the technical and economic performance of the TSUs when integrated with a baseload power plant will be estimated.

PROJECT STATUS:

The work is about half completed. Electroslag welded steel slab sandwiches are less expensive than the original concept of hollow steel ingots, although both can be commercially produced. Pouring concrete around steel pipes will not provide a reliable TSU because thermal stresses will cause separation of the concrete from the pipes, degrading thermal performance. Sand instead of concrete around the pipes appears to be a better choice for an inexpensive storage medium. Most of the materials and stress research is completed, and the thermal analysis is proceeding. An analysis to integrate the TSUs into a baseload power plant will be conducted.

RESULTS:

Two concepts were originally advanced for study as TSU candidates: the hollow steel ingot and concrete poured around pipes. The hollow steel ingot concept is indicated in Figure 1, where by an extrusion process a long billet with axial hole is produced. The ingot is 60 feet long, which length can be transported by rail. Since the ingot serves as a pressure vessel, pressurized fluid (water or steam) can be passed through the hole to thermally charge or discharge the unit. Many ingots are stacked to constitute the overall thermal storage unit (TSU) as shown in Figure 2. A header and valve arrangement allows fluid to flow through one and then another ingot in some series-parallel arrangement. Because the ingot is essentially a very thick pipe, the loss of strength of carbon steel above 650°F (343°C) is not a severe impediment, and our studies indicate that such an ingot system can contain pressurized steam to 750°F (400°C).

Many steel companies were contacted, but only one, Cameron Iron in Houston, is presently equipped to fabricate the steel member shown in Figure 1. Alternative ways to fabricate a hollow steel ingot were considered, such as purchasing a long steel ingot without the hole and then contracting to have the hole trepanned or even drilled with a flame lance. Drilling the hole is more expensive than extruding a finished ingot, which according to Cameron Iron will cost 45¢/pound.

To reduce the cost of the hollow steel ingot member, a two face "sandwich" approach has been adopted as the baseline concept; this is depicted in Figure 3. Basically, two identical steel slabs are separated by spacer bars and then electroslag welded together, so there is an interior passage for (pressurized) working fluid to contact the steel.

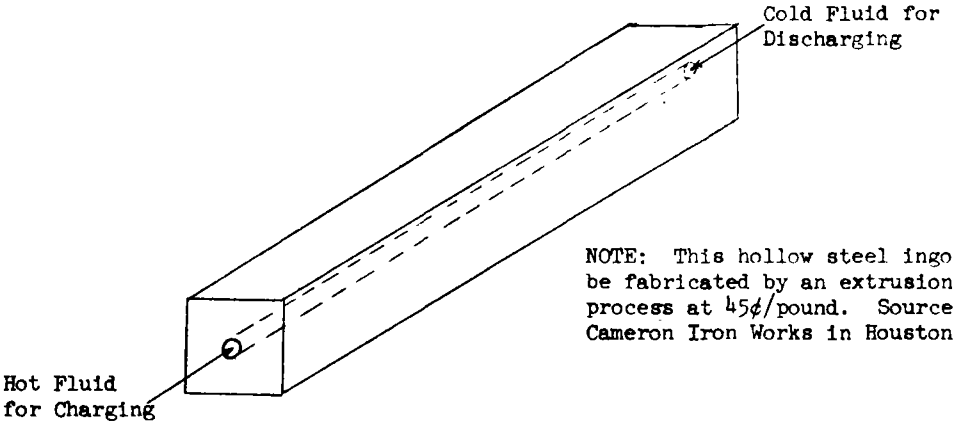
Near the end, of the passage narrows down so that header tubes can be attached to direct the flow between units. The necessary slab dimensions for different conditions have been determined, and the fabricated "sandwich", including welding, will cost around 30¢/pound. Many "sandwich" units are stacked to form the TSU, as in Figure 2.

The other concept which is being investigated is the desirability of pouring a very inexpensive solid material around a bundle of closely spaced tubes. The tubes could contain pressurized fluid which would bring heat to or from the solid. Originally it was felt that (inexpensive) concrete poured around the pipes would provide a continuous heat transfer path between the pipes and solid storage medium. The low thermal conductivity and thermal diffusivity of the solid storage medium would require close spacing of the heat transfer tubes, at considerable expense, but this would be traded off against the very low cost for the thermal storage medium. However, stress studies revealed that the concrete would crack and separate from the tubes, breaking the conduction heat transfer path and degrading performance. The use of concrete has been abandoned in favor of pouring sand, which should cost even less than concrete. A systems thermal analysis is being conducted to estimate technical and economic performance of such a TSU operating in different environments.

FUTURE ACTIVITIES:

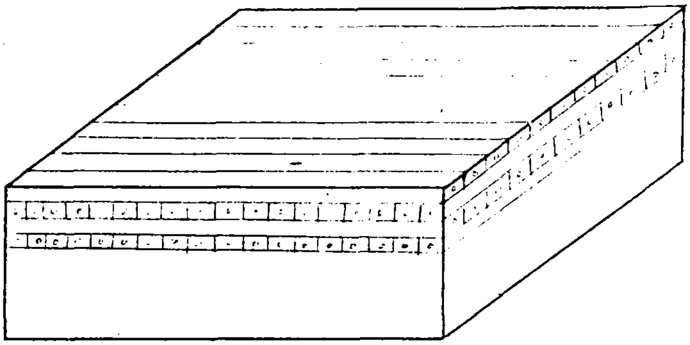
A systems analysis is in progress to determine how the considered TSUs will thermally perform for different storage conditions of interest. In the case of the sand-around-pipes approach this will provide design data from which necessary tube spacing can be specified, which will allow the system cost to be estimated, since the major cost will be for the pipes. For the steel sandwich concept it is necessary to design required flow routing to assure that adequate heat transfer area is made available on the fluid side, especially if superheated steam is used as the transport fluid. Also, flow length requirements must be understood and controlled to avoid wasting both pump work and pressure drop.

A system analysis to determine the effect of a TSU integrated with a baseload power plant is also being conducted. This will consider three modes of heat release for use in a steam power plant: feedwater preheating only, feedwater preheating and boiling, and preheating, boiling and superheating.



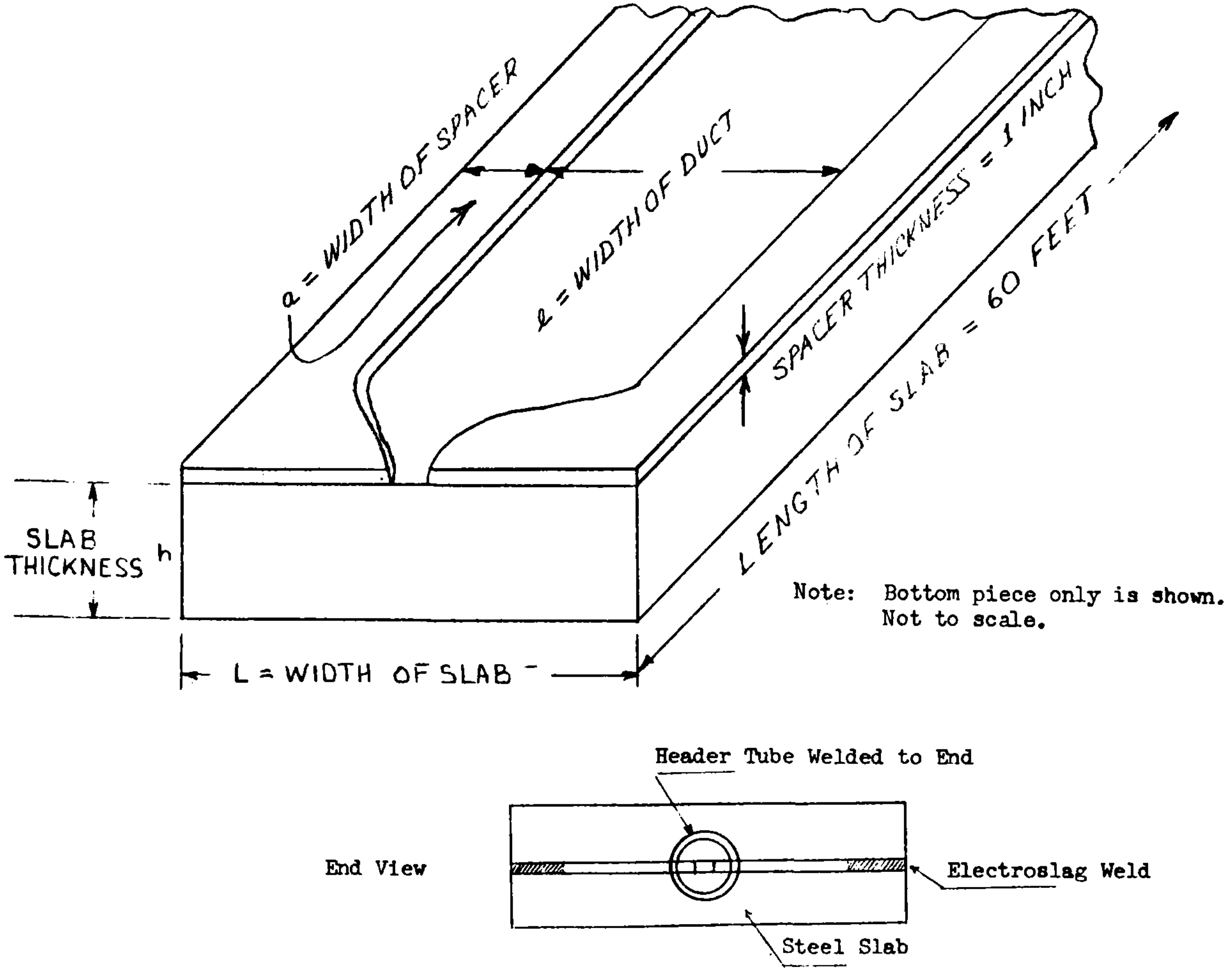
NOTE: This hollow steel ingot can be fabricated by an extrusion process at 45¢/pound. Source: Cameron Iron Works in Houston

FIGURE 1 Hollow Steel Ingot TSU, Original Concept



NOTES:
- * Header system not shown
- * Blanket insulation exterior, not shown
- * Ingots cross-stacked for stability

FIGURE 2 Many Ingots Stacked to Form a TSU



Note: Bottom piece only is shown.
Not to scale.

NOTES:

- Estimated cost is 30¢/pound
- Fluid passes through the duct, directly contacting steel slab

FIGURE 3 Electroslag Welded Steel Sandwich with Interior Passage

PROJECT SUMMARY

Organization: Martin Marietta Corporation
Denver Division

Address: P. O. Box 179
Denver, Colorado 80201

Project Title: Applications of Thermal Energy Storage in the Cement Industry

Principal Investigator: F. A. Jaeger

Telephone: (303) 979-7000
Extension 3748

Contract No.: EC-77-C-01-5084

Contract Period: September 1977 through

Contract Amount: ERDA $89,000

Project Goals:

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. Various energy storage systems and applications will be compared. The most promising of these will be selected for further technical and economic analyses. As a result of these analyses, a technology validation program and program plan for commercialization of the selected concepts will be developed.

Project Status:

Contract signed in September 1977. Work has just started on the definition of energy consumption, sources of waste heat and potential uses of the waste heat.

PROJECT SUMMARY

ORGANIZATION: Naval Research Laboratory

ADDRESS: Code-7120
Washington, DC 20375

PROJECT TITLE: Energy Storage Boiler Tank

PRINCIPAL INVESTIGATOR: Talbot A. Chubb
(202)-767-3580

PROJECT MANAGER: Joseph J. Nemecek
(202)-767-3530

CONTRACT NO.: EC-77-A-31-1024 CONTRACT PERIOD: March 1977
March 1978

PROJECT GOALS:

Studies and small-scale experiments leading toward the construction of a 2-MWHr thermal storage system utilizing the latent heat of fusion of a eutectic made up of naturally occurring salts.

PROJECT STATUS:

Commercially prepared salts have been melted by means of condensing terphenyl vapor. The heat transfer fluid composition is being optimized for cost and heat transfer properties. General specifications are being written for procurement of material and hardware to build the 2 MWHr system scheduled to operate in October of 1978.

ENERGY STORAGE BOILER TANK, PROGRESS REPORT

T.A. Chubb, J.J. Nemecek and D.E. Simmons
Naval Research Laboratory
Washington, D.C. 20375

Abstract

The energy storage boiler tank stores energy in molten salt eutectic and uses evaporation/condensation of a heat fluid for energy transport within the tank. In laboratory tests 54 lbs of NaCl, KCl, $MgCl_2$ eutectic has been melted by terphenyl condensation with a ΔT of less than 12°C between the pool of liquid terphenyl in bottom of tank and salt meltpoint. In large tanks costs are estimated to be ~\$2800 per MWh (thermal) of storage capacity.

The Energy Storage Boiler Tank(1) (ESBT) is a means for providing energy storage at moderately high temperature. The goal is to provide storage of large quantities of energy at low cost and in a form suitable for generation of on-demand superheated steam. One application is to provide energy storage for municipal utilities, especially utilities energized by sunlight(2), where storage is needed to permit full power production during night time periods, cloudy days and peak power intervals.

NRL is currently working on a first version of the ESBT, Figure 1. This version uses fusion of a salt eutectic mix (NaCl, KCl, $MgCl_2$) as a means of energy storage. The salt mix melts at a temperature of 385°C with a heat-of-fusion somewhat greater than that of ice. Energy flow into and out of the salts is achieved by heat pipe techniques, using the evaporation and condensation of a terphenyl heat transfer fluid. By packaging the salt in containers with a large aggregate surface area, the ESBT compensates for the poor thermal conductivity of the salts, achieving acceptable temperature drops (ΔT) associated with energy input and withdrawal. The ESBT also uses a condensation boiler heated by the same terphenyl heat pipe fluid. As a result it serves as a demand responsive source of high temperature steam.

Version 1 of the ESBT promises low cost energy storage estimate of \$2804 per MWh (thermal). A materials cost estimate of \$1407 per MWh (thermal) is arrived at by using salt costs taken from the US Fact Book, unofficial transportation costs from the Union Pacific railroad and using a \$300 per ton cost for steel. Costs of salt dehydration are based on use of electrical heating, and are included in the salt costs. Details are shown in Table 1. It is assumed that fabrication and construction costs will equal material costs once development costs and production methods are worked out.

The ESBT program is still in the laboratory stage with work directed toward construction of a pilot 2 MWh (thermal) storage tank and steam generator about a year or so from now. Laboratory tests are carried out in a 14" diameter tank containing 54 lbs of packaged salt

Table 1. Cost Estimate for 1000 MWh (th) Energy Storage Boiler Tank

Material Costs - 20-m Tank

Item	Costs per Unit	Units Required	Costs	Cost per MWh(th)
Anhydrous eutectic salt	\$64. ton^{-1}*	9,771 tons	\$625.3K	
Salt containers (paint cans)	\$0.15 can^{-1}	1,304,000 cans	195.6	
Transportation	\$ .015 ton-mile^{-1}	15,000,000 ton-miles	225.0	
½" tank	\$300. ton^{-1}	241 tons	72.3	
Internal pipings	\$300. ton^{-1}	8 tons	2.4	
Heat transfer fluid (terphenyl)	\$2000. ton^{-1}	141 tons	282.7	
			\$1403.3K	
		Total Material Costs		\$1403.3 per MWh
		Estimated Labor Costs		\$1403.3 per MWh
		Total Costs		\$2807 per MWh

*Breakdown of Salt Costs (55% MgCl, 24.5% NaCl, 21.0% KCl, by Weight)

Material	1972 Value	Ref	1976 Value
NaCl	\$ 6.60 ton^{-1}	U. S. Fact Book	
$MgCl_2$	37.1 (based on MgO equiv. in brines)	"	
KCl	25.4 (based on K_2O equiv.)	"	
MIX	\$27.2 ton^{-1}		\$39.8 ton^{-1}
Dehydration cost	(based on 1010 cal gm^{-1} energy to dehydrate $MgCl_2$ $6H_2O$ and melt eutectic, using electrical cost of \$.028 KWh^{-1})		24.5 ton^{-1}
		Total salt cost	\$64.3 ton^{-1}

eutectic. We are currently studying the energy input process and melt cycling problems using condensation of terphenyl heat transfer fluid as the means of distributing heat and melting the salts. Late in the spring we passed the first important milestone in the development, namely that of melting the salt eutectic by terphenyl condensation.

Terphenyl in its most readily available form is bought as Therminol 88 from Monsanto. Therminol 88 is a mixture of 3 terphenyls, each with a different boiling point. Our studies indicate that it is desirable to remove the lowest boiling component from the mix prior to its use in the ESBT. Recently, we have operated our lab ESBT using a largely m-terphenyl fraction obtained from Eastman with an approximate composition: 8% p-terphenyl, 91% m-terphenyl, 0.6% o-terphenyl. With this material we have succeeded in melting our 54 lbs of salt under conditions such that the temperature of the liquid terphenyl at the bottom of the tank never exceeded the melting point of the salt by more than a ΔT of 12°C (Figure 2). We expect a similar ΔT at energy withdrawal in a fully developed ESBT, in which case the total ΔT cost of energy storage will be about 25°C.

An attractive feature of the ESBT is the condensation boiler which is included inside the tank. The boiler for the 2 MWh tank has been initially designed and analyzed(3). As designed the boiler will be able to provide energy withdrawal at a 0.5 MW rate, at a steam temperature of 340°C and a steam pressure of 800 psia. At lower withdrawal rates, steam temperatures should approach the 385°C of the molten storage salt.

There are still a number of important questions to be answered and decisions to be made. How low should the o-terphenyl content of the heat transfer fluid be kept? Can the tank be designed to provide continuous removal by fractionation of o-terphenyl and possible low boiling dissociation fractions? Can the tank be designed to provide continual vapor circulation, so as to reduce stratification of vapors of varying p-terphenyl/m-terphenyl ratio? How low should the p-terphenyl and quatraphenyl content be kept? Most importantly, how stringently should the salt be separated from the heat transfer vapor? Present tests have been carried out with open salt cans. Crusting of the salt surface is observed. Nonetheless we have melt cycled the salt several times without apparent difficulty.

We will shortly make decisions on several of the above questions as regards the 2 MWh ESBT. Experience with the 2 MWh tank will then determine the wisdom of our decisions or the need to back-track and redesign portions of the unit.

Acknowledgement

This program is jointly supported by DoD and ERDA.

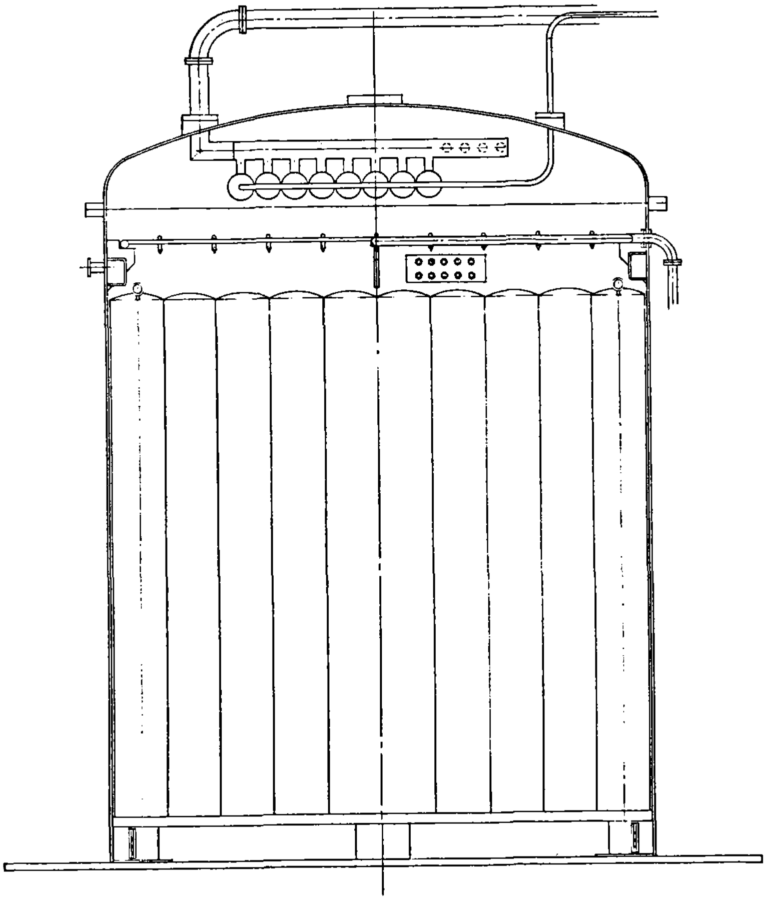


Figure 1. Drawing of 10-foot energy storage tank. The tank is designed to receive 150 kw of electrical heat and to store 2 MWh of thermal energy. The design option illustrated uses 10-foot long, 12" diameter salt containers with interior aluminum members for conductivity enhancement. The salt containers are separately manifolded to an inert atmosphere, so as to avoid contact between molten salt and heat transfer fluid. Such separation may not be necessary. Drawing shows spray ports used to keep containers wetted with heat transfer fluid during the energy withdrawal period. Also shown is a condensation steam boiler and superheater assembly inside the domed tank lid.

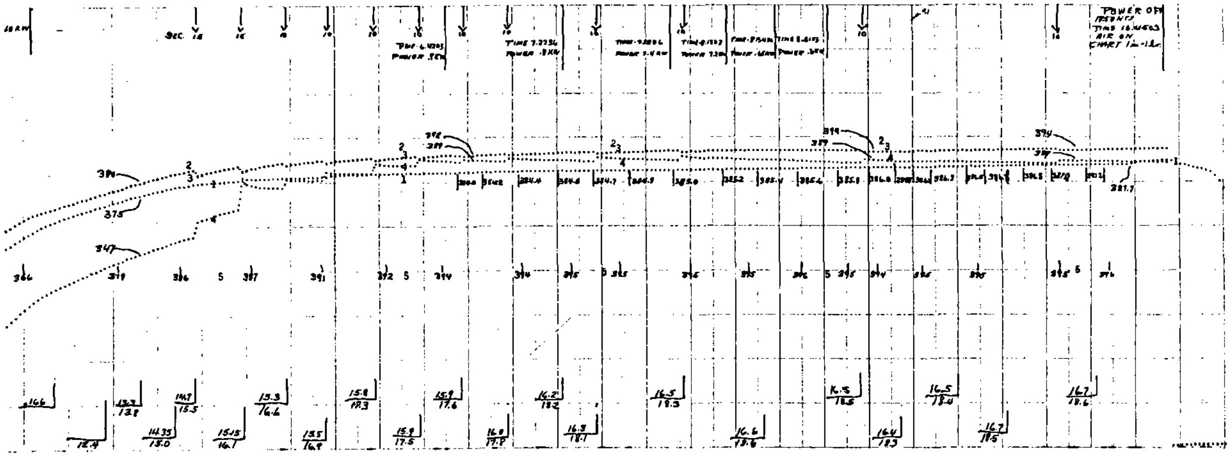


Figure 2. Energy input run demonstrating melting of 54 pounds of salt eutectic by terphenyl condensation. Trace 1 shows salt temperature vs. time. Traces 2, 3, and 4 measure vapor temperatures near the bottom, middle, and top of the tank. During the melt process the temperature of liquid m-terphenyl at the bottom of the tank differed only slightly from that of the vapor and never exceeded the melting point of the salt by more than 12° C.

References

(1) Nemecek, J.J., D.E. Simmons and T.A. Chubb, "Demand Sensitive Energy Storage in Molten Salts", Solar Energy 19, , 1977.

(2) Chubb, T.A., "A Chemical Approach to Solar Energy", CHEMTECH 6, 654, 1976.

(3) Chubb, T.A., J.J. Nemecek and D.E. Simmons, "Energy Storage-boiler Tank: Boiler Design, Materials Compatibility Tests", Proceedings of the ISES Meeting, Orlando, FL, 18-10, 1977.

PROJECT SUMMARY

ORGANIZATION: PENNWALT CORPORATION

ADDRESS: 900 FIRST AVENUE
KING OF PRUSSIA, PENNSYLVANIA 19406

PROJECT TITLE: INVESTIGATION OF METAL FLUORIDE THERMAL ENERGY STORAGE MATERIALS

PRINCIPAL INVESTIGATOR: JOHN L. EICHELBERGER

TELEPHONE: 215-265-3200

CONTRACT NO.: EY-76-C-02-2990*000

CONTRACT PERIOD: 7/1/76-12/30/76

CONTRACT AMOUNT: ERDA: $54,055

PROJECT GOALS:

1. Assemble and evaluate the thermophysical and kinetic properties of metal fluorides for thermal storage applications.
2. Determine the potential future availability of metal fluorides if large quantities are required for thermal storage.
3. Estimate the potential future costs of metal fluorides if they were manufactured on a large scale.

PROJECT STATUS: PROGRAM COMPLETED; FINAL REPORT SUBMITTED

BACKGROUND AND PURPOSE

One result of early thermal storage studies was the recognition that metal fluorides possess many of the qualities required for storage of energy by virtue of the latent heat of fusion. In addition to latent heats on a volume basis that surpass those of any other potentially practical material, the metal fluorides were recognized to have high thermal conductivities, good stabilities, low vapor pressures, and no supercooling. It was also shown that addition of a small quantity of getter material to fluoride eutectics inhibits corrosion of stainless steel.

Because the metal fluorides appear to be attractive candidates, several engineering studies have selected them for further investigation and development. In general, however, it was still necessary to determine the future availability of metal fluorides if large, new markets were found for them, as well as the potential costs of metal fluorides if they were manufactured on a large scale. In addition, a compilation of the thermophysical data available for these materials was needed.

This study, consequently, was undertaken to fill these needs and to assemble the available knowledge about metal fluorides that would be useful in the material selection process. As part of this effort, we have endeavored to select the most cost-effective metal fluorides for each of a number of different temperature ranges.

RESULTS

Availability

The availability of metal fluorides for heat storage applications is dependent on the reserves and resources of fluorine and the metals selected as well as the supply-demand relationships of fluorine, the metals, and the metal fluorides.

The primary source of fluorine is and will remain the mineral fluorspar, CaF_2. The North American continent holds 26% of the world's known high quality deposits of fluorspar, principally found in northern Mexico, the mountain states, and a region of southern Illinois and western Kentucky. The particular richness of Mexican deposits and the Mexican labor structure permit that country currently to control the world fluorspar market. Production is well below capacity and can be increased at least 10% on demand.

A significant secondary source of fluorine is fluosilicic acid, H_2SiF_6, currently a waste byproduct of the phosphate industry. For a large demand of metal fluorides, 226,000 tons/year of fluorine could be available from this source under current economic and technical conditions. This figure is expected to grow to 726,000 tons/year by 2000. From all sources 294,000 tons/year of fluorine, or greater than 590,000 tons/year of metal fluorides could be provided now without competition with existing markets for fluorine. This would be sufficient quantity for construction of 50 central power plant TES systems per year.

Cost

The current prices and estimated production costs of selected fluorine compounds are presented in Table 1. Current prices, with the few exceptions of those for HF, CaF_2, H_2SiF_6, AlF_3, and Na_3AlF_6, are based on low production volumes. The production cost estimates are based on state-of-the-art chemical reactions, production volumes of 91,000 metric tons/year, and 99% purity. Note that the estimated production costs are significantly lower than current market prices, indicating economies of scale. In all cases, fluosilicic acid appears to be the reagent of choice on a cost basis. The least expensive metal fluoride compounds are those containing Ca, Na, Mg, Al, Si, Ba, K, and Sr. These compounds and most of their mixtures have melting points above 450°C. If fluoride materials are desired that have lower melting points, then mixtures that contain the expensive compounds, LiF, SnF_2, and ZrF_4 are required.

Properties

Detailed chemical, thermophysical, and kinetic properties of many metal fluoride compositions were assembled from the literature and are tabulated in the final report. In many cases, data were obtained from compilations and their accuracy, therefore, is not verified.

Table 1. **Current Prices and Estimated Production Costs of Selected Metal Fluorides**

		Estimated Production Costs ($/kg)					
Metal Fluoride	**Current Selling Price**	**Based on HF @ 91¢/kg**	**Based on HF @ 62¢/kg**	**Based on H_2SiF_6 @ 36¢/kg**	**Based on H_2SiF_6 Free 1976**	**1985**	**2000**
NaF	0.74	0.58	0.44	0.33	0.11		0.18
KF	1.46	0.73	0.64	0.58	0.42	0.49	0.76
MgF_2	0.87-1.71	0.76	0.58	0.47	0.18	0.18	0.18
CaF_2	0.12					0.13‡	0.16‡
BaF_2	1.29	0.56	0.49	0.44	0.33	0.36	0.36
TiF_4	77.78	1.27	1.04	0.93	0.67	0.69	0.78
AlF_3	0.39	0.84	0.62	0.49	0.18	0.18	0.18
SrF_2	50.44	0.84	0.73	0.69	0.53	0.60	0.78
PbF_2	30.27	1.00	0.96			0.93*	0.93*
LiF	5.38	3.27	3.04	2.93	2.58	2.78	2.78
CuF_2	121.11	2.91	2.80	2.31	2.13	2.78	3.13
NiF_2	202.22	3.96	3.82	3.73	3.56	3.71	4.00
CrF_3	1.80	5.91	5.58	5.16	4.91	5.13	6.44
SnF_2	12.44					16.89*	25.16*

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*Based on HF @ 62¢/kg

‡Mined; selling price

All of the metal fluorides interact with water at high temperatures to give volatile products. Therefore, use of metal fluorides for thermal storage is practical only in closed containers where many metal fluorides have very low vapor pressures, even at temperatures of 100° above their melting points.

In general, the rate of corrosion is very dependent on the type of container material as well as the particular fluoride salt being studied. The data suggest that a number of alloys look promising for the containment of fluoride salts. Those that partially consist of molybdenum or columbium have the best corrosion resistance. Some research has been done to decrease the corrosion of less expensive alloys by either purification of the fluoride salts or by addition of a getter such as aluminum to the fused salt. The latter approach pioneered by Philips Corp. is reported to be quite promising. The alkali, alkaline earth, and silicon fluorides appear to be the least corrosive. Titanium fluorides and non-transition metal fluorides such as ZnF_2, AlF_2, SnF_3, SnF_2, and PbF_2 may also be useful for heat storage on the basis of corrosive stability.

Heats of fusion of greater than 1673 MJ/m^3 (based on ambient densities) were found for 24 fluoride materials. On a volume basis, magnesium fluoride is the most interesting, having a ΔHm of 2920 MJ/m^3. Determination of the heats of fusion of mixtures containing NaF and increasing amounts of SiO_2 indicates that small amounts (< 1%) of impurities will have little effect on this property, but that large amounts (2-5%) will have a significant effect.

Sensible heat contents, a function of temperature, were calculated for a variety of fluoride materials between ambient temperature and the melting points. They vary between 1310 MJ/m^3 for LiF/LiOH and 5561 MJ/m^3 for CaF_2. Sensible heat content for a variety of fluoride materials for the 100° temperature intervals above their melting points fall in the 238-812 MJ/m^3 range.

Thermal conductivities range from 0.84-4.18 J/m·sec.°C.

Volume changes vary between 7% to 49% from ambient to greater than the melting point temperatures.

Viscosities are on the order of 1.7-15 centipoise at the melting point.

Supercooling of metal fluorides is not observed.

Investigations of melting points and phase diagrams of metal fluorides and their mixtures have shown the existence of a variety of suitable candidates for at least every 50° temperature interval between 450 and 1000°C. Other candidates above 1000°C were found, and higher cost candidates were even found for the 200-450°C range. Some of these candidates are given in Table 2.

FUTURE WORK

A plan of work has been prepared to carry out accelerated and real-time thermal cycling to determine the long term effects of any corrosion that might occur and to determine expected system lifetime. The effects of purity on performance are to be studied. Certain thermophysical and kinetic data for prime candidates must yet be measured. Cost-effective techniques for composition preparation and material handling are to be developed.

Table 2. Selected Metal Fluoride Salts

Temperature Range °C	Composition (Wt. %)	Melting Point °C	Estimated Selling Price		ΔH_m		
			$/kg	$/m³	kJ/mole	kJ/kg	MJ/m³‡
200-250	$75.5NaF/24.5SnF_2$	240	5.29				
250-300	$70Na_3AlF_6/30AlCl_3$	300	0.66				
300-350	$85.3KF/14.7SnF_2$	320	3.62				
350-400	$31.0KF/4.1AlF_3/64.9ZrF_4$	400	3.64				
401-450	$27.1LiF/11.9NaF/55.1KF/5.9MgF_2$	449	1.33	3.424	7.0	699	1807
451-475	$29.2LiF/11.7NaF/59.1KF$	454	1.42	3.567	4.09	414	1046
476-500	$1.9LiF/42.6KF/55.5AlF_3$	490	0.47				
501-525	$20.1NaF/79.9ZrF_4$	510	4.27	16.322	6.4	255	983
526-550	$5.8NaF/28.9KCl/65.3Na_2CO_3$	538	0.07				
551-575	$25.9Na_2CO_3/38.8NaCl/35.3NaF$	575	0.09				
576-600	$11.5MgF_2/88.5MgCl_2$	596	0.16				
601-625	$35.2LiF/38.3NaF/26.5CaF_2$	615	1.36	3.790	5.83	636	1795
626-650	$45.2NaF/54.8ZnF_2$	635	0.64				
651-675	$56Na_3AlF_6/6.2AlF_3/37.8CaF_2$	675	0.53				
676-700	$27.9NaF/72.1NaCl$	680	0.07				
701-725	$32.5NaF/67.5KF$	721	0.47	1.157	7.22	585	1469
726-750	$51.7NaF/34.1CaF_2/14.2MgF_2$	745	0.16	.457	6.7	565	1678
751-775	$24.5Na_3AlF_6/62.1KF/8.9LiF/4.5Al_2O_3$	750	0.84				
776-800	$53.6NaF/17.8KF/28.6MgF_2$	798	0.27	.752			
801-825	$51.8NaF/48.2CaF_2$	810,818	0.13	.378	7.65	590	1686
826-850	$66.9NaF/33.1MgF_2$	830	0.18	.517	9.27	649	1920
851-875	$25.1NaF/74.9SrF_2$	855	0.60				
876-900	$75NaF/25AlF_3$	882	0.18				
901-925	$87Na_3AlF_6/18MgF_2$	921	0.53				
926-950	$74Na_3AlF_6/26CaF_2$	945	0.36				
951-975	$33.5NaF/46.2KF/20.3MgF_2$	975	0.38				
976-1000	NaF	995	0.16	.394	7.97	795	2033
1001-1025	$29.5KF/70.5MgF_2$	1008	0.36				
1026-1050	$NaMgF_3$	1030	0.20	.564	17.7	711	2025
1051-1100	$KMgF_3$	1070	0.42				
1251-1300	MgF_2	1252	0.24	.761	13.9	933	2920
1301-1500	CaF_2	1418	0.11	.419	7.1	380	1448

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‡Based on ambient densities.

PROJECT SUMMARY

ORGANIZATION: Rocket Research Company
(Bethlehem Steel Corp. and Seattle City Light)

ADDRESS: York Center
Redmond, Washington 98052

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

TELEPHONE NO.: (206) 885-5000

CONTRACT NO.: EC-77-C-01-5081

CONTRACT PERIOD: 8/30/77 – 5/30/78

CONTRACT AMOUNT: ERDA $91,349
OTHER

PROJECT GOALS:

Identify applications for existing thermal energy storage technology in the iron and steel industry, and to assess the economic benefits which could be derived therefrom.

PROJECT STATUS:

Several energy streams have been identified at the industrial partner's site which would be technically suitable to charge a thermal storage system. In all cases, the temperature is high enough so that solid phase storage materials are indicated, although the optimum choice of which solid medium is not yet clear. Slag, mill scale, and scrap iron are candidate materials, in ascending order by cost. Final choice of storage material will be based upon detailed results from computer modeling. A survey of major steel manufacturing plants is underway by both letter and telephone. Some reticence to respond to the survey has been found.

I. Purpose

This project is designed to investigate whether existing thermal storage techniques can effect significant energy savings for the iron and steel industry.

II. Background

Technology is available which allows straightforward design for the storage of sensible thermal energy in water, several petroleum based oils, and a number of solid materials including refractories, metals, and various types of rock. Design data is also available for storage systems using the solid-liquid phase transition of NaOH. Other energy storage concepts which achieve a full-scale working demonstration status can be included.

Many energy streams exist in the steelmaking process which are variable in temperature or magnitude. Normal steady-state energy conservation methods applied to cyclical energy streams are limited by the minimum value during the cycle, thus showing minimal payback for energy conservation approaches. Energy demands are also variable with time, and may be out of phase with otherwise suitable waste energy streams.

III. Project Description

A preliminary investigation of the operations at the steel recycling facility, operated by Bethlehem Steel, Incorporated, in Seattle, reveals several locations where high-temperature energy is currently dissipated to ambient; in particular, the fume collected from the arc furnaces is cooled by a water spray system to temperatures consistent with filtration apparatus. This gas stream fluctuates in temperature and flow rate due to periodic removal of furnace covers during raw material charging.

An attractive use for this energy exists in electrical energy generation through a bottoming cycle, based upon preliminary calculations. A schematic of the baseline system is presented in Figure 1. An unusually efficient generating system (for a bottoming cycle) is possible as the fume temperature may be as high as 1,100°F. Additional benefits from working with this energy stream are expected from reduced or eliminated water usage, and decreased filter failure rate.

The baseline thermal storage system utilizes slag as a sensible heat storage medium. Slag is a byproduct of the operations, and is currently disposed of by landfill. This is a negative cost item. A relatively high specific heat is expected, as the material is primarily metallic oxide. Metallic inclusions, commonly present, should provide significant improvement in thermal conduction over more commonly used metallic oxide materials (refractory bricks). Figure 2 presents the approach taken to this project. The project begins with an industry survey and literature search to assure that the baseline approach is not an isolated instance; hence, the results will have reasonable utility to the industry as a whole. Backup approaches are carried against this eventuality for the early stages of the project. Once the approach is fixed, instrumentation will be installed to better fix critical energy stream parameters (temperature versus time, flow rate versus time, etc.). A study of the site plan will be made, in conjunction with Bethlehem personnel, to assure that equipment location will be consistent with existing operations. This study essentially sets minimums upon flow lengths required for the various fluids in the system.

The major task of the study is in the assembly of a dynamic model of the system. All system critical dimensions will be input parameters. Thermal and hydraulic and cost relationships will compose the bulk of the model. Tradeoffs associated with storage materials other than the baseline slag can be assessed by inputting the appropriate thermal properties. Likewise, "optimum" dimensions for the system will be found from multiple exercise of the model. Final tasks include the assembly of a system design drawing package, and a plan for system installation consistent with minimum impact to steelmaking operations.

IV. Results

The project is currently in its first month; hence we are in the literature search – industry survey phase. No information has been found which would require a shift from primary approach. Samples of slag have been obtained, and specimens are being prepared for thermal property measurement.

V. Future Activities

Thermal property measurement of slag specimens will include density specific heat and thermal conductivity. In addition, measurements of granular bed thermal conductivity are planned for two granule sizes. All preliminary investigation data (industry survey, plant thermal data, thermal property measurements, and existing site limitations) are expected to be sufficiently well defined to allow the sizing and performance analysis task to begin on schedule during the third program month.

SCHEMATIC DIAGRAM OF THERMAL ENERGY STORAGE SYSTEM

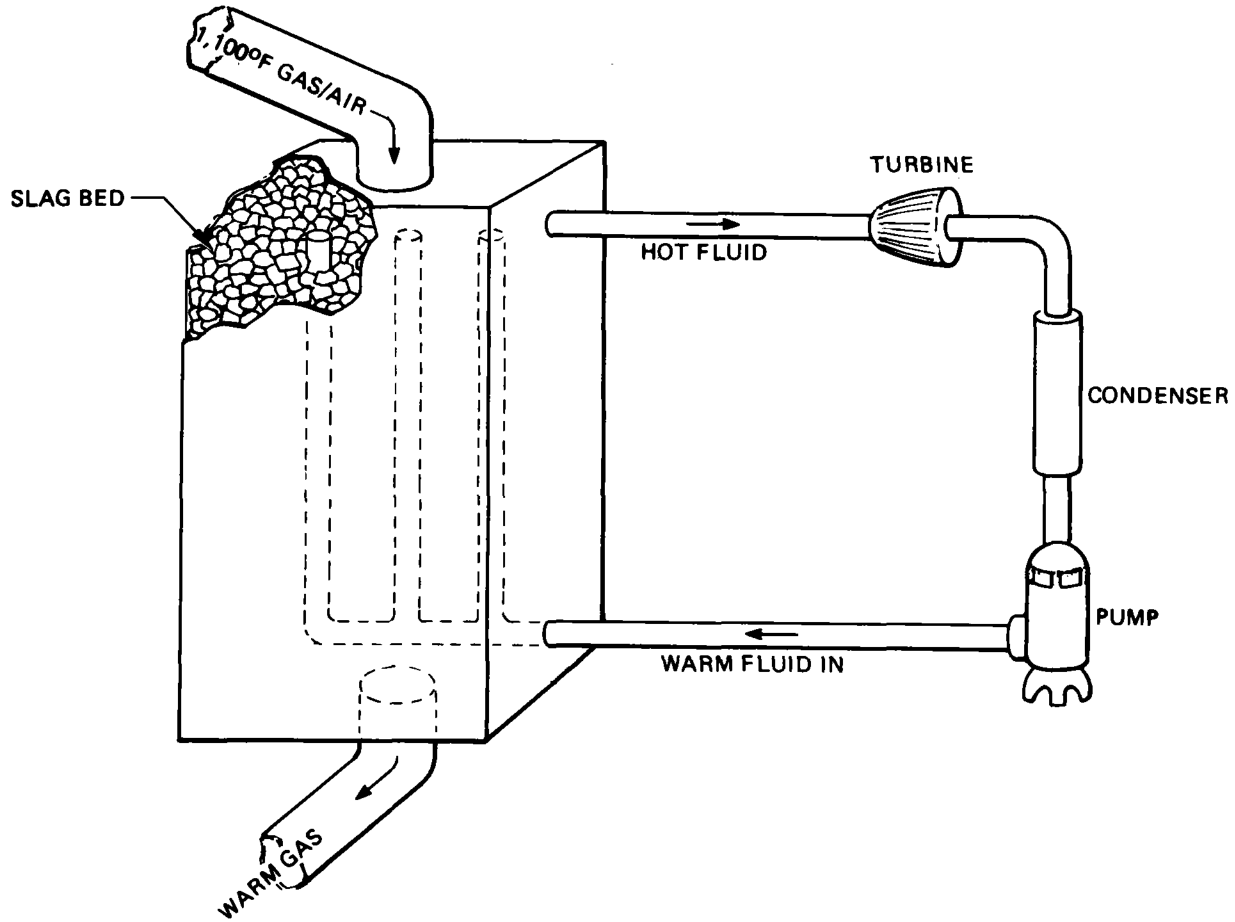

Figure 1

PROGRAM APPROACH

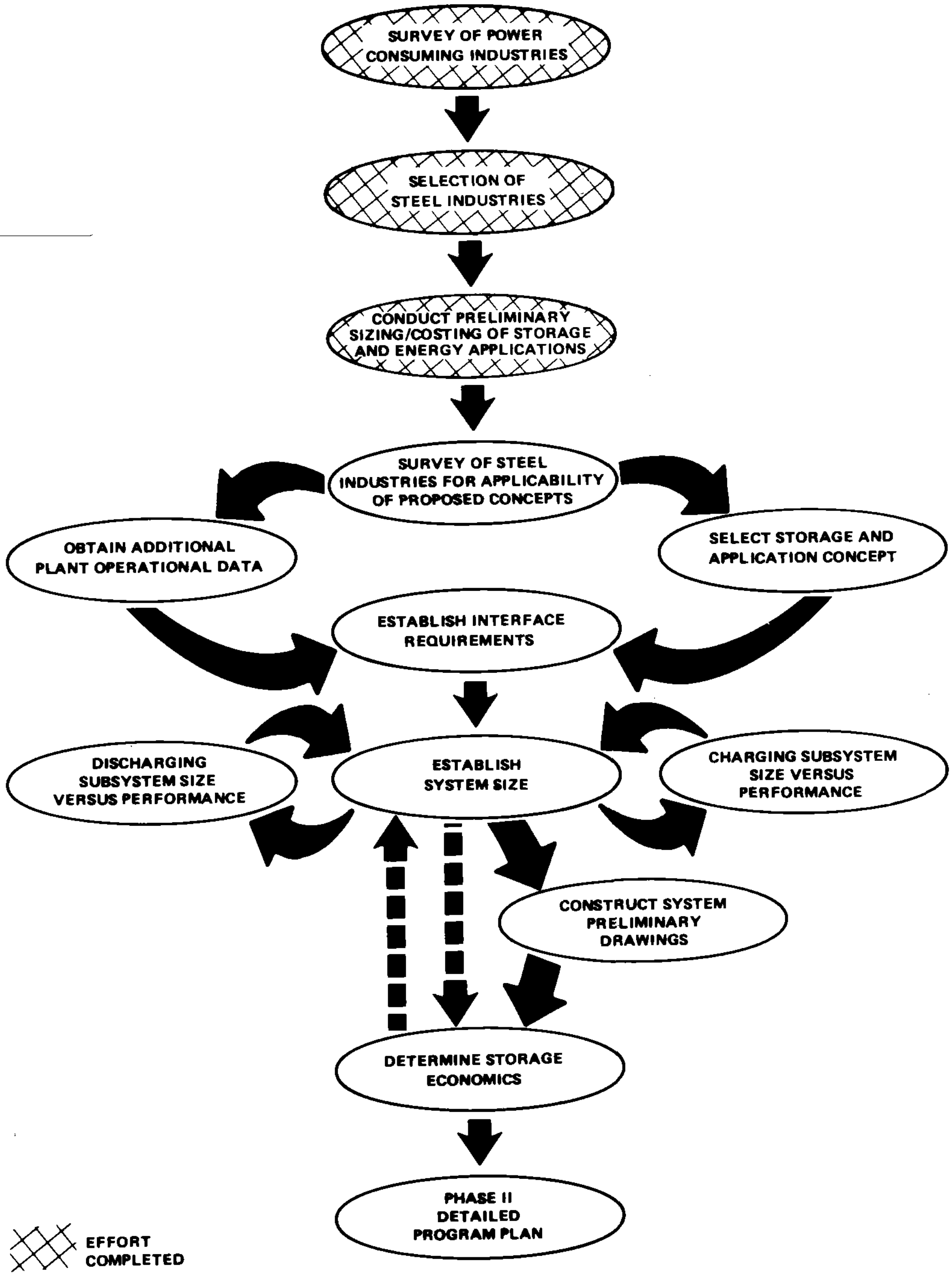

Figure 2

PROJECT SUMMARY

ORGANIZATION: University of Delaware

ADDRESS: Newark, Delaware

PROJECT TITLE: Alloy Thermal Storage Media

PRINCIPAL INVESTIGATOR: Prof. C. E. Birchenall
Mr. A. F. Riechman — Thermal Measurements
Dr. A. J. Harrison — Volume Change Measurements

CONTRACT NUMBER: E(11-1)-4042

CONTRACT PERIOD: July 1, 1976—October 31, 1977

PROJECT GOALS:

1. Survey properties of fusible alloys for use as thermal energy storage media above 200°C.
2. Measure heat of transformation, specific heat and volume change on transformation of selected binary alloys.

Market information on metals and alloys indicated the following (approximately decreasing) order of desirability for large-scale, low-cost application: Al, Si, Zn, Na, Cu, Mg, Ca. Sulfur and phosphorus are cheap enough to consider as alloy components. Iron might play some role at very high temperatures. Lead may be marginally inexpensive.

The heat of fusion data indicated that silicon is outstanding and aluminum better than most other metals for heat storage density contributions. The thermodynamic theory favors the use of eutectic transformations with large numbers of components which participate in nearly equal proportions in the liquid with little short range ordering, but which form ordered solid intermetallic compounds with high heats of formation or have very limited ranges of solid solubility in the primary metal phases. Using these criteria, several binary eutectics and two ternary eutectics of approximately known composition and transformation temperature were chosen for study. Measurements of heat of transformations, which determine the maximum possible storage densities, and heat capacities were done below 750 C in the Perkin-Elmer Differential Scanning Calorimeter. The reproducibility of repeated measurements was on the order of one percent. The melting points of pure metals were within 1°C of the accepted values. The heat capacities were less precise, probably uncertain to the order of 5 to 10 percent.

Above 750 C heat of transformation was measured with lower precision on the Du Pont Differential Thermal Analyzer. Calibration for heat capacity determination now is in progress. The summary of the results for 5 binary and 2 ternary eutectics is given in Table 1. Table 2 compares the energy storage capacities of these

THERMAL PROPERTIES OF SELECTED METAL EUTECTICS

Alloy (Mole Fractions)	Eutectic Temperature (K)	• ΔT (K)	Maximum Heat Storage Calculated (kJ/kg)	Maximum Heat Storage Measured (kJ/kg)	Heat Capacity (kJ/kg-K)
Mg-0.29Zn	616	2-4	247 (464)	138	1.04s 1.15ℓ
Al-0.375Mg	724	5-9	458 (477)	310	1.73s 1.62ℓ
Al-0.175Cu	821	1-3	359 (380)	351	1.11s 1.11ℓ
Al-0.13Si	852	2-3	571	515	1.49s 1.27ℓ
Mg-0.529Si	1210	1-2	1212	805	- -
Al-0.17Cu-0.162Mg	779	4-10	406 (400)	360	1.09s 1.18ℓ
Al-0.126Si-0.051Mg	833	5-6	549 (449)	545	1.39s 1.21ℓ

COMPARISON OF PHASE-CHANGE MATERIALS

Material	Transformation Temperature K	Maximum Heat Storage kJ/kg	Solid Density kg/m^3	Volumetric Heat Storage kJ/m^3	Solid Heat Capacity kJ/kgK	Coeff. of THERMAL Conduction W/mK
Mg_2Si/Si	1210$^{\neq}$	805$^{\neq}$	(2000)$^{\bullet}$	1.61 x 10^6		
LiF/MgF_2	1019	947	2630	2.49	1.42	
$NaF/CaF_2/MgF_2$	1018	574	2760	1.58	1.17	
$Na_2B_4O_7$	1015	VITRIFIES				
Li_2CO_3	998	605	2200	1.33	2.64	
$CaMg_2$	990	554	(1550)$^{\bullet}$	0.85		
$MgCl_2$	988	454	2240	1.01	0.75	
LiH	956	2582	790	2.03	8.04	7.0
Al	934	400	2370$^{\bullet}$	1.050	1.29$^{\neq}$	204.2
Mg	922	368	1590$^{\bullet}$	0.59		131
$MgZn_2$	861	275	5200	1.43		
Al/Si	852$^{\neq}$	515$^{\neq}$	(2250)$^{\neq}$	1.16	1.49$^{\neq}$	
$Ca(NO_3)_2$	834	130	2500	0.325	0.88	
Al/Si/Mg	833$^{\neq}$	545$^{\neq}$	(2300)$^{\neq}$	1.25	1.39$^{\neq}$	
Al/Al_2Cu	821$^{\neq}$	351$^{\neq}$	(2500)$^{\bullet}$	0.88	1.11$^{\neq}$	
Mg/Mg_2Ca	790	(353)	(1570)$^{\bullet}$	0.55		
$Al/Al_2Cu/Al_2CuMg$	779$^{\neq}$	360$^{\neq}$	(2550)$^{\bullet}$	0.92	1.09$^{\neq}$	
LiOH	744	1100	1340$^{\bullet}$	1.47		2.8
Al/Mg_3Al_5	724$^{\neq}$	310$^{\neq}$	(2300)$^{\bullet}$	0.71	1.73$^{\neq}$	2.8
$NaCl/MgKCl_2$	713	326	2240	0.730		
LiOH/LiF	700	1163	1150	1.80	2.14	2.6
Zn	693	112	7140	0.80		
Mg/Mg_2Zn	616$^{\neq}$	138$^{\neq}$	(4900)	0.68	1.04$^{\neq}$	
NaOH	593	160	2070	0.331	1.47	1.54
$NaCl/Na_2CO_3/NaOH$	555	316	2130	0.674	2.51	
LiCl/LiOH	535	530	2120	1.12	1.50	1.70
Li	452	663	534	0.354		

$^{\bullet}$DENSITY AT TRANSFORMATION TEMPERATURE; OTHERWISE, AT ROOM TEMPERATURE.
$^{\neq}$MEASURED IN THIS WORK

alloys with other materials that have been suggested. Although thermal conductivities of the alloys are not known precisely, they are about one order of magnitude better than the most conductive nonmetal, lithium hydride, and up to two orders of magnitude better in conductivity than the more conventional salts. The alloy heat storage capabilities on a mass or volume basis are close enough to the best of the less conductive materials that they should be advantageous. The choices may be dictated by the stabilities, fabricabilities and overall costs of container-structure materials.

It should be emphasized that the alloys investigated were known approximately with respect to composition and transformation temperature. Other ternary and higher eutectics may have higher energy storage density and different transformation temperatures. A systematic search for more alloys is being initiated at the same time that the container material compatibilities with the more promising of the presently known eutectics are under study.

A new method has been developed to measure volume change during an isothermal melting or freezing process by measuring the absorption of a collimated X-ray beam of proper wavelength. If the material under study is able to flow plastically at moderate temperatures, the coefficients of thermal expansion also can be measured with adequate precision. The method has given values that agree with those tabulated for the expansion and melting of aluminum, and it has been applied successfully to the eutectic transformation of $Al/CuAl_2$. Improvements in the apparatus are being made to increase its precision.

PROJECT SUMMARY

ORGINIZATION: University of Houston

ADDRESS: 4800 Calhoun, Houston, Texas 77004

PROJECT TITLE: Heat Transfer Aspects of Solar Energy Systems -- Development of Design Procedures for Thermal Storage in Molten Salts.

PRINCIPAL INVESTIGATOR: N. Shamsundar TELEPHONE NO: 713-749-2683

CONTRACT NO: EG-77-C-04-3974 (Task V) CONTRACT PERIOD: May 1, 1977 - April 30, 1978

CONTRACT AMOUNT: ERDA $45,455
Other ------

PROJECT GOALS:

This is an analytical study of the heat transfer characteristics of thermal storage in molten salts. Computational techniques and analytical models will be developed which can be used for studying novel heat exchanger designs for thermal storage, and design and performance data will be obtained for the same.

Studies are undertaken to ascertain the influences of the supercooling and volume change associated with solidification, the effect of operating with non-eutectic or impure mixtures, and the effect of fouling with age.

The work encompasses solar as well as non-solar thermal storage at high, medium and low temperatures.

PROJECT STATUS:

The project is on schedule in the sixth month at the time of reporting. One foreseen problem is difficulty in obtaining experimental results from other research efforts for the purpose of verifying the analytical models and computational results.

I. Purpose

The data and knowledge needed for designing passive systems for latent heat storage systems will be obtained. While extensive work is being devoted to the development of storage materials, the heat transfer aspects have received less attention, and there are few guidelines for designing thermal storage heat exchangers. For efficient and economical storage and recovery of energy, accurate design procedures and data are necessary. This project is intended to obtain that information.

Design and performance data are lacking for several advanced storage systems. Optimum tube sizes and layouts will be ascertained for applications of various kinds. Computational techniques available at present do not account for many of the phenomena that accompany phase change, and development work will be directed to make progress in this regard. Even where a capable computational technique exists, the expense of perfoming the computations is so great that there is a need to generate simple and reasonably accurate approximate formulae for design purposes.

Experimental confirmation of the analytical methods is necessary since previous experiments have been performed either with metals, which are good conductors of heat, or with water, which behaves quite differently from other substances. The computational results obtained in the project will be tested against experimental results obtained by other research groups.

II. Background Information

Thermal Storage in the form of latent heat has several attractive aspects. Large amounts of energy can be stored in small volumes when substances with high latent heats are employed. With careful design, the temperature fluctuations between the storage and discharge portions of the cycle can be kept tolerably small. But before these advantages can be realized, several problems have to be overcome. Firstly, suitable phase change materials have to be identified, tested and evaluated as to cost, ease of handling, high latent heat and thermal conductivity, low corrosiveness, stability, etc. Secondly, the heat transfer characteristics of storage devices based on these materials need to be understood. Among other aspects, the temperature differentials, heat flux distributions and variations, the effects of supercooling tendencies and the effects of volume changes need study. Finally all the results of these studies need to be correlated to develop procedures for designing heat exchangers to various requirements, and to help in deciding on the optimum balance between low cost and high performance.

III. Project Description

1. Application of Available Computational Techniques to Promising Designs

Computer programs which were previously developed by the Principal Investigator will be modified to study the thermal performance characteristics of three storage heat exchanger designs under investigation by other groups. The computer program is based on the enthalpy method and assumes phase change under equilibrium conditions. The computer program is simple in structure and is capable of yielding temperatures, heat fluxes and the interface position, all as functions of time. The influences of liquid superheat, surface heat transfer coefficient, sensible heat and fouling on the thermal performance will be calculated. The results will be cast into graphical form and will cover a wide range of phase change temperatures, material properties and geometrical parameters.

The three designs studies are (a) the SOLCHEM system, in which a heat transfer fluid condenses outside circular tubes containing the storage material, (b) the THERMOCRETE system, in which air or water flows in ducts inside slabs of concrete with a phase change substance interspersed in it, and (c) a passive version of the Honeywell, Inc. design in which a phase change substance exhanges heat with a steam-water mixture flowing inside circular tubes.

2. Development of New Analytical Models for Phase Change

Presently used computational methods fail to account for many of the factors that affect the performance of a storage unit. Some of the factors are:

- Volume change accompanying freezing
- Liquid motion caused by volume change
- Liquid motion caused by buoyancy
- Liquid superheat
- Supercooling during solidification; effect of adding nucleation promoters
- Influence of adding conduction promoters
- Effect of using an off-eutectic or impure mixture composition

Analytical models will be developed to assess the importance of each of these factors on thermal performance. At first, the models will be restricted to one dimensional phase change. If, as a result of this study, a factor is shown to be of importance, extension of the model to more dimensions will be undertaken.

3. Development of Simplified Design Formulas

The computational techniques developed for phase change could indeed be powerful and accurate, but it is expected that the costs of computation will be high enough to discourage avoidable, repetitious calculations. Since the computational results obtained in this project will cover a range of parameters, advantage should be taken of this opportunity to fit equations of simple form to the results. By comparing the numbers predicted by the simple design formulae to those of the more precise computer calculations, confidence limits will be established for the formulae. The use of these formulae instead of expensive-to-run programs should ease the designer's task.

4. Development of Design Procedures

Based on the quantitative information obtained in items 1 to 3, design procedures will be formulated. These will be kept as simple as possible, and will be detailed in terms that are suitable for non-specialists in thermal analysis. The procedures will be based on the design charts and formulae that were mentioned previously.

5. Evaluation of Results in Cooperation with Other Researchers

The analytical models, results and data generated, as well as the associated computer programs, will be placed at the disposal of interested research groups as early as possible after they become available. We shall do our best to cooperate with other workers, especially the several teams working under the supervision of ERDA. In turn, we shall evaluate the models and results in the light of the findings of these groups, and improve the models accordingly.

6. Small-Scale Experiments for Model Verification

For evaluating our analytical results, primary reliance will be placed upon previously published work and the experimental findings of other research groups as these become available. However, if circumstances warrant it, we shall undertake laboratory experiments on a small scale to verify the analyses. No major experiments are planned in this project during the first year.

IV. RESULTS

1. Application of Available Computational Techniques to Promising Designs

The literature was reviewed to find out if any major progress had been made with regard to computational techniques for phase change processes. The result was negative, and the presentations at the Symposium/Workshop on Moving Boundary Problems in Gatlinburg, Tennessee (September 26-28, 1977) confirmed this.

The extent of results necessary and the range of parameters for the calculations have been decided upon. Previously existing computer programs were modified (mostly rewritten, because of using a different computer system) to analyze the THERMOCRETE storage system; sensitivity analyses were performed to select suitable step-sizes for the finite difference calculations, and verification of the program was performed by comparing the results with one-dimensional solutions where permissible and by applying an overall energy balance in other cases. The program is now functional, and the production runs are well under way.

Modifications of the programs to treat the two other systems have been recently put into action.

2. Development and Testing of New Models

Two models have been developed so far. The first model serves to account for the effects of having superheated liquid on the heat transfer, while retaining the computational simplicity of models that do not account for superheating. This model is based on the Nesselmann approximation, in which a fictitious latent heat equal to the true latent heat plus the superheat energy is studied under conditions of no superheat. The model is now being tested by computations.

The second model is intended to address the problem of supercooling, which besets low temperature applications. The effect of supercooling is to reduce the phase change temperature and to increase the latent heat released. The analytical model we have developed to weigh these competing influences skirts the complications of nonequilibrium solidification thermodynamics because the degree of supercooling is assumed as a parameter whose influence is to be studied.

3. Development of Simple Design Formulae

A set of formulae have been compiled for calculating surface heat flux and rate of phase change for one-dimensional phase-change on a plane, inside and outside circular cylinders. Using accurate solutions where available, we are calculating error bounds for these formulae. The formulae are suitable for evaluation with the help of a hand-held calculator.

V. FUTURE ACTIVITIES

During the rest of the contract period, we expect to complete the project goals to schedule. We will obtain performance data for the SOLCHEM and (passive) Honeywell designs, and compare our results with experimental findings if possible. We will continue to develop and test new physical models and computational techniques. We will undertake small-scale experiments to test some of these models.

During subsequent years, we expect to continue development of more versatile and efficient computational design techniques and apply these methods to get reliable design data and design charts for diverse applications. Experimental apparatus to test if storage modules conform to design expectations will be built and tests will be run. As a result of these investigations, it should be possible to standardize heat exhanger designs for thermal storage, and to develop designs that are more efficient and cost-effective.

Our thermal studies will be fitted into the overall thermal storage program of ERDA so that all relevant aspects of storage technology will be given due attention.

PROJECT SUMMARY

ORGANIZATION: University of Houston

ADDRESS: Cullen Boulevard
Houston, Texas 77004

PROJECT TITLE: Underground Storage of Solar Energy

PRINCIPAL INVESTIGATOR: R. Eugene Collins TELEPHONE NO: (713) 749-3887

CONTRACT NO: EG-77-C-04-3974 (Task II) CONTRACT PERIOD: 5/1/77-4/30/78

CONTRACT AMOUNT: ERDA $104,545

PROJECT GOALS:

The basic objective of this project is to establish the feasibility of high temperature, high pressure thermal storage of energy from a central focus solar collector in deep saline aquifers or solution caverns created in salt domes.

PROJECT STATUS:

The project is now in its fifth month and most tasks are on schedule.

UNDERGROUND STORAGE OF SOLAR ENERGY

Background

A potential solution to the problem of storage of solar energy is storage in the form of heat in permeable subsurface rock formations(saline aquifers). Such storage can be accomplished by injection of superheated water (steam) into these permeable rock layers through wells, with retrieval accomplished by back-flowing the wells. Alternatively, underground storage can be accomplished by injecting hot oil into a solution cavern in a salt dome which has been filled with nitrogen, back flow being achieved by expansion of the nitrogen. Much of the engineering technology required for the design of wells for injection of hot fluids into subsurface formations has already been developed in the petroleum industry and the sulphur mining industry; steam or hot gas injection is a technique now commonly used to improve the production of highly viscous oil by reducing the oil viscosity through heating. Injection of high pressure hot water is the basis of the Frasch process for the recovery of sulphur through wells.

The very high surface to volume ratio of the solid matrix of any porous rock leads to almost instantaneous local thermal equilibrium of the rock matrix with the fluids contained in the rock pores, but the very low thermal conductivity of rocks and earth leads to a very slow loss of heat to surrounding rocks not permeated by injected hot fluids. For a spherical domain of radius R contacted by hot fluid the heat losses in cyclic storage and retrieval can then be estimated from the asymptotic solution of the heat conduction equation:* to a very good approximation the ratio of rate of heat loss to the quantity of heat stored is

$$\frac{\text{Rate of Heat Loss}}{\text{Heat Stored}} \approx \frac{3\kappa}{R^2}$$

where κ is the thermal diffusivity of surrounding rocks

$$\kappa \approx .038 \text{ ft}^2/\text{hr}$$

and R is the linear dimension (sphere radius) of the region directly contacted by hot fluid. Thus if τ is the time period of storage and retrieval, the ratio of heat lost during a cycle to the total heat stored is

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*Collins, R. E., "Geothermal Storage of Solar Energy," in "Governor's Energy Advisory Council Report, Project NT-3," A. E. Dukler, Executive Director. The University of Houston, Houston, Texas, (Nov. 1974).

Collins, R. E. and Davis, K. E., "Geothermal Storage of Solar Energy for Electric Power Generation," Proceedings of Clean Energy Conference, Verziglie, Editor, Univ. of Miami, 1976. (in press).

$$\frac{\text{Heat Loss per Cycle}}{\text{Heat Stored}} \approx \frac{3\ \kappa\tau}{R^2}$$

Hence, as the time period of the storage cycle is increased, the size of the storage system must be increased in order to maintain as reasonable loss rate.

The above equation shows that in order to sustain a small heat loss per storage cycle it is necessary to store, on a permanent basis, a much larger quantity of heat than is injected and retrieved during a cycle; this is strictly determined as a surface to volume ratio effect. Consequently an initial investment of a very large quantity of energy is required in order to establish this large heated region. Thereafter it is necessary only to inject a slight excess during the injection portion of each storage cycle over that retrieved during the cycle, in order to compensate for heat lost by conduction to surrounding rock. Thus, a geothermal storage system of practical dimension could be developed where the rate of heat loss would be .05% per day, or less. Hence if the quantity of heat injected during sunlight hours and retrieved during the night were 10% of the stored heat, the heat lost would be only 0.5% of the quantity of heat stored and retrieved on a daily basis. These figures would apply to a spherical storage region on the order of 200 feet in diameter. Furthermore, such storage and retrieval on a daily cycle could be accomplished with only negligible degradation of the heat; that is, the retrieved heat would be a quantity of hot fluid of almost the same volume and temperature as that injected. This means that retrieved heat can be used to drive a suitable heat engine with almost identical efficiency to that attainable using the injected fluid.

Even longer term geothermal storage of solar energy is practical but with a more significant heat loss. In fact geothermal storage of even larger quantities of solar energy would make storage during summer for winter retrieval a practical reality. The critical factors determining the heat loss and the thermal degradation of retrieved heat are the time period of the storage and retrieval cycle and the bulk surface to volume ratio of the earth region occupied by injected hot fluids.

Thus, it is not heat losses which pose the major problem to practical realization of geothermal storage of solar energy; rather it is some practical problems of well design. For example, in order to store one-third of the daily energy collection from a 700 megawatt system it would be necessary to inject into a well at a rate on the order of 2000 gallons per minute, for a 400°F temperature increment. The attainment of such high rates without excessive pressures calls for multiple wells of special design. Backflowing will also present problems because of potential sand production. A problem of perhaps even more concern is that of dissolved salts in the produced liquid which can create scale in the well bore and surface equipment.

Project Description:

This project is being carried out by the University of Houston and a subcontractor, Subsurface, Inc., under a general contract to the Energy Foundation of Texas. The first phase of this project will evaluate the geophysical, technical and economic feasibility of underground thermal storage. Assuming the system is completely feasible, the second phase will be the construction and testing of a prototype system. All the work done so far indicates that the system is feasible, but the final well location, sizing, and the drilling decision will be explicitly contingent upon the detailed results of the first phase of this study.

Our study considers injection of super-heated water at temperatures on the order of 650°F and pressures on the order of 3000 psi into deep (several thousand feet) permeable aquifers and steam production on the recovery cycle. We also consider high temperature oil storage in caverns dissolved in salt domes.

There are four general topics which must be examined in order to arrive at a realistic evaluation of a well design for underground thermal storage of solar energy, or heat from other sources, namely:

(1) Thermal losses and degradation of stored heat
(2) Pumping requirements
(3) Geophysical constraints
(4) Thermal, mechanical and chemical constraints on equipment design.

These topics are being addressed through an extensive literature survey and evaluation and also by exploitation of numerical simulators.

A mathematical model of steam injection into a permeable earth stratum containing brine is being constructed to evaluate thermal losses, thermal degradation of retrieved heat and injection and retrieval pumping requirements in various operational modes. The model also simulates the solution and transport of soluble salts in the aquifer. Later, when a prototype storage well is in operation, this model will be used to evaluate test data obtained from the well.

We are also constructing a mathematical model to study the operation of a cavity storage system in which a hot liquid is alternately injected and retrieved from a deep impermeable cavity partially or completely filled with inert gas. This model will be used to study storage capacity, thermal losses and energy requirements for pumping in various modes of operation.

A general survey of potential sites for construction of thermal storage wells is being carried out to evaluate the compatibility of geophysical and geological constraints on wells and solar requirements for large scale solar collectors. This will of course be based upon the geological constraints on storage wells as formulated from our mathematical studies, i.e. aquifer characteristics and operating pressures, or, in the case of cavities, the existence of suitable salt formations. These geological assessments will also provide general evaluation of potential areas where underground thermal storage of excess heat from industries might be implemented.

The evaluation of thermal, mechanical and chemical constraints on down-hole and surface equipment will be initiated in two stages. The first stage is being carried out in the literature survey by studying similar problems associated with steam stimulation of oil wells and exploitation of natural geothermal sources, as reported in the literature. The second stage will be based upon the specific operating conditions deduced from our mathematical models. This will culminate in specific recommendations for all equipment associated with the installation and operation of thermal storage wells, interfacing to the solar tower and to steam-electric power conversion. These recommendations will be set forth in complete design drawings and specifications.

The final state of this program will be the construction and testing of a prototype thermal storage well to be operated in conjunction with a suitable energy source. We will investigate the 10 megawatt central focus solar collector for this purpose.

The efforts of this first year of this project will address three specific tasks:

(1) Review of literature on thermal wells
(2) Design, program and debug computer simulators for aquifer and cavern storage
(3) Carry out a preliminary review of potential sites for thermal storage wells

Task (1) is being carried out by both University of Houston and its subcontractor, Subsurface, Inc. Task (2) is being carried out by University of Houston. Task (3) is being carried out by the subcontractor, Subsurface, Inc.

At the time of this writing Task (1) is well underway with special emphasis being given to the problems associated with dissolved salts (scale).

Two different versions of the simulator for steam (super-heated water) storage in a saline aquifer are being constructed; one is in the debugging stage, the other is being input at this time; both treat two-phase flow, with gravity effects and simulate coupling to infinite overburden and underburden by using a Green's Function technique.

The cavern storage model is now being debugged. This model simulates coupling of the cavern to an infinite surrounding earth by Green's function techniques, similar to those used in our aquifer models.

Subsurface, Inc. is only just starting the site study because of delay in formalizing the subcontract but this should now go forward quickly.

PROJECT SUMMARY

ORGANIZATION:	UNIVERSITY OF MINNESOTA
ADDRESS:	MINNEAPOLIS, MN 55455
PROJECT TITLE:	ROCK BED HEAT ACCUMULATORS
PRINCIPAL INVESTIGATOR:	M. RIAZ; TEL NO.: (612) 373-2472
CONTRACT NO.:	EY-76-S-02-4009
CONTRACT AMOUNT:	$172,174
CONTRACT PERIOD:	JUNE 16, 1977 - SEPT. 15, 1977

PROJECT GOALS:

The project goals are: a) to investigate the technical and economic feasibility of storing large amounts of thermal energy (in the tens of MWt range) at high temperature (up to 500°C) over extended periods of time (up to 6 months) using native earth or rock materials; b) to conduct studies to establish the performance characteristics of large rock bed heat accumulators (RBHA) at various power and temperature levels compatible with thermal conversion systems; c) to assess the materials and environmental problems associated with the operation of such large heat accumulators.

In the generic configuration of the RBHA, a large bed of crushed or naturally formed porous rock is heated by hot air flowing from a central manifold toward two outer cold manifolds; on discharge, the flow is reversed with cold air introduced at the top and bottom manifolds being heated in its passage through the porous media so that hot air is harvested from the central manifold.

The results of the study indicate that rock bed heat accumulators for seasonal storage are both technically and economically feasible, and hence could be exploited in various applications in which storage plays an essential role such as solar power and total energy systems, district and cogeneration heating systems. The economic advantage of RBHA stems from the low cost inherent in the preparation of on-site native materials using a variety of construction techniques that can be adapted to local geological conditions and siting constraints with minimum environmental impact.

PROJECT STATUS:

Complete (final report in preparation).

I. PURPOSE:

The principal objective of the project is to determine the technical and economic feasibility of large-scale thermal energy storage at high temperature in native rock or earth materials with minimum environmental impact.

II. BACKGROUND INFORMATION:

Thermal energy storage on a large scale in terms of both time and volume of rock material can play an important role in energy conservation and management. In electric utility systems, load leveling provides for improved utilization of capital equipment resulting in substantial cost savings; in district heating systems, the use of waste or process heat in cogeneration modes can reduce premium fuel requirements; in solar power generation and/or heating systems, the inherent cyclic and intermittent nature of solar energy requires the use of efficient storage systems to achieve optimum energy utilization. While most of these applications have been concerned with short-term storage (hourly, daily, or weekly), there is a need also to consider long-term storage (seasonal or yearly).

III. PROJECT DESCRIPTION:

The concept of the rock bed heat accumulators, as originally presented [1], involves heating crushed or naturally formed porous rock by forcing hot air to flow from a central manifold to collector manifolds located at the top and bottom of the bed; on discharge, the air flow is reversed: cold air is introduced through the top and bottom manifolds and hot air is harvested through the central manifold. Input and output temperatures of up to 500°C and charging and discharging times of four to six months are possible with storage capacity limited only by the size of the bed. Various configurations of rock bed heat accumulators can be envisioned with local geological conditions, environmental constraints, and cost dictating the appropriate selection. Figure 1 illustrates two particular configurations applicable to surface and underground construction techniques.

IV. RESULTS:

1. System Performance

- Performance Characteristics: The design and performance of rock bed thermal storage systems are governed by these principal requirements: (a) heat leaks to surrounding (uninsulated) earth or groundwater must be minimized, thereby also insuring high first-law efficiency; (b) volume and second-law efficiencies must be optimized by proper selection of rock materials and of bed dimensioning; (c) pumping losses (pressure drop) associated with the charging and discharging of the bed must be minimized relative to the input energy; (d) the stability of the flow through the porous bed heated from below must be maintained by inhibiting the onset of free convection.

- Dynamic Containment: This requirement is achieved in the generic triple manifold system by stopping the charging of the bed when the temperature begins to rise at the outer cold manifolds. Furthermore, the follow-up discharge process is allowed to continue until the temperature of the central hot manifold falls substantially. These conditions imposed on the cyclic operation of the bed are necessary in order to inhibit the build-up, after two or three years, of a temperature gradient that would otherwise fill the entire bed regardless of its length [3].

- Mathematical Models: Analytical and computer models of one- and two-dimensional configurations of earth storage beds have been developed [2,3,5]. The simple single-phase one-dimensional model in which air and rock are at the same temperature and which uses an effective thermal conductivity of the bed $[k_e = k_{bed} + (v_{air}\rho_{air}c_{air})^2/h_v]$ is particularly suited to estimate the long-term performance. The single-blow solutions provide a good approximation to the dynamic containment operation that can be visualized in terms of moving thermal wavefronts having simple mathematical closed forms. Such analyses serve to identify the basic parameters which affect the design and performance of earth thermal storage systems in terms of such criteria as volume, first- and second-law efficiencies. In particular, volume efficiency η_v is a function of $H/\sqrt{\alpha\tau}$ as illustrated in Fig. 2 for two dimensionless outlet temperatures θ_f [H is the bed height, τ the charging time, and α the effective bed diffusivity]. Clearly with bed length and charging time prescribed, volume efficiency can be improved only with a reduction in diffusivity of the bed.

- Pumping and Stability Requirements: The work done in pumping the air through the rock bed must be minimized in relation to the energy input. This ratio (which must be less than a few percent) is proportional to the square of the bed length and inversely proportional to the permeability of the porous material. The flow stability requirement that no free convection occurs in the portion of the bed heated from below is satisfied when the Rayleigh number is less than 40; this criterion constraints the product of bed height and permeability to be less than some critical value which depends on the temperature. The satisfaction of the constraints of pressure stop and stability establishes acceptable domains of operation from which the permeability and bed length can be selected as illustrated in Fig. 3 for the case of a 300 MWt storage system with a charging time of 4 months, 8 hours per day, assuming a 40% volume efficiency. In this instance, bed height cannot exceed 35 to 45 m and the optimum permeability is about 5000 darcys ($5\times10^{-9}m^2$) [6].

2. Construction and Material Evaluation

- Construction Techniques: Various geometric arrangements and excavation methods have been identified for the construction of earth heat storage units in a variety of soil/rock types [6]. Surface construction methods such as trenching, rock quarrying, and strip mining, as well as underground techniques in competent rock involving mass blasting or large excavation are examined and compared (see Table I). Of particular promise is the use of naturally occurring porous rock such as St. Peter sandstone or reconstructed aggregates of fine particles as the storage medium.

Table I: Comparison of construction techniques

CONSTRUCTION SCHEME	CRUSHED ROCK SUPPLY	ROCK QUALITY	TRANSPORTATION	SITING	ENVIRONMENTAL IMPACT	MAJOR COST	COST INDEX	BEST SUITED	CONSTRUCTION PERIOD (YRS.)
TRENCHING	EXTERNAL	GOOD AS SPECIFIED	OF CRUSHED ROCK	DEEP SOILS MUST BE AVAILABLE	PUMPING	TRANSPORTING CRUSHED ROCK TRENCHING	$6/TON	SMALL STORAGE	?
STRIP MINING	SORTED ON SITE	MIXED	ON SITE OF CRUSHED ROCK AND FINES	SANDY SOIL MOST APPROPRIATE	LAY IMPERVIOUS BED	?	$2 to $3/TON	LARGE STORAGE	2
ROCK QUARRY	ADJACENT	GOOD BY SELECTION	ON SITE OF CRUSHED ROCK ONLY	OUTCROPS OF SUITABLE MATERIAL	LAY IMPERVIOUS BED	DRILL AND BLAST IN QUARRY	$2 to $3/TON	ALL SIZES	2
NATURAL POROUS ROCK	NATURAL	NATURAL	REMOVAL OF ACCESS	LOCALLY FAVORABLE CONDITIONS	PUMPING IF NECESSARY	ACCESS HORIZONTAL DRILL HOLES	$1 to $2/TON	WHERE NATURAL CONDITIONS APPLY	3
UNDERGROUND WITH MASS BLASTINGS	MASS BLASTING	GOOD	20% to 40% EXTRACTION DISPOSED ON SURFACE	ROCK AND GROUNDWATER CONDITIONS DICTATE	IN TIGHT ROCK IN FLOW LOW	ACCESS AND SHAFT IF AT DEPTH	$3/TON	LARGE STORAGE	2-3
UNDERGROUND, CRUSHED ROCK BACKFILL	CRUSHED EXCAVATION MATERIAL	GOOD	ON SITE ALL MATERIAL MOVED	ROCK AND GROUNDWATER CONDITIONS DICTATE	IN TIGHT ROCK IN FLOW LOW	EXCAVATION	$4 to $6/TON	LARGE STORAGE	3-6

- <u>Material Evaluation</u>: A literature survey [4] of the thermo-mechanical properties of rocks over the temperature range of 0°C to 500°C shows that for most rocks the thermal properties are temperature dependent and indicates that very little data is available on the mechanical properties of rock in this particular range. A series of laboratory experiments were conducted to evaluate the possibility of thermo-mechanical degradation of seven rock types subjected to up to 100 thermal cycles at 100° to 500°C. All samples showed dimensional changes and weight loss. The granites and sandstone experienced a significant strength loss after thermal cycling whereas the other rock types tested (limestone, basalt, and quartzite) had no strength reduction. Even after the 100 thermal cycles, all rock samples, still had significant strength, and thus would be suitable for a RBHA.

3. Environmental Considerations

The mode and degree of interaction of the accumulator with the hydrogeologic environment strongly influences its technological and ecological feasibility. A digital model based on finite-element techniques has been used to simulate two-dimensional heat transport from a RBHA unit into and with the groundwater flow system. It investigates the influence of different hydrologic parameters on the spatial evolution of dimensionless isothermal lines with time. The controlling parameters are groundwater flow velocity, aquifer dispersivity, thermal diffusivity, and position of the unit in the unsaturated soil zone, with the first two being the most important. The main results are that isotherms move very slowly under average flow and operating conditions, and that the most critical situation is one where intermediate velocities and dispersivities allow temperature buildup over a relatively large aquifer volume. However, if the temperature at the bottom of the RBHA is only 10 to 20°C higher than ambient soil temperature, this temperature rise will damp out quickly, and, within a distance of 2 to 3 times the lateral extent of the RBHA, it will not be distinguishable from normal soil temperature fluctuations [9].

4. Economic Assessment

The physical configurations and excavation methods considered for the various heat storage schemes are the primary cost determinants. For comparison and estimation purposes, it is convenient to express the total construction cost in dollars per ton of in-situ material removed and backfilled. Construction cost estimates were compiled from comparisons with similar construction projects, such as crushed rock quarrying and pipe laying, and do not include input/output heat exchangers, air pumping equipment, nor cost of energy input to the system. The construction cost indices for the various heat accumulator schemes studied ranged from a low of \$1.77/m^3 (\$1.00/ton) to a high of \$10.60/m^3 (\$6.00/ton) of rock material. An economic analysis computer program was developed that considered interest during construction, cost of capital, interest on debt, debt ratio, operation and maintenance with escalation, overhead, federal tax on profits, federal investment credit, other taxes, and depreciation. For an annual storage heat accumulator with a 300 MWt rating operating at 500°C, and assuming construction costs of \$1/ton to \$3/ton, energy costs and capital costs are in the range of 5 to 15 mills/kWht and 150 to 400 \$/kWt, respectively. Such costs for long-term thermal energy storage in rock materials appear economically attractive.

V. FUTURE ACTIVITIES:

Based on the results of the project, it is recommended that further research be carried out on RBHA along the following main lines:

(a) Conduct a small-scale experiment on a long-term storage module constructed in St. Peter sandstone to validate the concept feasibility and assess environmental impact.

(b) Perform laboratory tests and measurements on natural and reprocessed rocks and sandstone with improved thermal and mechanical properties.

(c) Develop analyses for beds with non-homogeneous porous materials, and for hybrid bed configurations suitable for combining both long- and short-term storage.

(d) Establish the preliminary design of a rock bed accumulator unit for seasonal storage appropriate to a cogeneration heating system operating at moderate to low source temperatures.

VI. PUBLICATIONS:

(The research work reported in the following publications was performed by the University of Minnesota with the support of ERDA under the present contract.)

1. M. Riaz, P. L. Blackshear, and H. O. Pfannkuch, "High Temperature Energy Storage in Native Rocks". Proc. of ISES Joint Conference: Sharing the Sun, Winnipeg, Canada, vol. 8, pp. 123-137, Aug. 1976 (Permagon Press).

2. M. Riaz, "Transient Analysis of Packed-Bed Thermal Storage Systems". Proc. of 1977 ISES Meeting in Orlando, FL, vol. 1, pp. 17.11-17.15, June 1977.

3. P. L. Blackshear, P. Emerson, B. R. Baliga, and M. Riaz, "Gravel-Filled Trenches in Earth for Annual Thermal Energy Storage". Ibd., pp. 16.16-16.19.

4. H. O. Pfannkuch and M. H. Edens, "Rock Properties for Thermal Energy Storage Systems in the 0° to 500° Range". Ibd., pp. 18.5-18.9.

5. M. Riaz, "Analytical Solutions for Single- and Two-Phase Models of Packed-Bed Thermal Storage Systems". J. of Heat Transfer, ASME Trans., vol. 99, pp. 489-492, Aug. 1977.

6. M. P. Hardy, V. D. Albertson, R. P. Bligh, M. Riaz, and P. L. Blackshear, "Large-Scale Thermal Storage in Rock: Construction, Utilization, and Economics". Proc. of 12th Intersociety Energy Conversion Engineering Conference in Washington, D. C., vol. 1, paper no. 779093, pp. 583-590, Sept. 1977.

7. R. P. Bligh, "Thermal Energy Storage in Large Underground Systems and Buildings". Proc. of Rockstore 1977/Conference, Stockholm, Sweden, Sept. 1977.

8. M. Riaz, "Long-Term Storage of Solar Energy in Native Rock". Submitted for presentation at the International Solar Energy Congress to be held in New Delhi, India, Jan. 1978.

9. D. W. Pollock, "Numerical Simulation of Energy Transport in Shallow Aquifers Subjected to a Thermal Stress from High-Temperature Energy Storage in the Unsaturated Zone". MS thesis, July 1977.

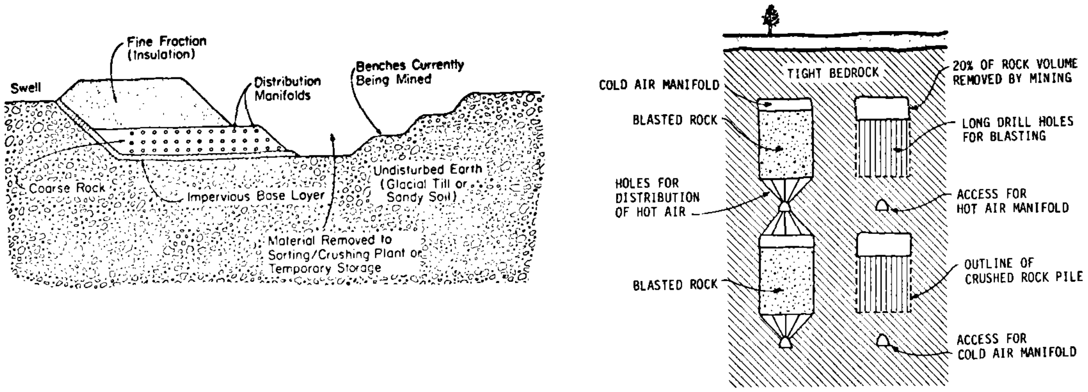


Figure 1. Examples of surface and underground RHBA

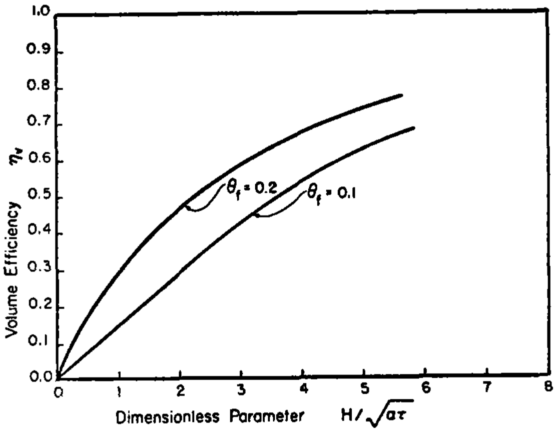


Figure 2. Volume efficiency

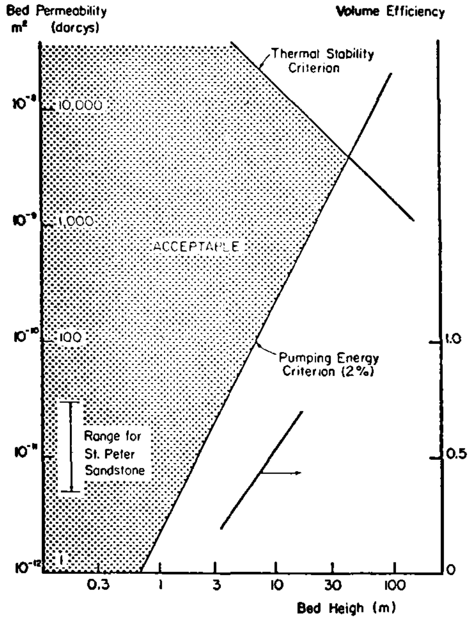


Figure 3. Pumping and stability constraints

Organization: Xerox Electro-Optical Systems

Address: 300 North Halstead Street
Pasadena, California 91107

Project Title: "RESEARCH ON ENERGY STORAGE FOR SOLAR THERMAL CONVERSION"

Principal Investigator: J. A. Carlson (213) 351-2261
J. L. Clayton

Contract No.: NSF-C7522234 Contract Period: July 1976 - Nov. 1977

Contract Amount: $125,000

Project Goals:

- Provide subsystem definition for thermal energy storage equipment for improved solar thermal electric power systems.
- Study sensible and latent heat delivery in two temperature regimes:
    - (1) 400° to 600°F
    - (2) 900° to 1100°F

Project Status: 68% complete

1. PURPOSE

The purpose of this program is to provide identification, definition, and conceptual design of improved storage systems and component subsystems for solar thermal electric power systems. Thermal storage modes to be considered include both sensible and latent heat. Energy delivery from storage to an electric power system is to be evaluated in two temperature regimes, 400° to $600^{\circ}F$ (feed water heating and boiling) and 900° to $1100^{\circ}F$ (superheating).

Subsystem specifications are to be generated for three hypothetical use cases:

- 10 mW_e peak power - Central Station Bus Bar
- 100 mW_e peak power - Central Station Bus Bar
- 200 $kW_e/2000\ kW_{th}$ - Total Energy System

2. BACKGROUND INFORMATION

Typical electric power systems use a fossil fuel fired Rankine steam cycle to convert thermal energy to electrical. A representative block diagram of such a system is shown in figure 1. Heat, or thermal energy, is added to the cycle for feed water heating, boiling, and steam superheating. A solar-thermal power system utilizes solar energy to provide the necessary heat input to the cycle.

The function of a thermal energy storage unit in a solar-thermal power cycle is shown in figure 2. The storage unit accepts energy from the solar collector over, at most, a 12-hour period and provides energy to the cycle over a 24-hour period. Thermal energy may be stored as sensible heat or as latent heat. Various molten salts are being considered as storage media.

3. PROJECT DESCRIPTION

The following tasks have been and are being addressed as a part of this program:

a. Literature Search - A survey of the literature has been conducted to obtain data on thermal energy storage materials. An additional survey has been made to obtain published analytical techniques and solutions treating heat transfer across a moving boundary (fusion).

b. Analytical Studies - Parametric analytical studies have been conducted to correlate storage material properties and storage unit configuration with design requirements. Computer analyses have been conducted for a variety of configurations using modal models. The phase change phenomenon was accommodated by using a weighted specific heat, input as a function of temperature.

   Thermodynamic analyses of latent and sensible heat storage concepts have been conducted and a baseline established.

c. Design Studies - Design studies are being conducted, trading off the baseline concept against alternate systems. These tradeoffs will include performance, cost, reliability, safety, and environmental effects.

4. RESULTS

Thermodynamic and preliminary cost studies show that the storage temperature should be near the collection temperature and that the cycle use temperature should be near the storage temperature. Large temperature differences between collector and storage and/or storage and cycle results in the loss of available energy. The loss of available energy approaches zero as the energy transfer process becomes isothermal (reversible). In addition, the average solar collector temperature should be kept as low as possible. The solar collection to receiver area ratio (concentration ratio) increases with collector temperature raised to the fourth power. For a given receiver, the collector field area is proportional to the concentration ratio, hence collector field cost increases with temperature to the fourth power. The manner in which these two concepts impact the selection and design of a thermal energy storage unit is discussed below.

Consider the temperature-entropy diagram for a latent storage system, shown in figure 3A. This scheme employs latent storage at two temperature levels. Large temperature differences occur between collector and the lower storage level and between the upper storage level and the cycle. Note also that the collection temperature is high, being dictated by the upper storage level. The average collection temperature may be lowered by going to a sensible storage system as shown in figure 3B. However, a large temperature gradient exists between storage and the power cycle.

An improved system is shown in figure 4. This system is hybrid, employing both sensible and latent modes of storage. Latent storage is used for feed water heating and boiling, and sensible is used for superheating. Solar collection is effected at two temperature levels, one for each mode of storage.

This system results in minimum temperature differences between collector and storage and storage and cycle, minimizing loss in available energy. The average collection temperature is basically the lowest attainable with a Rankine cycle minimizing concentration ratio and collection field cost. This is the system that will be used as the baseline for the storage system tradeoff studies that follow.

5. FUTURE ACTIVITIES

The storage system presented herein will be used as a basis for comparison with alternate storage systems. Tradeoffs will include performance and cost, as well as reliability, safety, and environmental effects. A preliminary design layout of the most favorable system will be generated and included in the final report.

Figure 1.

POWER CYCLE

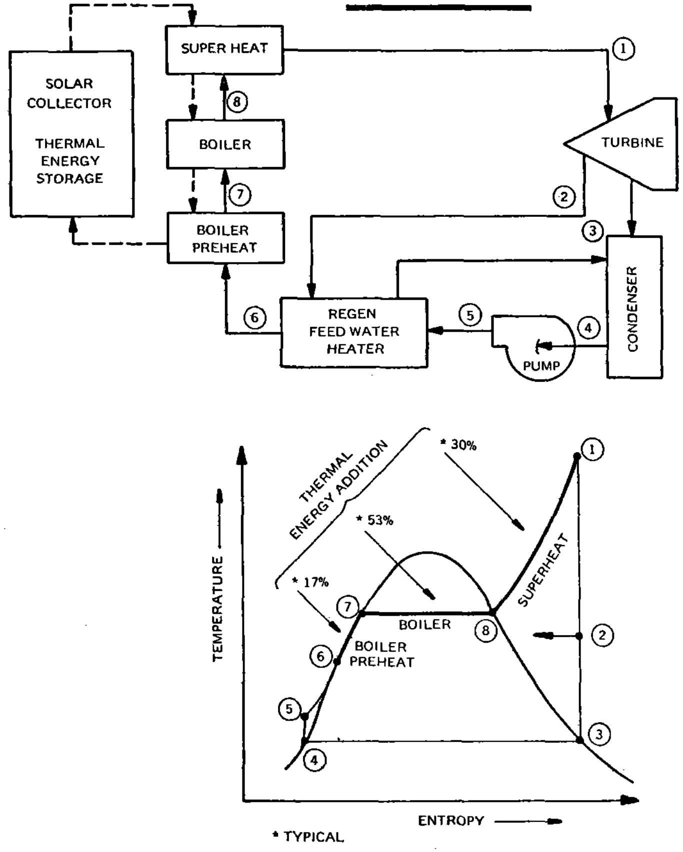
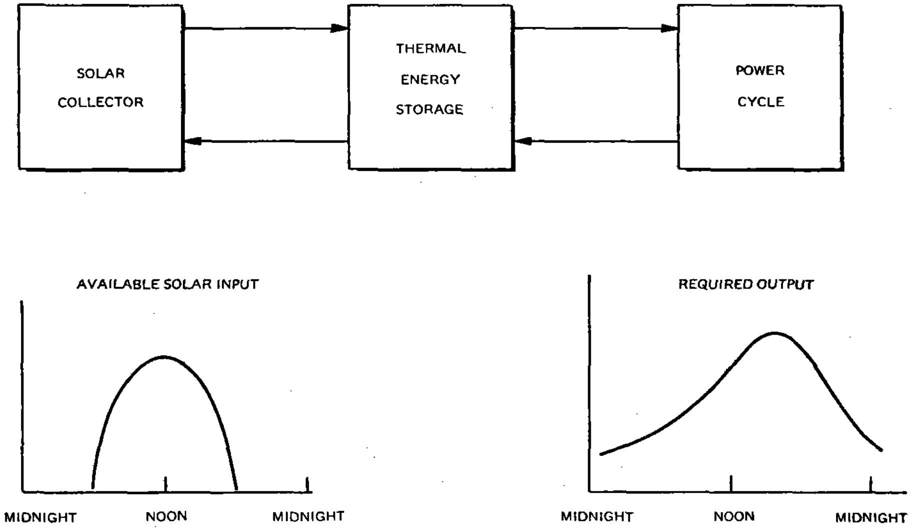


Figure 2.

SOLAR THERMAL POWER CYCLE



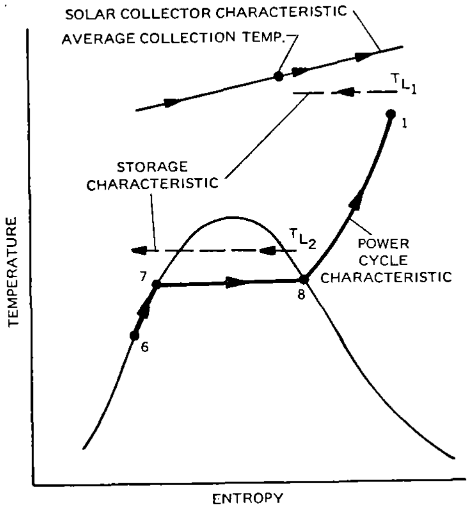


Figure 3A.

LATENT HEAT STORAGE SYSTEM

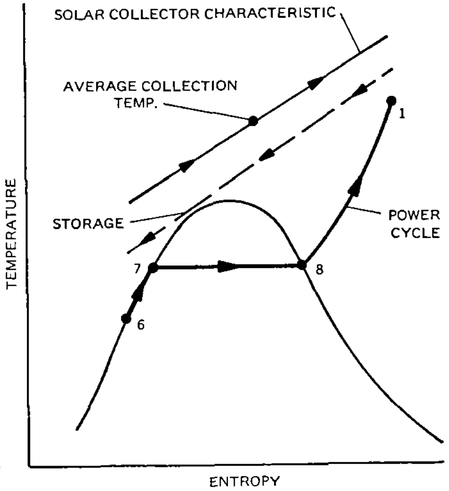


Figure 3B.

SENSIBLE HEAT STORAGE SYSTEM

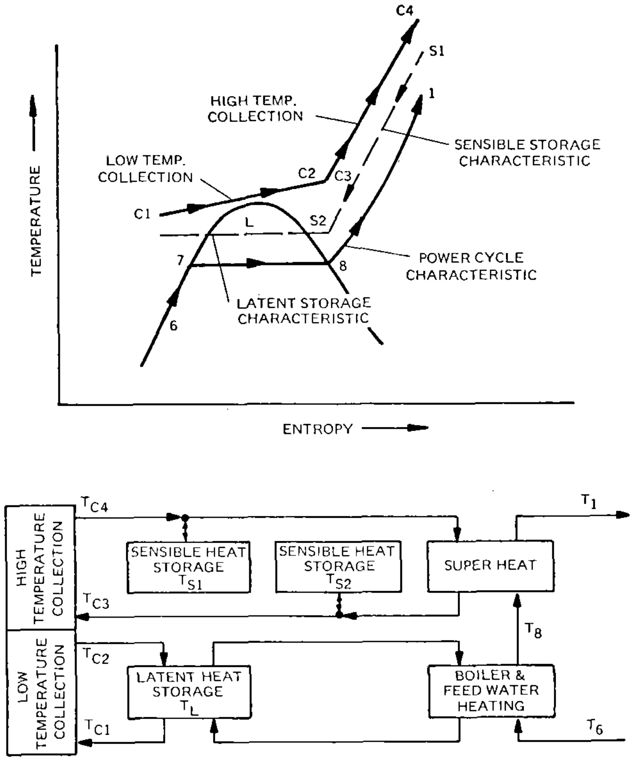


Figure 4.

HYBRID STORAGE SYSTEM

III. THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT

THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT PROGRAM OVERVIEW

Raymond W. Mar
Sandia Laboratories
Livermore, CA 94550

Introduction

The Chemical and Thermal Storage Branch of the Energy Research and Development Administration (ERDA), Office of Conservation, Division of Energy Storage Systems has implemented a National Thermal Energy Storage (TES) Program. The objective of the National Program is to develop and disseminate thermal and thermochemical energy storage technology. The program consists of three sub-programs:

1. Low-Temperature Thermal Energy Storage Program - The objective is to develop sensible and latent heat technologies for low-temperature ($\leq$ 250°C) applications.
2. High-Temperature Thermal Energy Storage Program - The objective is to develop sensible and latent heat technologies for high-temperature ($\geq$ 250°C) applications.
3. Thermochemical Energy Storage and Transport (TEST) Program - The objective is to develop reversible chemical reaction technologies for thermal energy storage and transport applications.

The Chemical and Thermal Storage Branch has delegated the management responsibility for the Thermochemical Energy Storage and Transport Program to Sandia Laboratories, Livermore. (Oak Ridge National Laboratories and NASA Lewis Research Center are responsible for the Low-Temperature and High-Temperature Thermal Energy Storage Programs, respectively.)

Program Scope

The Thermochemical Energy Storage and Transport (TEST) Program will include research and development of reversible thermochemical reaction technologies as they apply to the storage and movement of thermal energy. The program considers all classes of reactions, with the exception of hydrogen generating and photochemical reactions. All potentially viable applications for energy storage and transport will be considered.

Program Objective

The basic objective of the TEST Program is to develop the technologies required to commercialize energy storage and transport systems at the earliest possible date. These technologies will be advanced and developed by the development of specific concepts or systems.

The specific objectivies of the Program are:

- identify and evaluate preferred users (current and future) of reversible chemical reactions for energy storage and transport
- identify specification requirements and evaluate available technology and technology needs for selected storage systems
- formulate and evaluate energy storage and transport concepts which meet the requirements established above
- develop the most promising concepts and systems to a point of demonstration on a scale commensurate with commercial application. Only those concepts with potential for commercialization will be developed to completion.

Technical Breakdown Structure

The technical contents of the TEST Program have been divided into technology elements according to a Technology Breakdown Structure (see Figure 1). The four Technical Breakdown Structure elements are: 1) thermal energy storage, 2) chemical heat pipe, 3) chemical heat pump storage, and 4) generic research. Each major element has been further divided into subelements which represent specific concepts/applications which are being pursued in this program.

The use of thermochemical storage technology in solar thermal electric systems is of interest, with particular attention given to the long duration storage capabilities. The role of thermochemical technology in non-solar utilities is also being addressed. Chemical heat pipes for the transmission of thermal energy for industrial process heat and district heat applications appear to hold significant promise. The current TEST Program is investigating this end-use application coupled to three potential energy sources: 1) a coal gasification plant (open loop heat pipe), 2) a very high temperature nuclear reactor (high temperature heat pipe), 3) moderate temperature sources available in the United States including nuclear, solar and fossil (low temperature heat pipe). In addition, the use of chemical heat pipes for transmission in distributed solar systems in also being addressed. The only application of current interest for chemical heat pump storage technology is solar heating and cooling.

Long Range Plans

The various activities which comprise the long range (five-year) TEST Program are given in Figure 2, along with a very brief description of each. A long range plan has been formulated for each of the above mentioned Technical Breakdown Structure subelements; these plans are presented on Figures 3 -9 in the form of network diagrams. The networks illustrate the interactions required between various projects if the concept/application is to be successfully developed. Each activity shown on the flow sheets is numbered to be consistent with those used on

Figure 2. Interactions between activities are depicted by nodes; the nodes are indicative of "decision to proceed" points or "technical information exchange" points, although continual information flow between all activities is assumed.

The basic strategy adopted for development of each application/concept is briefly described below:

1.1 TES for Long Duration Solar - the basic objective is to develop the technologies required for long duration storage applications in solar thermal electric systems. During FY78, the emphasis will be on determining the economic feasibility of extended duration storage. All solar systems are currently of interest, including central and dispersed power systems. Concurrent with the economic systems studies, several promising technical concepts are being developed: SO_3/SO_2, $Ca(OH)_2$/CaO and NH_4HSO_4 decomposition (activities 1.1.4, 1.1.5, and 4.5). Continued concept development work into FY79 will require positive results from the systems studies (activities 1.1.1, 1.1.2, and 1.1.6).

1.2 Thermal Energy Storage for Non-Solar Utilities - the potential role of thermochemical technologies for storage in non-solar utilities will be assessed in a joint ERDA/EPRI funded study. Future development activities (1.2.2) will be planned if warranted.

2.1 Open Loop Heat Pipe - the open loop heat pipe has been addressed by General Electric/Corporate Research and Development under contract to ERDA/STOR (contract No. E(11-1)-1976), and in greater detail by IGT (activity 2.1.1). Pending favorable results from the IGT study, a system development effort (activity 2.1.3) may be mounted.

2.2 High Temperature Chemical Heat Pipe - a duplex steam reformer design will be fabricated and tested at the Kernforschungsanlage (KFA) facility as part of a joint United States/Federal Republic of Germany technical cooperative program agreement (activity 2.2.2). An alternate catalyst design worthy of testing will be sought (activity 2.2.3).

2.3 Low Temperature Heat Pipe - the benzene/cyclohexane reaction has been identified as an attractive candidate in a previous study (activity 2.2.1), and concept development will be initiated in FY78 (activity 2.3.1). Alternate reactions will continue to be of interest, and alternate concepts will be pursued if attractive ones are identified (activity 2.3.5). Ultimately, one concept will be selected for continued development to the prototype development and test phase (2.3.2). Concurrent with the benzene/cyclohexane project, systems studies will be performed to comparatively evaluate competing concepts for the delivery of industrial process heat (activity 2.3.3) and characterize the potential users (2.3.4).

2.4 Transmission in Distributed Solar Systems - the potential of thermochemical heat pipes in distributed solar energy systems will be critically assessed in FY78 (activity 2.4.2), and a development program initiated (activity 2.4.3) if warranted.

3.1 Solar Chemical Heat Pump - four different chemical reactions are currently being investigated (3.1.1, 3.1.2, 3.1.3, 3.1.4) and studies will continue into FY78. One (or more) reaction concept will be selected (activity 3.1.5) in FY79 for continued development to the prototype design, fabrication, and test phase (activity 3.1.6).

The long range plans were established by assessing the technology issues, and our best estimates of the times to their resolution. Realistic TEST Program budget levels were considered, as well as the relative importance of each concept/application with regard to potential impact on energy conservation. As the Program progresses and as data are generated and evaluated, the development of some concepts/applications may be accelerated at the expense of others. The long range plans are flexible, and will be updated as required.

THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT PROGRAM

TECHNOLOGY BREAKDOWN STRUCTURE

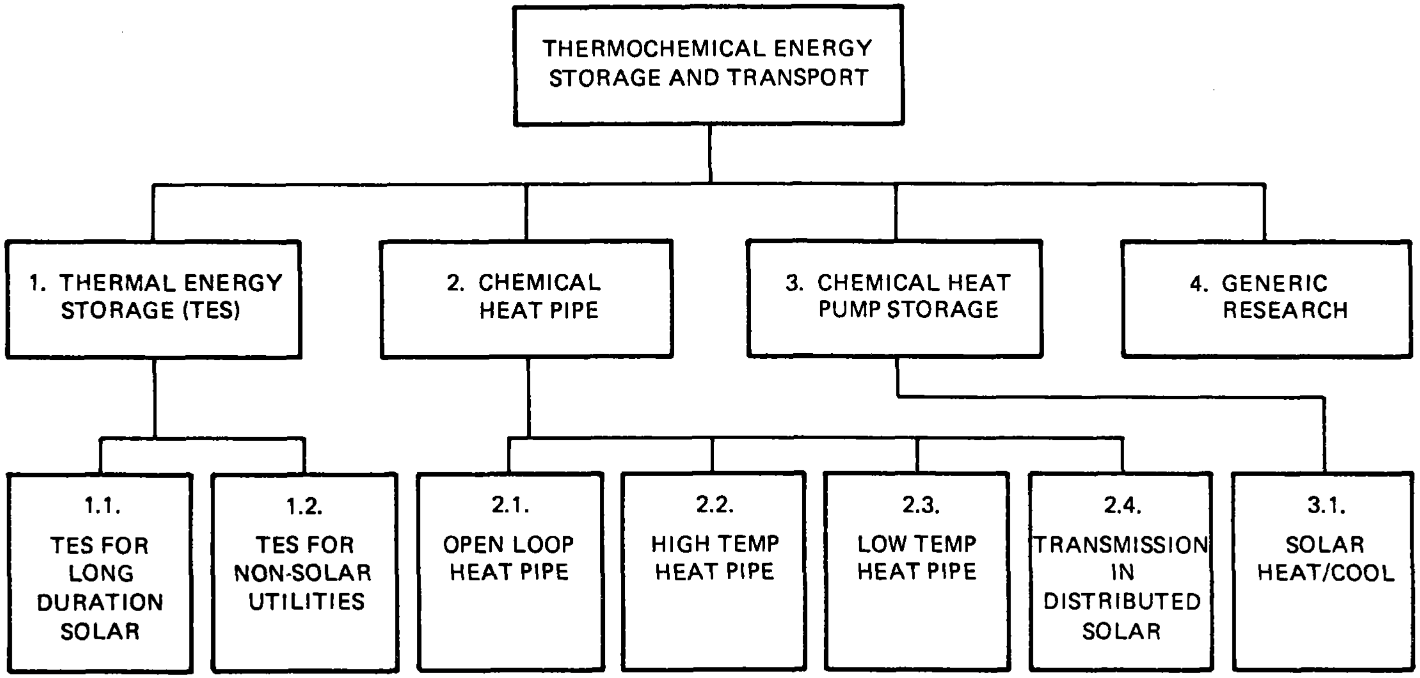


FIGURE 1

FIGURE 2. THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT PROGRAM - LONG RANGE ACTIVITIES

TECHNICAL BREAKDOWN STRUCTURE		ACTIVITY	CONTRACTOR*
PRIMARY ELEMENT	SUBELEMENT		
1. Thermal Energy Storage	1.1. Thermal Energy Storage for Long Duration Solar	1.1.1. Extended Storage Feasibility - a system study to evaluate the technoeconomic feasibility of thermochemical storage concepts in solar energy systems.	Rocket Research Corporation
		1.1.2. Extended Storage Feasibility - an activity complementary to activity 1.1.1.	Sandia
		1.1.3. TES Concept Development - if a need for alternate ideas and concepts for use in solar applications is identified, this activity will seek to fill the need.	
		1.1.4. Ammonium Hydrogen Sulfate Decomposition - to develop an energy storage concept based upon the decomposition of ammonium hydrogen sulfate.	Univ. Houston
		1.1.5. $Ca(OH)_2/CaO$ Reaction - to develop an energy storage concept based upon the hydration and dehydration of CaO and $Ca(OH)_2$ respectively.	Atomics Int'l
		1.1.6. High Temp. Storage and Heat Pipe Analysis - system studies to formulate and evaluate operational chemical cycles.	Lawrence Berkely Lab.
		1.1.7. SO_2/SO_3 Concept Development - to develop an energy storage concept based upon the reaction $2SO_3 = 2SO_2 + O_2$.	
		1.1.8. TES System Development - the continued development of a thermal energy storage concept(s) to the prototype demonstration phase.	

FIGURE 2. (CONT.)

TECHNICAL BREAKDOWN STRUCTURE		ACTIVITY	CONTRACTOR*
PRIMARY ELEMENT	SUBELEMENT		
	1.2. Thermal Energy Storage for Non-Solar Utilities	1.2.1. TES for Non-Solar Electric Utilities - a system study to evaluate the techno-economic potential of thermochemical storage concepts in current and near term electric utilities.	
		1.2.2. TES Development - concept development activities for promising applications identified in 1.2.1.	
2. Chemical Heat Pipe	2.1. Open Loop Heat Pipe	2.1.1. Open Heat Pipe Feasibility - a system study to determine the technoeconomic feasibility of the open loop methane based heat pipe.	IGT
		2.1.2. Program Planning - the competitive solicitation and procurement of an activity to develop the open loop methane based heat pipe (see 2.1.3).	Sandia
		2.1.3. Open Pipe Development - the development of an open loop methane based heat pipe.	
	2.2. High Temp. Heat Pipe	2.2.1. Heat Pipe Feasibility - a systems study to determine the technical and economic feasibility of chemical heat pipes.	General Electric/ Corporate Research
		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.	General Electric/ Energy Systems Program Department
		2.2.3. Alternate Catalyst Development - to develop alternate catalyst designs used in methanation/reformation reactions	General Electric/ Energy Systems Program Department.

FIGURE 2. (CONT.)

TECHNICAL BREAKDOWN STRUCTURE		ACTIVITY	CONTRACTOR*
PRIMARY ELEMENT	SUBELEMENT		
		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.	Univ. Houston
	2.3. Low Temp. Heat Pipe	2.3.1. Benzene/Cyclohexane Reaction - to develop the benzene/cyclohexane reaction for use in chemical heat pipe systems which can be coupled to thermal sources available in the United States.	General Electric/ Corporate Research
		2.3.2. Low Temperature Heat Pipe Development - the continued development of a heat pipe concept(s) to a point of prototype demonstration and test.	
		2.3.3. Heat Pipe Application Study - system study to critically evaluate and compare alternate means of transporting industrial process heat.	
		2.3.4. Heat Pipe Users Market Analysis - a study to obtain detailed information concerning potential users of process heat delivered by chemical heat pipes. This information is required for the completion of 2.3.2.	
		2.3.5. Alternate Heat Pipe Concept Development - to identify and develop concepts other than the benzene/cyclohexane reaction for use in heat pipe systems.	

FIGURE 2. (CONT.)

TECHNICAL BREAKDWON STRUCTURE		ACTIVITY	CONTRACTOR*
PRIMARY ELEMENT	SUBELEMENT		
	2.4. Energy Transmission in Distrib. Solar Systems	2.4.1. Feasibility Study - the use of thermochemical reactions to transport thermal energy in a distributed solar energy will be comparatively evaluated with other approaches.	
		2.4.2 Heat Pipe Concept Development - assuming a need is identified in 2.4.1, reactions and concepts will be developed for use in distributed solar systems.	
3. Chemical Heat Pump Storage	3.1. Solar Heating and Cooling	3.1.1. Sulfuric Acid Concentration/Dilution - a chemical heat pump system based on the concentration/dilution of sulfuric acid will be developed.	Rocket Research Corporation
		3.1.2. Methanol-Salt System - a chemical heat pump storage system using methanolated salt reactions will be developed.	EIC Corporation
		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.	Chemical Energy Specialists
		3.1.4. Ammoniated Salt Heat Pump - to develop a chemical heat pump system based upon the use of coupled ammoniated salt reactions.	Martin-Marietta Corporation
		3.1.5. Program Planning - the comparative evaluation of all chemical heat pump concepts and the selection of a concept(s) for continued development to the prototype demonstration and test phase.	Sandia

FIGURE 2. (CONT.)

TECHNICAL BREAKDOWN STRUCTURE		ACTIVITY	CONTRACTOR*
PRIMARY ELEMENT	SUBELEMENT		
		3.1.6. Prototype Development - the development of a chemical heat pipe concept to prototype demonstration and test.	
		3.1.7. Alternate Concepts - to identify and develop concepts and reactions for solar heating and cooling in addition to those described in activities 3.1.1, 3.1.2, 3.1.3, and 3.1.4.	
4. Generic Research		4.1. Experimental Heat Transfer - to determine various heat transfer parameters required to model and characterize fixed bed heat exchangers as they are used for gas/solid thermochemical reactions.	Colorado State Univ./Martin Marietta
		4.2. Thermal Decomposition Kinetics - detailed mechanistic studies of various thermal decomposition reactions will be carried out.	Univ. California at Davis
		4.3. SO_3/SO_2 Catalyst Development - the applicability of current catalysts for use in SO_2/SO_3 storage systems will be determined, and new catalysts developed if required.	Rocket Research Corporation
		4.4. Ammoniated Salt Storage - the chemical system characteristics of dissociating ammoniated salts will be determined, (complementary to activity 3.1.4).	Martin-Marietta Corporation

*A contractor is identified if the activity is currently in progress. The extension of the activity beyond the current contract period does not imply continued participation by the listed contractor.

TES FOR LONG DURATION SOLAR

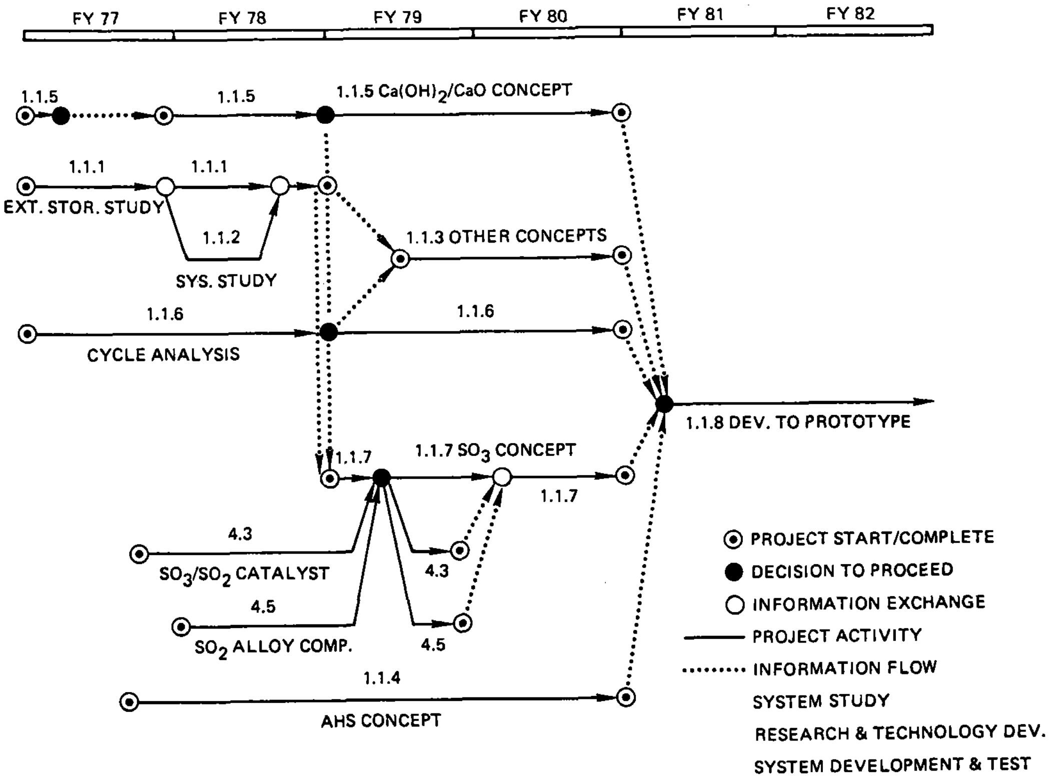


FIGURE 3

TES FOR NON-SOLAR UTILITIES

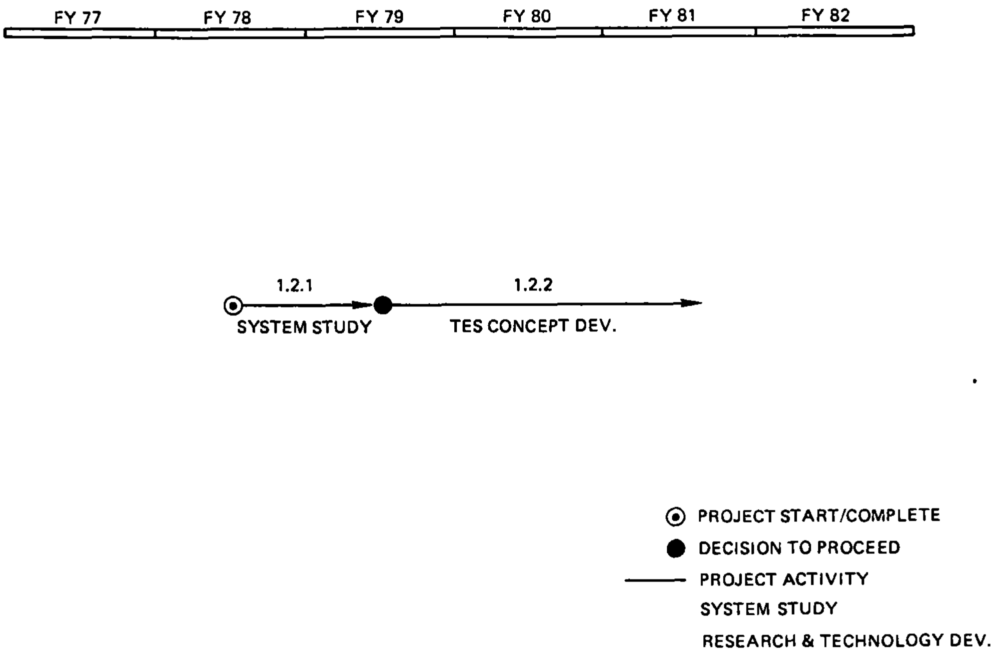


FIGURE 4

OPEN LOOP HEAT PIPE

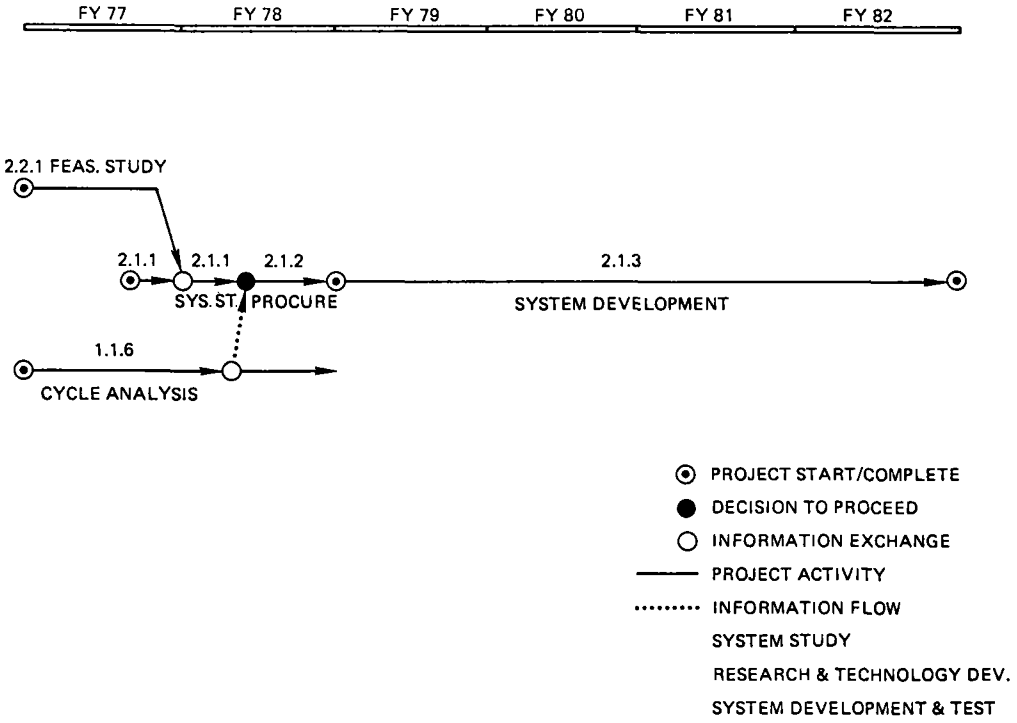


FIGURE 5

HIGH TEMPERATURE HEAT PIPE

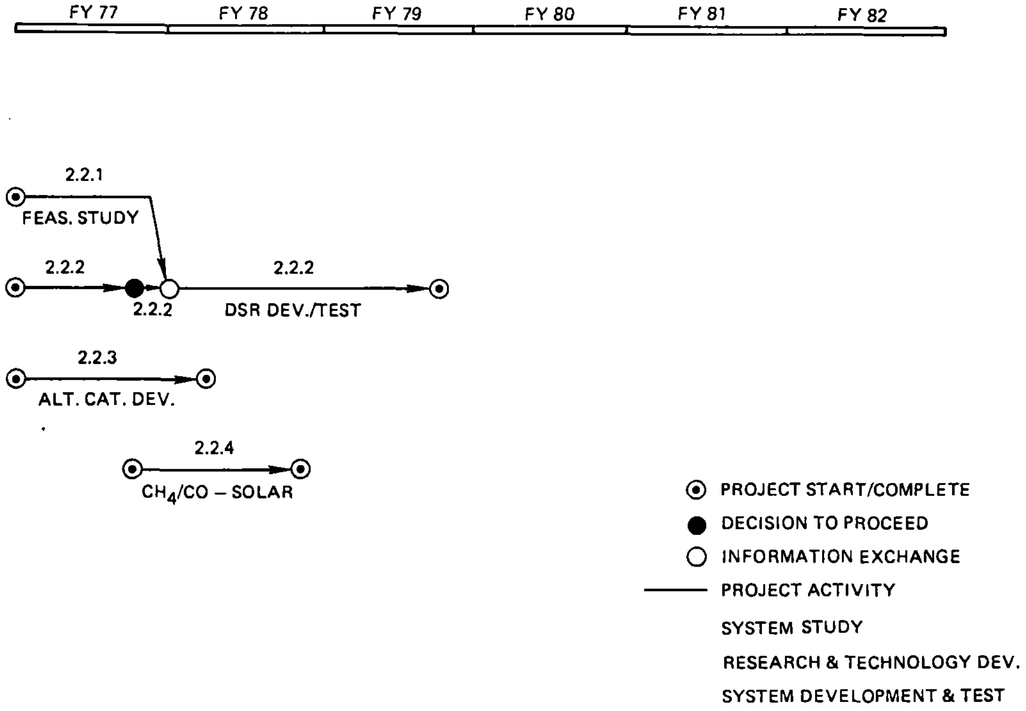


FIGURE 6

LOW TEMPERATURE HEAT PIPE

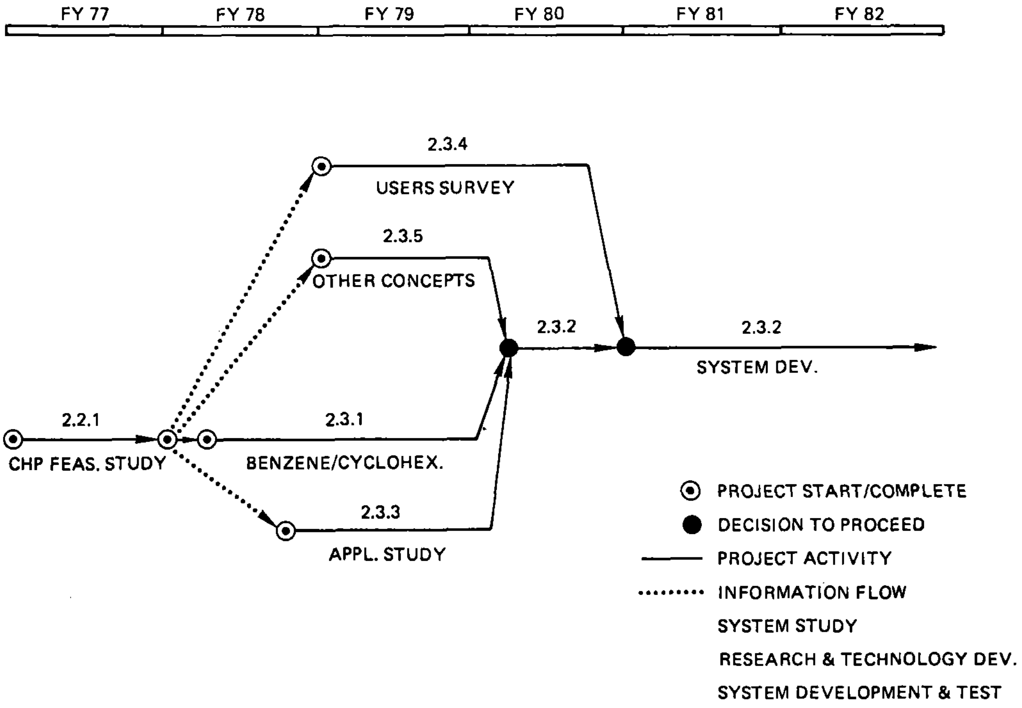


FIGURE 7

ENERGY TRANSMISSION IN DISTRIBUTED SOLAR

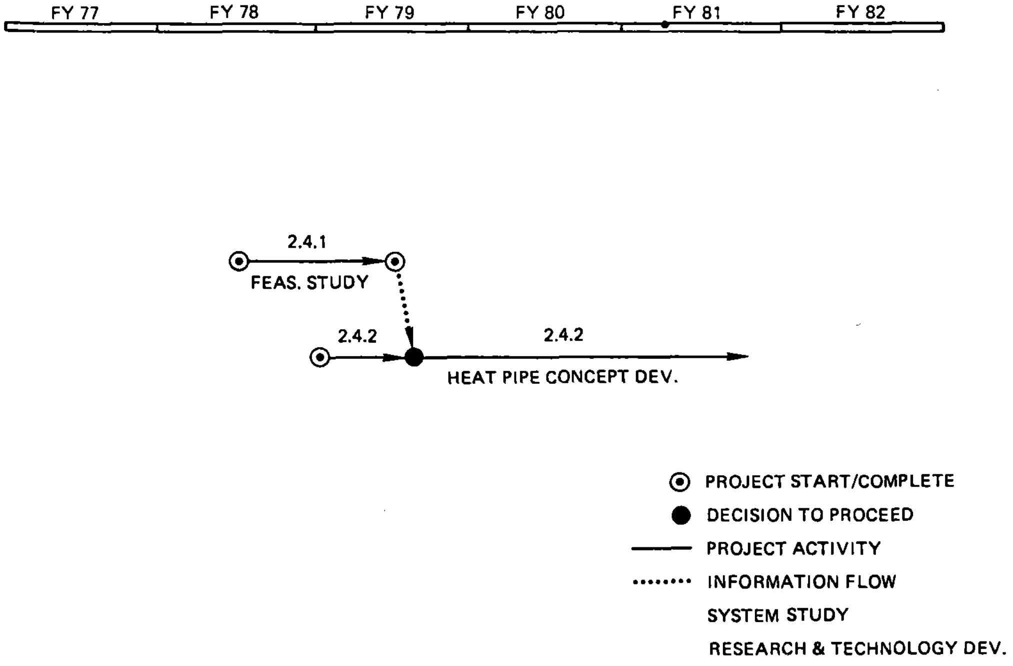


FIGURE 8

SOLAR HEATING/COOLING

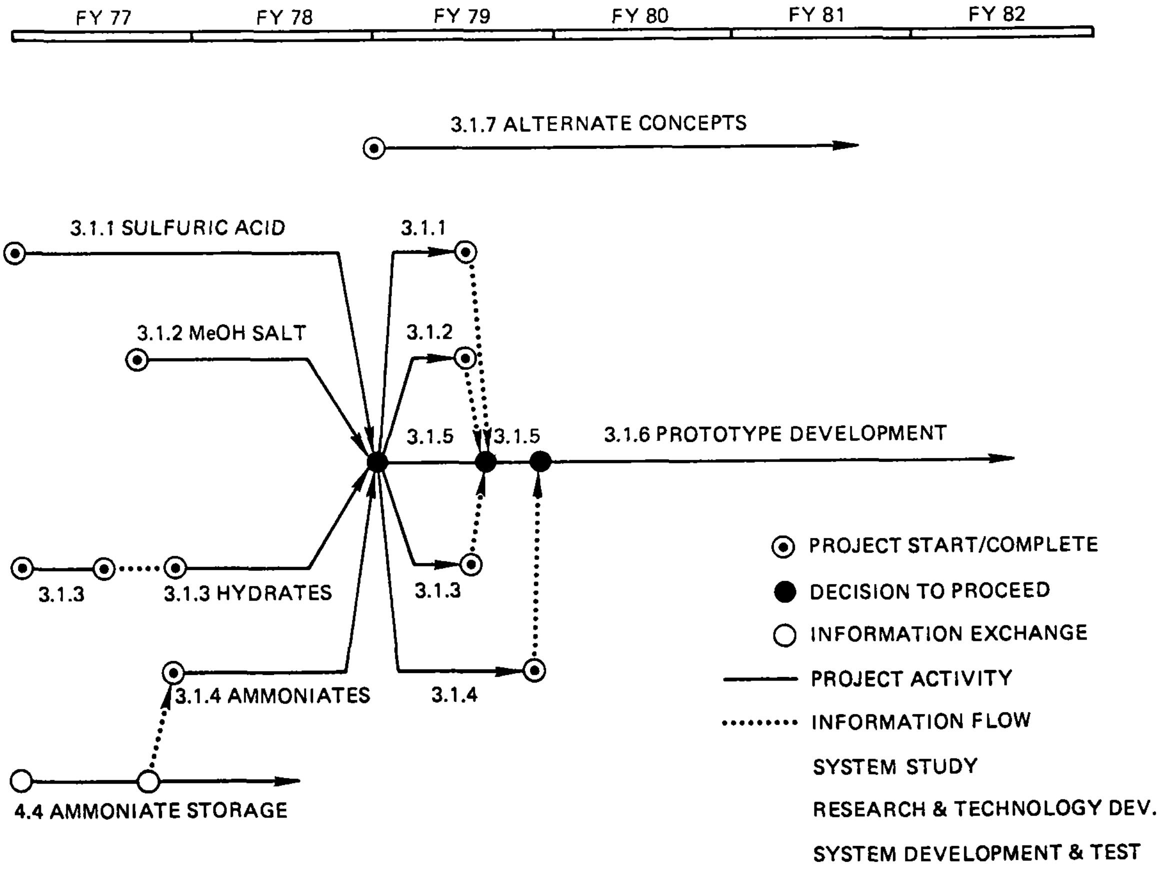


FIGURE 9

PROJECT TITLE: THE CHEMICAL HEAT PUMP (Hydrated Salt Heat Pump)

PRINCIPAL INVESTIGATOR: LEONARD GREINER
TELEPHONE NO.: 714-557-6483

CONTRACT NO.: ERDA, EY-76-C-03-1332
SANDIA, 87-9835A
CONTRACT PERIOD: Sep 76-Feb 77
Aug 77-Dec 77

CONTRACT AMOUNT: ERDA, $62,395
SANDIA, $40,000

PROJECT GOALS:

Preliminary investigation of the chemical heat pump, based on vapor hydration of salts, as means of day and night heating and cooling of residences with solar energy. Its purpose is to integrate design and analytical studies and experimental studies to provide the background technology needed for design and fabrication of a pre-prototype. The design and analytical task includes theoretical and engineering analyses to refine an initial design sketch of the chemical heat pump towards a viable prototype, including external apparatus, interface requirements, control systems, estimated operating capabilities, and preliminary economic assessment. The experimental task is largely performed in laboratory models, and determines rates of water desorption from the salt as function of various physical parameters, rates of water condensation in selected configurations, cycling effects, and examination of inexpensive materials of construction with respect to mechanical life and chemical attack. Preliminary attention is given to $MgCl_2 \cdot xH_2O$ as salt absorbant.

PROJECT STATUS:

Analytical and design studies have resulted in a simplified collector-absorber design that appears capable of collecting the desired solar energy input at the required temperatures for operating the chemical heat pump. The experimental studies have established requirements for achieving the necessary conditions for absorption and desorption of water vapor. They show a strong dependance on the mechanical features of the system. These requirements are met by the collector-absorber design. Chemical corrosion problems have hampered the studies, but successful solutions appear at hand. Cycling studies appear initially promising.

THE CHEMICAL HEAT PUMP

I. Purpose

The purpose of the work is to obtain the necessary technical background for the design and fabrication of a pre-prototype Chemical Heat Pump, based on hydrated salts, for day and night heating and cooling of residences with solar energy, and to provide a preliminary assessment of the operability of the device.

II. Background Information

The Chemical Heat Pump consists of two containers and a valved conduit. Its principle involves the reversible transfer of water vapor between liquid water in one container and an absorbant chemical in the other, as the respective vapor pressures are affected by temperatures within the two containers. As consequence of this vapor movement, thermal energy is transferred to or from the environment of the containers, which results in energy storage and subsequent heating, or cooling.

Figure 1 shows imporant vapor pressure-temperature data for water and a magnesium chloride hydrate as absorbant. Point E on the right hand curves indicates the vapor pressure of the magnesium chloride hydrate at 250°F, which temperature is achievable with solar energy. Point C on the left hand curve is the vapor pressure of water at a normal ambient of 75°F. When the two containers are inter-connected, water vapor will move from the higher pressure within the hydrated salt container to the lower pressure within the water container, and this will result in the desorption (or recharge) of the salt by a daytime solar input. At night, when the air temperature is much lower, the situation reverses. Now, the pressure in the water container is represented by Point A at (say) 32°F, which is higher than that of point B on the absorbant curve at about 160°F. As a consequence, vapor passes from the water container to the absorbant where heat is liberated at a temperature high enough for home heating. The energy output in the latter fashion is about 360 BTU/lb of the absorbant plus water, which is the potential thermal storage capacity of the chemical pair.

Figure 2 represents a version of the Chemical Heat Pump on rooftop. Modules of the water and absorber containers, each in the form of closed, flat pans, are incorporated together in rows and columns to make up the proper overall thermal capacity. The absorbant container is located within the solar collector, and the water container in the shade of the latter. In the daytime, the sun supplies the necessary thermal input and temperature both to heat the home in the daytime and to desorb the absorbant. At night, the energy input results from vapor passage from the water container back to the absorber container. The thermal energy requirements for home heating are transferred by closed-circuit air ducts that pass over the area of the absorbant container.

III. *Project Description*

The project comprises an Analytical and Design Task and an Experimental Task, with the information obtained in the two continuously integrated.

The Analytical and Design Task comprises theoretical and engineering design analysis. It is intended to refine the initial design sketch of the Chemical Heat Pump *towards a viable pre-prototype.* A preliminary mechanical design of the system is to be developed. External apparatus, interface requirements, control systems, estimated operating capabilities, and other important information are to be identified. A theoretical study will attempt to model the process that occurs within the Chemical Heat

Pump Absorber. A preliminary economic assessment is to be made, detailing assumptions made and outlining gains and benefits.

The Experimental Task is to be carried out primarily within laboratory models derived from the integration of the Analytical and Design Task and Experimental Task. The studies are to include rates of water desorption from the absorbant as functions of temperature, bed thickness, surface concentration, water contents and internal pressures. Rates of water condensation onto selected vaporizer configurations are to be examined. Effects of cycling are to be studied. The potential of inexpensive construction materials and designs under use conditions is to be determined, with respect to mechanical life and chemical attack.

IV. Results

Normal solar collector designs do not provide the capacity needed by the Chemical Heat Pump, as indicated in Figure 1 (augmented by experimental studies) and with respect to the energy inputs needed. A detailed analysis of such collectors resulted in improved methods. Based on the latter, a preliminary design has been developed which appears capable of providing the necessary thermal and temperature inputs but, nevertheless, is relatively simple and potentially inexpensive in its construction. The computed time-temperature history of the collector at the absorbant surface is indicated in Figure 3. Temperatures up to 340^{o}F seem obtainable, even in cold days within the Los Angeles Area. The duration of such relatively high temperatures seems long enough to effect dehydration of the absorbant. The collector design permits absorption of sufficient thermal energy both to dehydrate the absorbant chemical and to supply the thermal energy needed to heat the house in the daytime. The design includes means for heating the home at night with the somewhat lower temperature capability provided by the absorber, strictly from the heat pump action. Thermal energy for home heating is transferred by closed-circuit air ducts that pass over the enclosed area of the absorbant container. Also, heat is transferred to, or from, the vaporizer by ambient air circulated over its container.

Mathematical modeling of the absorption process has been begun. In its very preliminary status, it is roughly predicting the behaviors noted experimentally.

Experimental studies are showing a great dependence between the operability of the Chemical Heat Pump and its mode and materials of construction. One primary problem is to maintain the powder particles of the absorber bed in close and continuous contact, despite volumetric changes that occur in the process. Designs to achieve this have been developed. Results of time-temperature history of a dehydration test are indicated in Figure 4A. At a surface temperature in the range of 240^{o}F, dehydration proceeded from the nominally completely hydrated salt ($MgCl_2 \cdot 4H_2O$) to 70% of its desired final concentration ($MgCl_2 \cdot 2H_2O$) in 10^2 hours. Data at higher temperatures show much faster dehydrations to lower concentrations: 300^{o}F will effect virtually the dehydration needed within about 3 hours. Important potential corrosion problems have been experienced due to formation of small amounts of hydrochloric acid vapor as a side reaction of the dehydration. The amount of such formation decreases at lower temperatures, but is not eliminated. Present experiments with materials resistant to chemical attack by HCl are very encouraging. We are also looking into other chemical couples that do not form HCl, but the more promising are relatively expensive.

Figure 4B shows temperature data at the absorber surface of the Chemical Heat Pump under simulated nighttime conditions, in which heating results only from absorpton of water vapor liberated at the vaporizer container. Apparently, water vapor is readily absorbed with attendant temperature and thermal outputs that are more than satisfactory, It appears that controls will be needed to lower the energy output.

Our present conclusion is that the use of the specialized collector design, the specialized absorber design, and the newly tested materials of construction will result in a viable Chemical Heat Pump system for day and night heating and cooling of residences with solar energy.

During parametric studies, we have performed four charge-recharge cycles on two experimental units, and 7 cycles on a third, before discontinuing the runs for reasons unrelated to life-cycle problems. In the latter regard, one must avoid hydration of the magnesium chloride beyond a mole ratio of 5 waters to prevent solidification of the powder bed.

V. Future Activities

The remainder of the present contract will be devoted to completing the studies indicated in II, Project Description.

In the succeeding contract, we should like to design and fabricate a small-scale pre-prototype Chemical Heat Pump, based on information then available, and subject it to simulated roof-top studies. In the next and final developmental contract, we would like to design and fabricate a full-scale prototype Chemical Heat Pump module and install it on roof-top, where its capabilities to heat and cool a simulated home volume with actual solar energy will be ascertained.

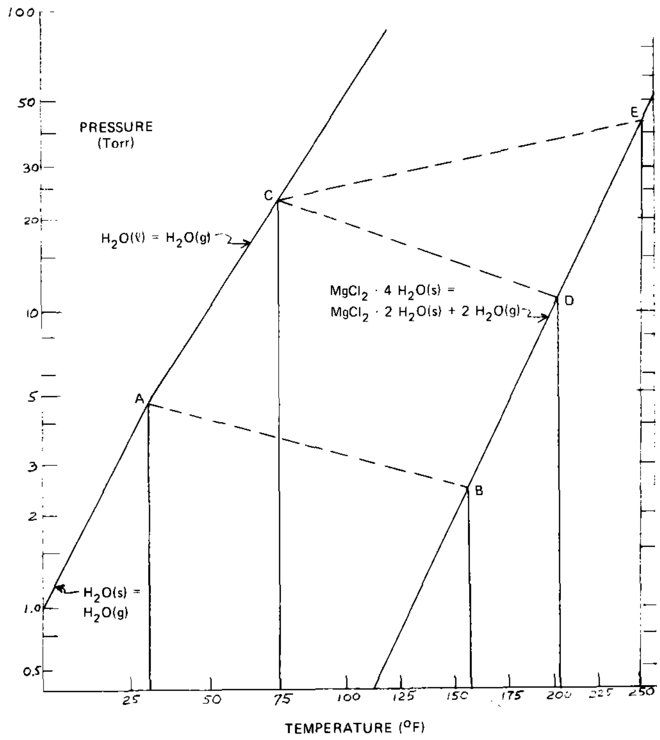


Fig. 1. Vapor pressure–temperature plot for a water–magnesium chloride system.

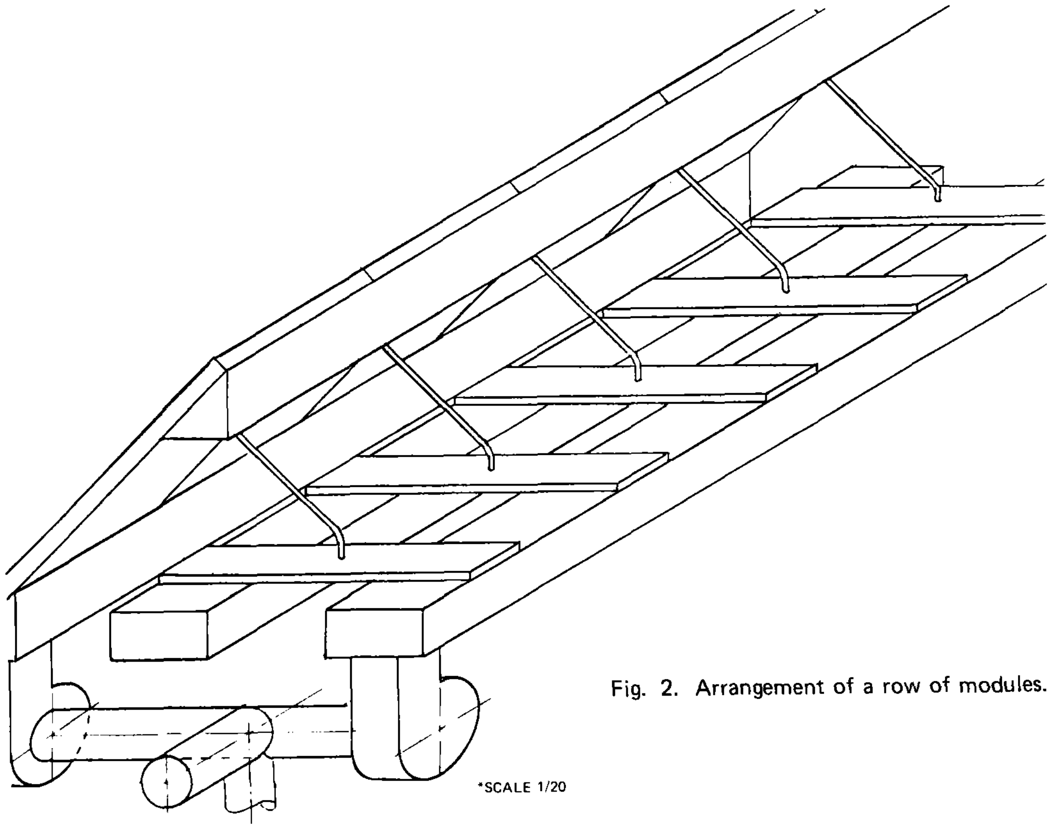
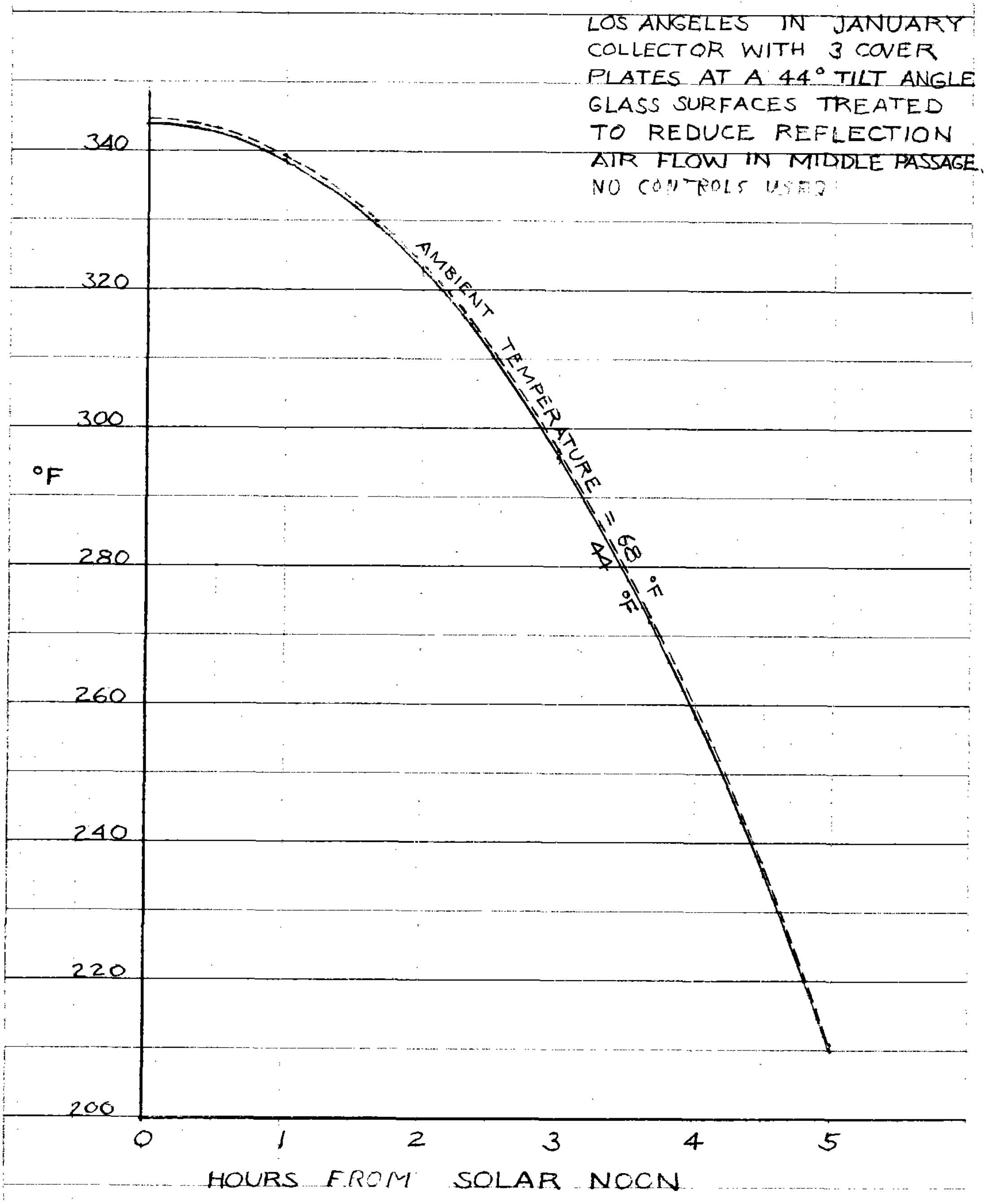


Fig. 2. Arrangement of a row of modules.

FIG. 3

ESTIMATED VARIATION OF ABSORBER TEMPERATURE WITH TIME OF DAY FOR A COLLECTOR OF FIXED GEOMETRY



LOS ANGELES IN JANUARY
COLLECTOR WITH 3 COVER PLATES AT A 44° TILT ANGLE
GLASS SURFACES TREATED TO REDUCE REFLECTION
AIR FLOW IN MIDDLE PASSAGE.
NO CONTROLS USED

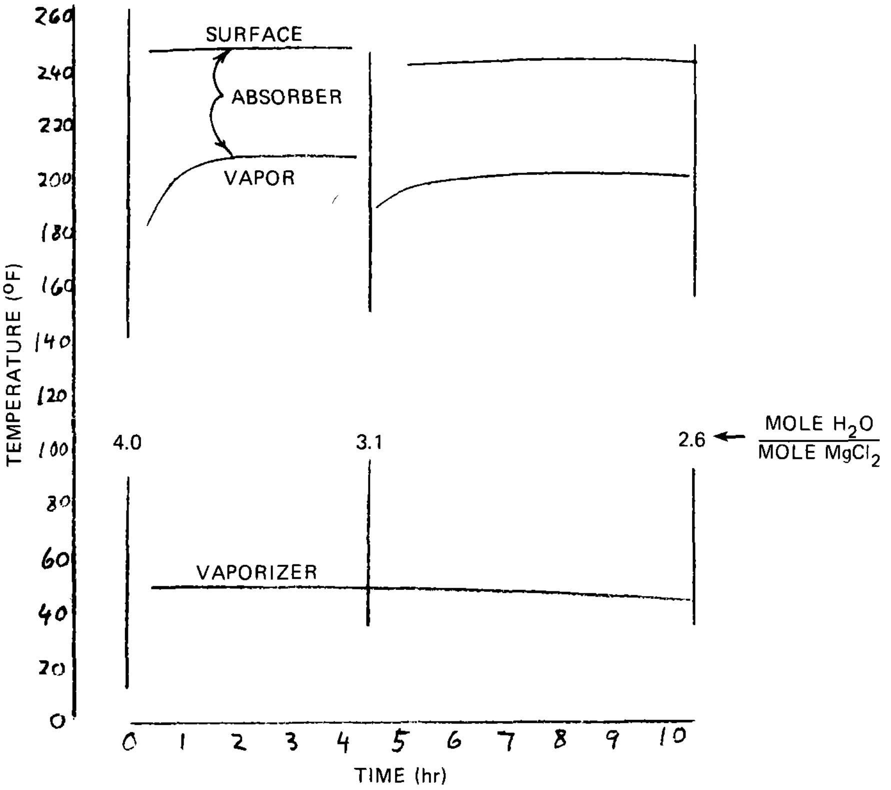


Fig. 4A. Typical dehydration.

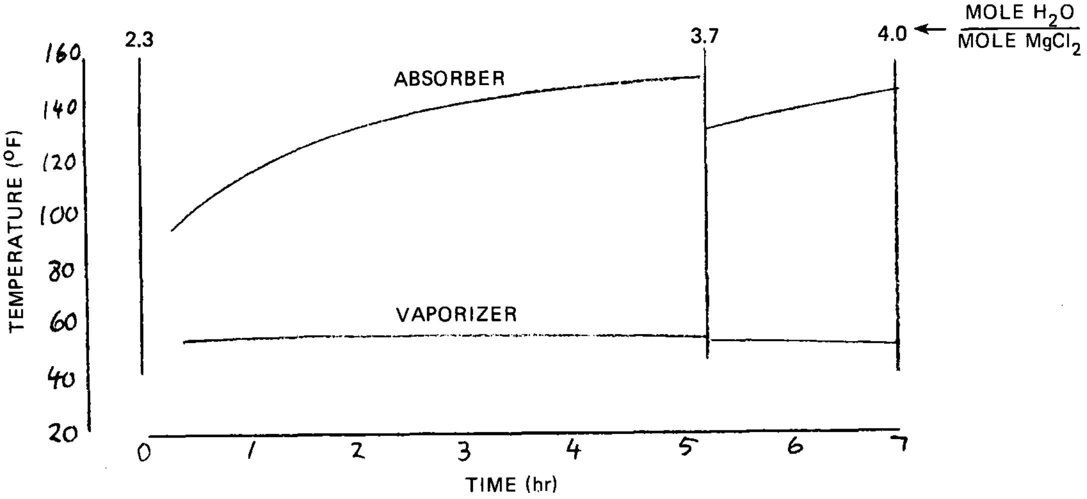


Fig. 4B. Typical hydration.

PROJECT SUMMARY

ORGANIZATION:	EIC Corporation
ADDRESS:	55 Chapel Street, Newton, Massachusetts 02158
PROJECT TITLE:	Methanol-Based Single-Substrate Heat Pump for Solar Thermal Storage
PRINCIPAL INVESTIGATOR:	Dr. Peter O'D. Offenhartz - Telephone No. (617) 965-2710
CONTRACT NO.:	87-9118
CONTRACT PERIOD:	April 25, 1977 - April 24, 1978
CONTRACT AMOUNT:	$119,498

PROJECT GOALS:

The objective of this program is to find combinations of inorganic salt substrates and carrier gases (CH_3OH) that are thermodynamically and kinetically suitable for use in the operation of a chemically driven heat pump for storage of solar thermal energy. As such combinations are found, the experimental thermodynamic, kinetic, and heat transfer data will be used as the basis for engineering design and economic analysis of various storage configurations.

Methanol-based thermally activated heat-pump systems offer the promise of long-term energy storage at high energy density. The projected coefficient of performance of the heat pump is ca. 1.6, which implies a substantial savings in collector area and cost compared to conventional systems. Inherent safety is provided by sub-atmospheric operating pressures.

PROJECT STATUS:

Over twenty inorganic salts have been investigated for their reaction with CH_3OH. Approximate pressure-temperature-composition profiles of these compounds have been measured at a constant CH_3OH pressure of 0.1 atm. Three compounds have been found that pass the initial screening tests:

$$MgCl_2 \cdot 2CH_3OH,\ FeBr_2 \cdot 2CH_3OH,\ \text{and}\ CoBr_2 \cdot 2CH_3OH.$$

Other salts have been found that could be suitable in warmer climates, in air conditioning, or in conjunction with low-temperature underground storage (i.e., minimum pumping temperature ca. 0°C). More detailed thermodynamic, kinetic, and heat transfer studies will begin shortly.

PROJECT DESCRIPTION

METHANOL-BASED SINGLE-SUBSTRATE HEAT PUMP FOR SOLAR THERMAL STORAGE

I. Objectives

The primary aim of this program is to obtain experimental thermodynamic, kinetic, and heat transfer data on combinations of inorganic salt substrates with CH_3OH vapor. These data will be used as a basis for the engineering design and economic analysis of single-substrate heat pumps for solar thermal storage. In Phase II of the program, prototype heat pump storage systems will be constructed and tested.

II. Background Information

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 relation freedom from hazards.

The reaction scheme is

$$\text{Salt}\cdot n\text{CH}_3\text{OH (solid)} \overset{T_2}{\rightleftarrows} \text{Salt (solid)} + n\text{CH}_3\text{OH (vapor)}$$

$$\text{CH}_3\text{OH (vapor)} \overset{T_1}{\rightleftarrows} \text{CH}_3\text{OH (liquid)}$$

In the storage mode, T_2 is the solar collection temperature, ca. 125°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. -20°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 de-methanolated salt, and a separate storage subsystem is not required.

III. Project Description

Phase I of this project, which is aimed at selecting one or more substrates suitable for heat pump use, has been broken down into six major tasks. A brief description of each of these tasks follows.

Task 1: Initial Selection of Substrates

Relatively few data are available in the literature on the reactions of CH_3OH vapor with inorganic salts. In Task 1, a number of inorganic salts will be screened using thermogravimetric analysis. By thermostatting a pool of CH_3OH at 15°C, the vapor pressure will be maintained at 0.1 atm, and the temperature of each salt will be cycled between 150°C and 25°C. In this way preliminary temperature-pressure-composition information will be obtained. The objective is to find salts that can take up a substantial amount of CH_3OH ($\geq$ 2 moles per mole of salt) when the temperature of the salt is ca. 65°C above the temperature of the CH_3OH pool. Salts selected after Task 1 screening will be examined in more detail in the subsequent Tasks.

Task 2: Pressure-Temperature-Composition Diagrams

For each salt, the solvate composition will be determined as a function of temperature and pressure. Temperatures will be varied in the range -30 to 150°C; pressures in the range 0.01 to 1 atm. Studies will be made by thermogravimetric analysis (TGA). The pressure-temperature-composition data will be used to derive enthalpies and entropies of reaction and will serve as a basis for quantitative (engineering) analysis and optimization.

Task 3: Gas-Salt Reaction Kinetics

The temperature increase or decrease rate will be varied to obtain quantitative estimates of gas-salt reaction kinetics. In suitable cases, the kinetics of complex formation and decomposition will be studied in more detail, using TGA with linear temperature scan and with a derivative computer. Rate equations, incorporating the effects of temperature, gas pressure, and solid-phase composition will be obtained.

Task 4: Heat-Transfer Coefficients

The rate of heat flow through the solid complexes will be measured using thermal cells. The influences of effective density, solid-phase composition, gas pressure, and mean temperature will be studied. Particular attention will be paid to the discontinuous changes in the heat-transfer coefficient that are expected to occur as different solid complexes are formed.

Task 5: Engineering Scoping and Economic Analysis

The thermodynamic and kinetic data obtained in the previous tasks will be used in scoping the system and obtaining estimates of cost for various storage configurations. Particular attention will be paid to the possibility of designing an economically feasible, long-term (seasonal) storage system.

Task 6: Side Reactions and Effects of Chemical Purity

Compounds will be checked for long-term stability and freedom from irreversible side reactions, as evidenced by hysteresis or irreproducibility in the TGA temperature-pressure-composition curves after the compounds have been subjected to accelerated aging at the highest temperature (150°C). The aged samples of solvate will be fully decomposed at higher temperatures, and the effluent gases analyzed for products from side reactions, using gas chromatography. Possible changes in kinetics due to sintering (decrease in specific surface area) will be examined, along with the potential effect of decrease in pore size due to particle decomposition. Such effects may be important to system performance after long-term cycling.

Since it is highly desirable to use industrial-grade chemicals in constructing thermal storage systems, the effect of purity will also be tested.

IV. Results

Task 1 is now essentially complete, and three salts that pass the initial screening have been selected for further study: $MgCl_2 \cdot 2CH_3OH$, $FeBr_2 \cdot 2CH_3OH$, and $CoBr_2 \cdot 2CH_3OH$. Data for 12 salts that react with CH_3OH vapor are shown in Table I; a number of other salts showed no appreciable reaction. In principle, the temperature of formation should equal the temperature of decomposition; the difference is due to the relatively rapid rate at which the temperature of the salt was varied. It is not immediately clear which of the two temperatures is closest to the true thermodynamic value; for screening purposes, we have conservatively chosen the formation temperature. Seven salts show evidence of compound formation at 80°C or above: $CoBr_2$, $FeBr_2$, $FeCl_2$, $MgCl_2$, $MnCl_2$, $MnBr_2$, and $NiCl_2$. However, the reaction rates of $FeCl_2$, $MnCl_2$, $MnBr_2$, and $NiCl_2$ appear quite slow, as can be seen by the large difference between formation and decomposition temperatures. Thus, these salts have not been selected for further study. $NiBr_2$ is still being investigated. $CaCl_2$ and $NiBr_2$ may be suitable for use when the evaporator temperature of the heat pump is $>0°C$.

V. Future Activities

It appears likely at this point that one or more salt substrates will be found that are suitable for use in a methanol-based system for solar thermal storage and heat pumping; $MgCl_2$ appears particularly promising. However, additional thermodynamic and kinetic data are required before engineering design can begin; in particular, thermal conductivity data are needed to design the salt-bed heat exchanger. The feasibility of any storage system depends on both cost and performance, and in the present system the heat exchanger promises to be an important fraction of the total system cost. Thus, a major effort is planned on heat exchanger design and analysis.

TABLE I

Salts that React with CH_3OH Vapor Equilibrated with Liquid at 15°C

			Temperature Range, °C	
Salt	Methanol, moles	Δmoles	Formation	Decomposition
$AlNH_3(SO_4)_2$	0.3		55	
$CaCl_2$	1.96		65-47	109-132
$Ca(NO_3)_2$	1.80		32	55
$CoBr_2$	3	0-1	82-73	113-132
		1-2	65-47	87-108
		2-3	45-38	65-80
$CoCl_2$	∿0.5			
$FeBr_2$	1.95	0-1	98-75	132-140
		1-2	72-55	101-115
$FeCl_2$	1.93	0-1	95-52	135-145
		1-2	32-26	80-95
$MgCl_2$	3.92	0-2	90-50	0-4 95-120
		2-4	50-30	
$MnCl_2$	1.91	0-1	82-55	140-178
		1-2	30-26.5	75-94
$MnBr_2$	1.87	0-1	80-55	130-159
		1-2	53-43	85-96
$NiCl_2$	>2		130-30	40-140
$NiBr_2$	>5		60-27	50-115

PROJECT SUMMARY

ORGANIZATION: General Electric Company
Corporate Research and Development

ADDRESS: P. O. Box 8
Schenectady, New York 12301

PROJECT TITLE: Closed Loop Chemical Systems for Energy Storage and Transmission (Chemical Heat Pipe)

PRINCIPAL INVESTIGATOR: Himanshu B. Vakil

TELEPHONE: (518) 385-8572

CONTRACT NO: EY-76-C-02-2676.*000

CONTRACT PERIOD 6/75-12/77

CONTRACT AMOUNT: $300,000

PROJECT GOALS:

The basic goal of the program was to identify the most promising options of the Chemical Heat Pipe (CHP) for the U.S. applications. This overall goal comprised several secondary objectives including evaluations of primary sources, alternate chemical systems and their technical feasibility, performance of the methane/steam and, to a lesser extent of benzene/hydrogen CHP systems, customer needs, and systems economics of the end use applications. Based on technical feasibilities of the available options, operating efficiencies, economics and market potentials, overall recommendations and priorities were determined as an input to future CHP programs.

PROJECT STATUS:

All the technical work on the project has been completed. The draft final report has been submitted to contract monitors (Sandia) and is currently in the process of being reviewed. The final report will be issued soon after the completion of the review process.

Background

The fundamental driving force to study novel forms of secondary energy carriers and transportation modes arises from several general needs for future energy management. Among these are the need to substitute current uses of prime fossil fuels by alternate sources such as nuclear and coal, the importance of energy conservation, and the motivation for achieving effective energy storage to cope with fluctuating demands.

There are several aspects in which the future energy sources and demands show a large mismatch: coal and nuclear plants are large, capital intensive, and remotely located; the demands for energy, on the other hand, require a supply in small sizes, in varying amounts at different times, and usually near populated areas. It is necessary, therefore, to find ways by which the primary energy can be converted to a secondary form that can be transported, stored, and distributed conveniently.

If economics of thermal energy are considered, one observes that the cost of heat at the nuclear or large coal plant is approximately \$1/GJ to \$2/GJ whereas the small industrial user often is prepared to pay up to \$6/GJ for process steam if he is prohibited (either by scarcity of natural gas or by a restriction on imported oil) from using oil or gas. The only current alternatives for a small process steam user (needing less than ∿200 MJ/s) are the use of electrode boiler at a steam cost of ∿\$9/GJ or of SNG-fired boiler at greater than \$6/GJ.

The principal rationale for the Chemical Heat Pipe program lies in the fact that it promises a new way of transporting relatively inexpensive thermal energy from a large central plant to many small users located in a radius of 200 km from the source and willing to pay a premium for the delivered thermal energy. If it can do so at an incremental cost of roughly \$3/GJ to \$5/GJ, then it may prove marginally profitable. If in addition, it can provide daily/weekly storage and extend the use of co-generation of electricity and heat to small industrial steam users, then it would make a valuable contribution towards improving the future energy management.

Chemical Heat Pipe (CHP)

The general concept of CHP is shown in Figure 1. The important elements of the concept are that the absorbed energy is converted to an increase in chemical enthalpy, the sensible heat in the reactor effluent is used to preheat the reactants in counter-current heat exchanger, and the transport and storage of energy takes place at ambient temperatures. In addition, by the choice of an intermediate chemical energy form that is lower in thermodynamic quality than that of the source, all of the primary energy can in principle be transported or stored just as if it were thermal in nature.

Chemical Reactions and Potential Sources

In spite of the fact that there are countless endothermic/exothermic chemical reactions that one could propose based on thermodynamics alone, our findings indicate that the constraints placed by the source temperatures and the requisite background of industrial technology to permit an operation at the enormous scale inherent in these applications result in an elimination of most of them. For high temperature sources ($T_{max} > 1000°K$) the methane-based CHP appears to be the best choice. Unfortunately, a coupling of steam-methane reforming reaction, which is the endothermic step, to either a coal-fired furnace or a high temperature solar cavity poses severe and, in our view, insurmountable problems. This leaves only the very high temperature gas-cooled reactor (e.g. the German Pebble Bed Reactor) as a suitable source. This PBR-based CHP is currently being pursued actively by the German PNP program. This high temperature chemical heat pipe (HTCHP) was the subject of a major part of our CHP effort in this contract.

Lower temperature sources such as the light water reactors, fossil steam boilers, liquid metal breeders, and solar furances are much more relevant to future CHP applications in the U.S. In this category, the most promising candidates appear to belong to a class of hydrogenation/dehydrogenation reactions - benzene/cyclohexane system being the most likely candidate among these. Unfortunately, the chemistry in this case is not as well proven and will require further work before a demonstration of successful cyclic operation can be undertaken.

High Temperature Chemical Heat Pipe (HTCHP)

The greatest asset of the methane-based HTCHP is the fact that both the endothermic and exothermic reactions have been demonstrated industrially - the former has been practiced for decades as steam-reforming of methane in fertilizer industries and in hydrogen production; the latter is the subject of considerable interest currently as the final step in coal conversion to SNG.

In view of the demonstrated cleanliness, as represented by the lack of significant byproduct formation, the technical feasibility of the HTCHP system appears to be reasonably well assured.

Our analyses of HTCHP technical performance has indicated that the overall energy efficiency can be quite high if reasonable care is exercised in achieving a good thermal exchange. Due to the necessity of cycling unreacted, excess H_2O the internal heat flows can be quite significant and play a dominant role in efficiency and, to a lesser extent, economics.

An important contribution of our study is the methodology of thermal histograms to analyze and optimize thermal exchanges amongst the various CHP streams and the associated power plant. A second important message from our analyses is the fact that a rigorous thermodynamic approach is not only useful but essential in optimizing the CHP design. In view of the lack of a unique definition of overall efficiency, particularly in systems like the CHP that involve inputs and outputs of various different forms of energy, the ambiguities inherent in popular definitions have been pointed out in the report. These difficulties notwithstanding, typical designs indicate that approximately 70% to 90% of the energy can be delivered for the end-use application. We consider this to be a highly acceptable performance.

The overall economics of HTCHP reflect the typical uncertainties of an unproven technology; however, we believe the numbers to be much more reliable than many other new and esoteric technologies that have been proposed. Typical designs lead to an incremental cost in transporting thermal energy over a distance of 160 km of approximately \$1/GJ - \$1.50/GJ. When one adds to this the cost of primary thermal energy from a PBR of \$2/GJ - a number that is at best marginally accurate - the total cost of delivered process steam appears quite attractive.

Investigations of end-use applications have revealed that the most favorable applications are for supplying baseload and intermittent uses of process steam and for combined electricity/process steam. Economics of on-site storage and baseload electrical transmission appear marginal. If sufficient credit can be taken for the distributed generation of peak electricity, then CHP may prove profitable in an all-utility application. By far the largest economic incentive appears to be in applications with combined heat/electricity delivery in situations where it would not otherwise be possible to use cheaper primary energy sources; an example may be a small intermittent user needing electricity and low-grade steam.

In conclusion, CHP applications are characterized by a high cost of the endothermic plant and the transport and a low cost of the exothermic plant. As a result, applications where the capacity factor is low at the source are not favored economically but those where the capacity factor is low at the end use location are highly favored.

Low Temperature Chemical Heat Pipe (LTCHP)

Based on the conclusions that the lower temperature CHP applications were of considerable importance in the future, and that the uncertainties of technical feasibility could only be resolved by a dedicated experimental project, it was decided to extend the HTCHP work to a LTCHP analysis based on the assumptions of a successful catalyst development. The objective was to find out whether the removal of technical barriers would result in favorable efficiencies and economics of LTCHP or not. Results from this extension indicate that with sources capable of providing energy at adequate temperatures (e.g., fossil fired boilers, LMFBR, and solar furnaces) the overall efficiency can be nearly as high as that in the case of HTCHP. For the base case design, the economics were somewhat more favorable than the HTCHP; this was primarily due to a lower cost of reactor materials, more efficient transport, and a reduced internal heat exchange. The overall conclusion was that the LTCHP would prove valuable if its technical feasibility can be experimentally demonstrated. The study also led to the formulation of the requirements of good LTCHP catalysts from the points of view of specificity, activity, and longevity.

Customer Analysis

The greatest disappointment in the course of this work arose in our attempts to obtain a detailed characterization of the Industrial Process Steam market to enable us to investigate the extent to which CHP could serve this sector. Unfortunately, the reported energy consumption data were too lacking in both consistency and detail to permit a breakdown by size, temperature, duty factor, and rough geographic distribution. An important recommendation resulting from our work was that a study aimed at obtaining a more detailed characterization of the process steam market, even if it has to be restricted to a specific location, be undertaken to aid not only the CHP application analyses but that for all proposed process delivery proposals.

Overall Conclusions

The CHP as a concept is judged by us to be novel, versatile, and highly useful for the U.S. energy future. It promises a whole new realm of applications aimed at fuel substitution, storage, and energy conservation. Getting down to the specifics, there are several avenues of future efforts that are attractive. Among these are attempts to resolve the gas-cooled reactor program for the U.S. so that the future likelihood of HTCHP can be better ascertained, to demonstrate the technical feasibility of LTCHP and its application to the most likely future energy sources, and to evaluate the viability of the open CHP concept based on coal gasification under current investigation internally at GE and with ERDA funding at IGT.

CHEMICAL HEAT PIPE (CHP) CONCEPT

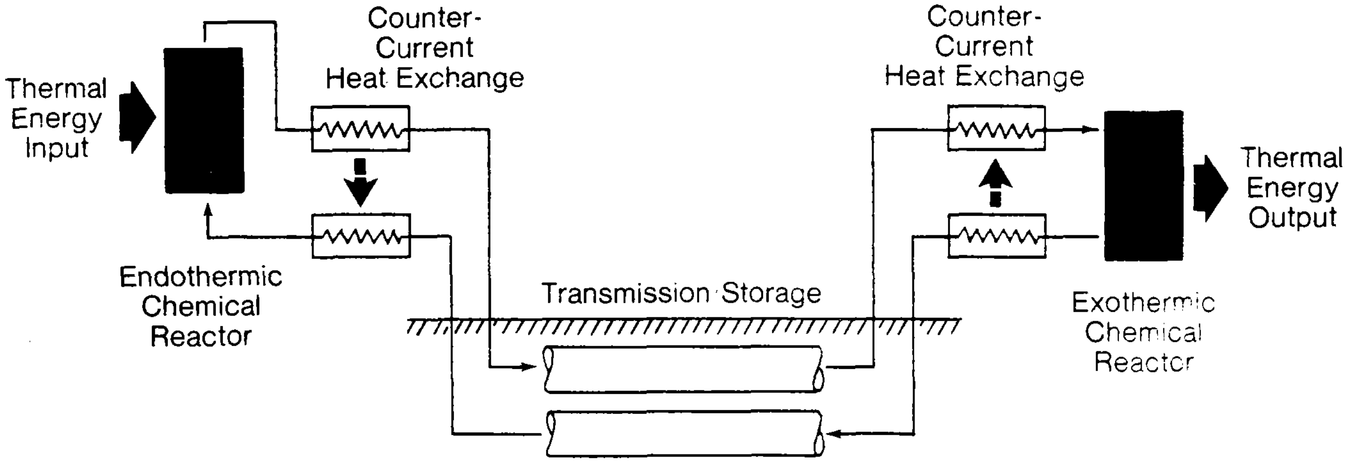


Figure 1 Chemical Heat Pipe Schematic

PROJECT SUMMARY

ORGANIZATION: General Electric Co., Energy Systems Programs Department

ADDRESS: Schenectady, New York 12345

PROJECT TITLE:	Duplex Steam Reformer	Alternate Catalyst
CONTRACT NO.:	EY-76-C-02-2841	EY-76-C-02-2926
CONTRACT PERIOD:	3 Dec. 75 - 30 Sept. 79	1 June 76 - 31 January 78
CONTRACT AMOUNT:	$976,663*	$69,469
PRINCIPAL INVESTIGATOR:	M.A. McDermott	M.A. McDermott
TELEPHONE:	518-385-5699	518-385-5699

*Jointly funded by ERDA Conservation and ERDA Nuclear.
Testing will be performed by KFA in Germany.

PROJECT GOALS:

Duplex Steam Reformer Design, develop fabrication techniques, fabricate, test and evaluate a duplex steam reformer tube which has potential use in conjunction with a high temperature heat source such as a high temperature gas-cooled reactor (HTGR). This is part of a GE-ERDA study to determine the potential use of HTGRs for process heat application in this Country and Germany.

Alternate Catalyst Develop and test a steam reformer catalyst which, when compared to conventional catalysts, reduces reformer costs, improves ease of installation and removal and increases catalyst life.

PROJECT STATUS:

The manufacturing feasibility of a duplex steam reformer tube has been successfully demonstrated. This technique consists of explosively expanding the inner tube into the outer tube. To successfully achieve the desired 0 to 3 mil radial gap between the tubes it is necessary to perform the expansion in two steps with an intermediate anneal. The next step in the program is fabrication of a 40-foot long tube for testing in the EVA facility in Germany. The estimated delivery date is early in 1979.

A catalyst design that would have replaced the conventional Raschig rings with a metal supported catalyst has been evaluated and it has been concluded that further development and testing are needed before fabrication of a full scale prototype is warranted. Consequently, the immediate contract efforts are directed towards reevaluating the incentives for developing a catalyst and the probability of successfully developing a catalyst that could be used for steam reforming.

I. PURPOSE

The duplex tube program, which is funded jointly by the Division of Nuclear Research and Applications and the Division of Energy Storage, and the alternate catalyst program are part of a GE-ERDA-KFA international program to study the use of a high temperature gas reactor for industrial process heat applications. The successful development of a duplex reformer tube will eliminate the need for a costly and complicated intermediate heat exchanger (IHX). The two walls of the duplex tube provide the required double isolation between the reformer process gas and the potentially radioactive reactor coolant. Replacing the IHX with a duplex tube will reduce the cost of construction of a 3,000 MW plant by an estimated 10%, increase the overall efficiency by an estimated 1.5%, and reduce the required temperature of the reactor by 50°F. The alternate catalyst program is intended to reduce the fabrication and operating costs of a steam reformer by developing a catalyst that can be readily replaced and reduces the diameter of the steam reformer tube. This program, which is currently the only demonstration program funded by the Thermal Energy Storage Branch, is done in cooperation with the German government and information obtained from this program will be shared with the German government.

II. BACKGROUND INFORMATION

The steam reforming process, which is a well developed 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 which has been studied by General Electric and is discussed in the paper by Dr. H.B. Vakil. 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-Tropsch Synthesis
- Oxosynthesis

Recognizing the potential advantages of the duplex tube, GE proposed a program for its commercialization and in 1975 ERDA awarded this contract to the General Electric Company. The duplex tube steam reformer (DSR) program is divided into four sequential phases:

Phase 1 - Study and Planning

Phase 2 - Test Section Procurement

Phase 3 - Steam Reformer Test & Performance Evaluation

Phase 4 - Steam Reformer Metal Evaluation

Phase 1 of this contract was completed in May 1976 and the results are described in Reference 1. In this Reference the performance characteristics of a Duplex Steam Reformer-HTGR application are reported and the recommendation made that Incoloy 800H be the material used in the fabrication of the duplex tubes. The recommendation on material 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 ID x 12 meters long) and thickness lead to the segmentation of Phase 2 into two parts. In Phase 2A the objective was to demonstrate the feasibility of kinetically forming the duplex steam reformer tubes. This procedure was successfully demonstrated by Foster Wheeler Development Corporation (FWDC) under subcontract to GE and a report describing this work was submitted in July 1977. 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.

III. PROJECT DESCRIPTION

Figure 1 compares helium heated and conventional reformers and Figure 2 shows the design of the DSR tube to be 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 gases. The tube will be 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.

A separate task in the duplex tube program is investigation of the licensability of the duplex tube. A preliminary licensing submittal will be submitted to the US Nuclear Regulatory Council to obtain their concerns on licensing a nuclear reactor using a duplex tube rather than an intermediate heat exchanger.

The alternate catalyst concept that has been under study is shown schematically in Figure 4. The catalyst is contained in the fins attached to the center tube. This design can be accommodated in smaller diameter tubes than the conventional Raschig ring-type catalyst. It also can be quickly removed and replaced, and has the potential for in situ activation. The catalyst development is independent of the duplex tube development. It could be used in a duplex or a single walled tube.

IV. RESULTS

The mechanical and thermal analyses of the duplex tube are complete. The heat transfer (and chemical performance) of the duplex tube is similar to that of a single walled tube. The gap between the tubes contributes 5% of the overall thermal resistance of the tube. Structural analysis shows that thermal and pressure stresses are acceptable and the mechanical design should meet the 100,000 hour goal.

In the duplex tube hydrogen and tritium permeation rates are predicted to be significantly reduced from those in a single tube if there is an oxide film on the walls at the tube gap. This causes a problem in the preparations for the EVA test where permeation rates will be measured since the film on the walls for the test should be typical of that expected in the tube after lengthy operation. During operation the gap will fill with hydrogen from the process gas and this is expected to slowly eliminate any oxide films that are placed on the tubes. This area is under investigation and must be resolved before the tubes are fabricated. Hydrogen permeation into the gap will have a maximum value of 10 to 100 liters per day per tube.

The 1/16" grooves on the outer wall of the inner tube, which ensure free flow of gases along the length of the tube, were formed by a grooving tool attached to a guided high speed air grinder in the demonstration phase. This is not a satisfactory process for commercial application and alternatives are being investigated.

The EVA facility where the duplex tube will be tested is a 1MW electrically heated helium loop. This facility will be extended to become the EVA ADAM facility which will include the methanation portion of a chemical heat pipe. The testing of the duplex tube is currently scheduled early in 1979 after the first EVA ADAM tests. If the duplex tube is not ready to support the planned schedule the next window in the facility availability will be several months later.

The alternate catalyst that was under development has been evaluated and it has been concluded that more experimental data are needed before a full scale prototype should be manufactured and tested. Such additional testing is beyond the scope of the current contract. The major technical concern is the lifetime characteristics of the alternate catalyst--sufficient data are not available to identify whether or not catalyst sintering would occur. Sintering would reduce the effective catalyst surface area and result in a reduction in the catalyst effectiveness.

The development of an alternate catalyst and the duplex steam reformer will enhance the economic viability of the HTGR as an industrial process heat source. The duplex tube can eliminate an intermediate heat exchanger which reduces the total plant capital costs by 10% and increases overall efficiency by 1.5%. The reduced reformer tube diameter associated with the finned catalyst will also reduce plant capital costs by approximately 10%. In addition, the estimated costs associated with a 3000 Mwth reactor downtime are ~$250,000/day and this provides an added incentive to develop a catalyst that can be readily replaced.

V. FUTURE ACTIVITIES

The future activities with the duplex steam reformer in this Country will depend on the future of the HTGR and the views of the Nuclear Regulatory Commission on the licensability of the duplex tube. If the LMFBR is developed the duplex tube may also have potential application in eliminating an intermediate heat exchanger in steam generation.

The timetable for development and testing of an alternate catalyst is dependent on the timetable for development of gas-cooled nuclear reactors. However, many incentives exist for the development of an improved catalyst, and because this influences the cost and size of steam reformers, this program should be continued so that the economics associated with supplying industrial users with nuclear process heat are properly evaluated.

REFERENCES

1. ESTD 76-06 "Design of a Helium Heated Duplex-Tube Steam-Methane Reformer" J.A. Bond et al. June 1976.

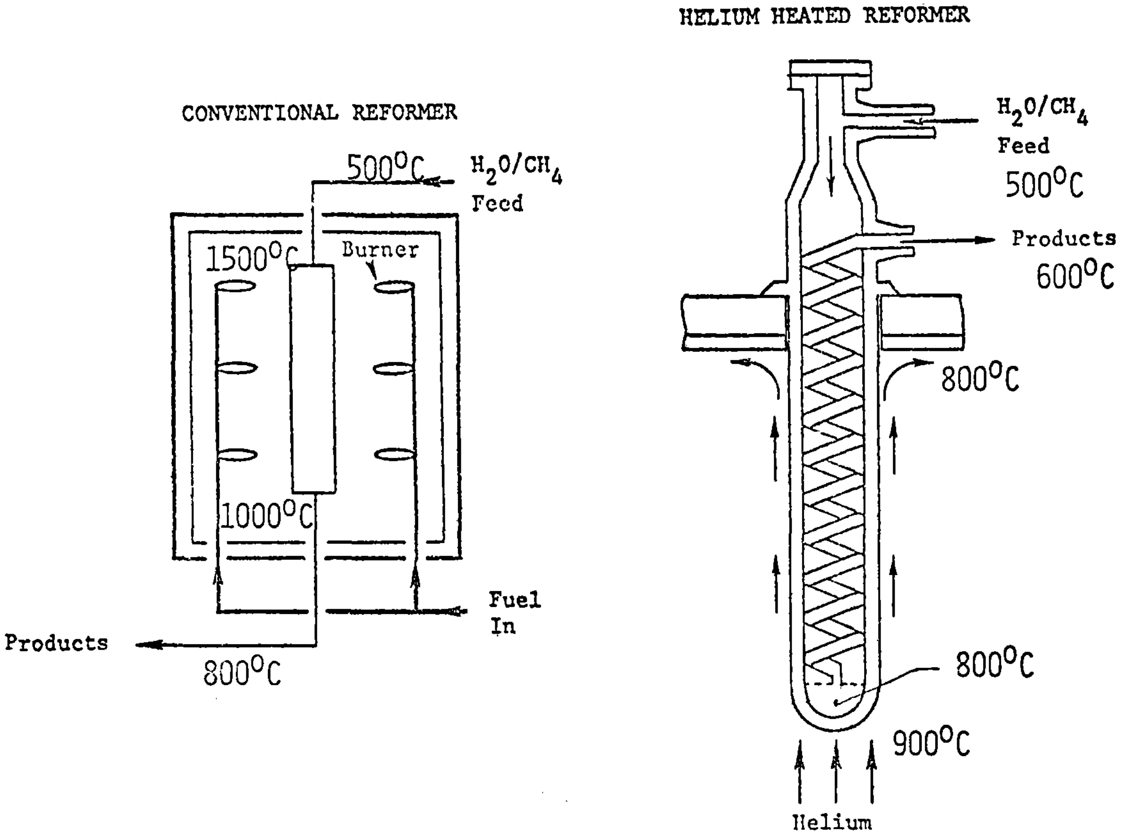
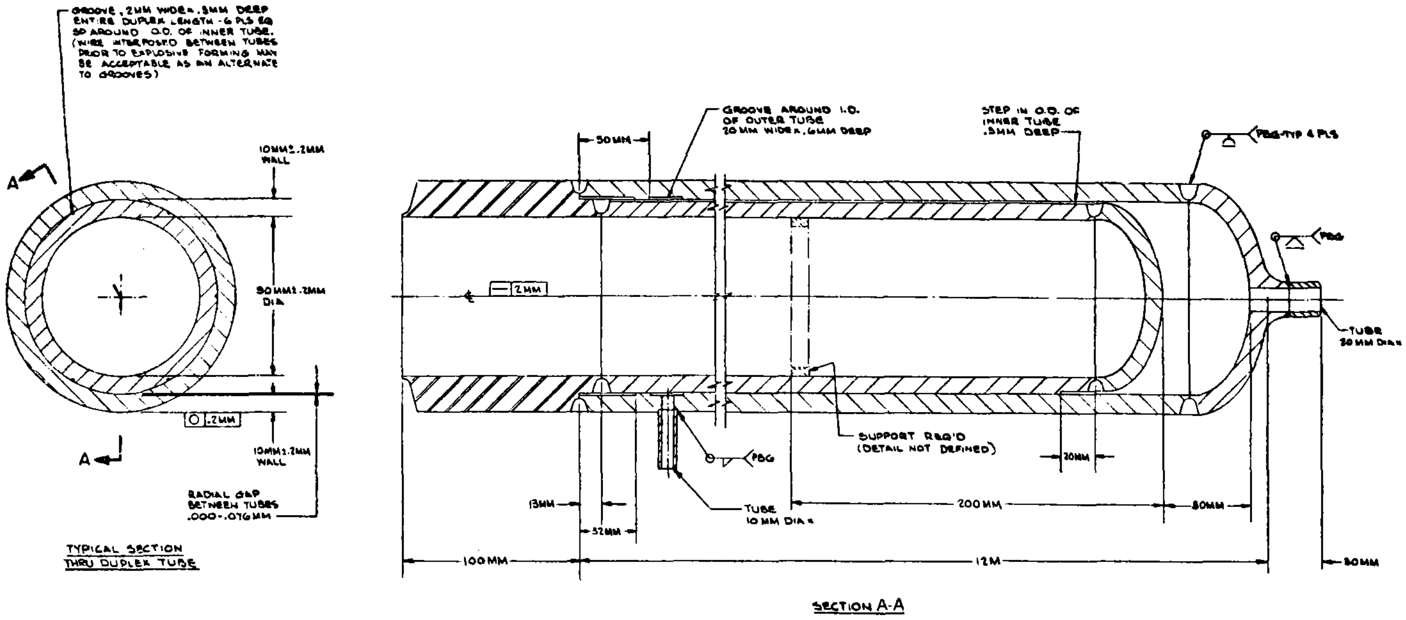


Figure 1. Conventional and Helium Heated Reformer Comparison

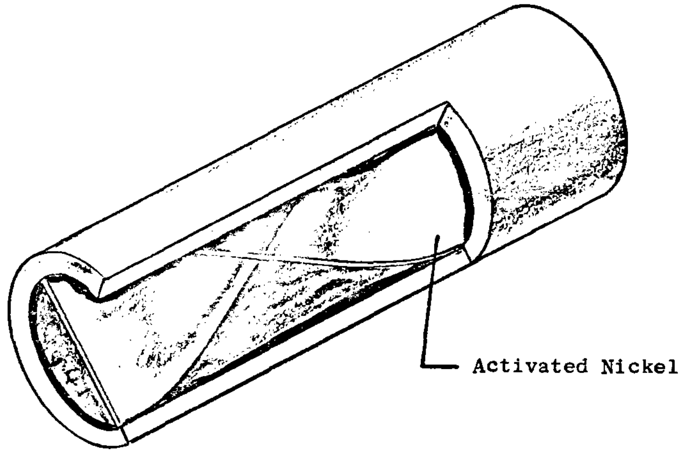


DUPLEX TUBE (Dwg. 101D9604)

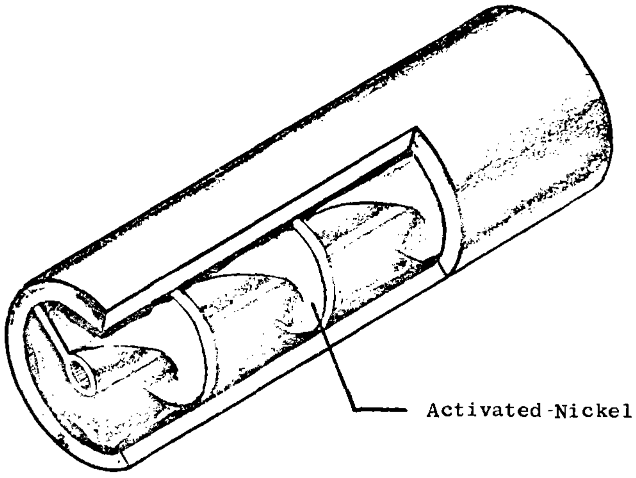
Figure 2. Duplex Tube Design

Helium Side	Metric	English
Inlet Temperature	950°C	1742°F
Outlet Temperature	700°C	1292°F
Inlet Pressure	39.4 b	571 psia
Max. Pressure Drop	.24 b	3.5 psi
Mass Flow Rate	0.202 Kg/s	0.446 lbm/s
Process Side		
Inlet Temperature	450°C	842°F
Reforming Temperature	825°C	1517°F
Outlet Temperature	600°C	1112°F
Outlet Pressure	40 b	580 psia
Max. Pressure Drop	6 b	87 psi
Methane Inlet Flow Rate	98 Kg/hr	216 lbm/hr
Steam Inlet Flow Rate	321 Kg/hr	709 lbm/hr
Duplex Reformer Tube Data		
Min. Tube ID	90 mm	3.54 inch
Tube Length	12 m	39 feet

Figure 3. Duplex Steam Reformer Operating Conditions



Twisted Tape



Helical Vane

Figure 4. Turbulator Catalyst Concepts.

PROJECT SUMMARY

ORGANIZATION: Institute of Gas Technology

ADDRESS: IIT Center, 3424 S. State St., Chicago, Ill. 60616

PROJECT TITLE: Transmission of Energy by Open-Loop Chemical Energy Pipelines

PRINCIPAL INVESTIGATOR: Nathaniel R. Baker TELEPHONE NO.: 312-567-3929

CONTRACT NO.: 87-9181 CONTRACT PERIOD: May 1977 - Jan. 1978

CONTRACT AMOUNT: ERDA $96,400
OTHER - -

PROJECT GOALS:

The primary objective of this program is to evaluate the technical feasibility and, in a preliminary fashion, the economic viability of transmitting and storing energy by an open-loop modification of the reversible chemical energy pipeline system known as EVA/ADAM. The work designed to achieve this objective includes –

- The preliminary design of a nuclear (HTGR) and methane-based open-loop system (Task 1)
- Evaluation of energy sources as alternatives to those in the preliminary design (e.g., coal gasification and HTGR/LNG) (Task 2)
- Assessment of the feasibility of using existing natural gas pipelines and storage systems for the synthesis gas (Task 3)
- Assessment of existing methanation technologies and interchangeability of the SNG with natural gas (Task 4)
- Evaluation of the various alternative energy end-uses for heat, SNG, and electricity (Task 5)
- Development of two conceptual designs and evaluation of their economics and environmental impacts (Task 6).

PROJECT STATUS:

The preliminary base-case design (Task 1) has been completed and forms the main body of the first quarterly report for the project issued in August. We are currently expending most of our effort in Tasks 2 through 4. Only preliminary work has been carried out in the remaining two tasks.

I. Purpose

The chemical energy pipeline is a method of converting thermal energy from alternative heat sources, such as nuclear, solar, or coal, to a gaseous chemical form that allows this energy to be transmitted by pipeline and stored for use at some distant location. It is based on the 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.

II. Background Information

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 combine in an endothermic reaction:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad (1)$$

At the other end of the pipeline, the reverse exothermic reaction occurs, producing heat and methane; i.e., the reformed gas (synthesis gas) is methanated over a suitable catalyst at approximately 700°K.

$$3H_2 + CO \rightleftarrows CH_4 + H_2O \qquad (2)$$

Simultaneously with these reactions, both the forward and reverse shift reactions take place:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (3)$$

III. Project Description

At IGT, we are assessing the possibilities of opening the loop, that is, supplying hydrocarbons to the reformer at the heat source and producing both heat and substitute natural gas (SNG) for end use at the methanator location. We are evaluating three open-loop systems. The first, which forms our base case, is an HTGR/reformer fed by natural gas, a 100-mile pipeline, and a methanator producing steam and SNG that is available for use in the existing natural gas distribution system. In what we call our 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 case, the HTGR/reformer is coupled to a liquefied natural gas (LNG) receiving terminal, and the whole complex is sited on a floating platform 3 miles or less off the U.S. coast. An undersea pipeline connects the complex to the shore and the remaining system components.

By implication we consider that the closed-loop chemical energy pipeline is a far-term system and that our near- and mid-term cases are transitional energy concepts because they allow the transition from the present fossil fuel system to a nonfossil energy transport system.

IV. Results

Our work on the base case, completed in July, involved the matching of system components taken from other studies. For example, the 3000-MW_t HTGR/steam reformer came from a study by General Atomic,[1] whereas the pipeline and methanator information was obtained in other IGT studies.[2,3] All had to be slightly modified to suit our less-than-optimal system.

No major technical problems were found through assembling the system conceptually. In order to establish a cost for the product heat, we gathered costing information on the components, which is summarized in Table 1.

Table 1. ESTIMATED BASE-CASE COSTS

	$ Million
Nuclear/Steam Reforming Plant[1]	
Total Capital Cost	626.56
Operation and Maintenance	30.6 /year
Fuel	41.957/year
Pipeline	
Total Capital Cost	121.3
Operation and Maintenance	1.4/year
Fuel	10.4/year
Methanation Plant[3]	
Total Capital Cost	283.9
Operation and Maintenance	28.3/year

Using a utility financing basis, the open-loop base case produced 587°K steam at a cost of 2.0¢/kWhr$_t$. We then extended the pipeline distance to 400 miles, which increased the cost only two-tenths of a cent. Shown in Figure 1 are the costs for pipeline distances between 40 and 400 miles. Sensitivity to the capitalization ratio was also determined by changing the incremental debt financing ratio of 75% to an industry-imbedded average ratio of 60%. The resulting changes in cost are represented by the dashed line in Figure 1.

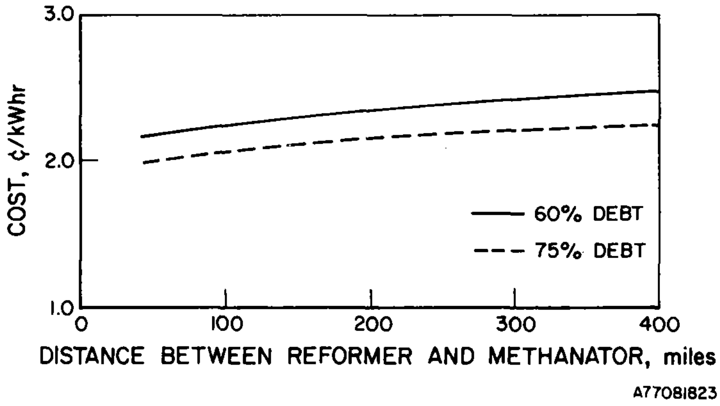


Figure 1. COST OF THERMAL ENERGY AS A FUNCTION OF PIPELINE LENGTH

Based on this analysis, it seems possible, at least from an economic viewpoint, to have the heat source sited remotely from the methanator.

Our work on the remaining tasks is in progress and is not at a stage, as of this meeting, for which firm results may be stated. We feel, however, that the following brief description of the areas we are investigating may be helpful.

A. Near-Term Case

Our work on the near-term case is primarily centered around the Koppers-Totzek and U-GAS® gasification processes. We are interested in these schemes because they are capable of being oxygen blown, they produce essentially no methane, and information is readily available for different types of feed coal. (Both nitrogen, from an air-blown process, and methane lower the energy density of the syngas.) We are sizing the plant on the same scale as most current gasification studies, i.e., 250 billion Btu/day, and are also reviewing in situ gasification.

B. Mid-Term Case

We are currently working out the design of a floating 3000-MW_t VHTR-steam reformer-LNG terminal for the mid-term case. Previous reactor studies have used smaller and/or lighter reactors. Thus we are trying to produce a design that is small and light enough to make this concept feasible. We have gathered information on LNG compositions in order to predict reformer operation. Two seawater desalination processes are being evaluated for integration into the system. Using IGT-developed computer programs, we have been seeking an optimal overall system efficiency by varying the steam reformer operating conditions, e.g., water to hydrocarbon ratio, temperature and pressure.

C. Use of Existing Gas Storage and Pipelines

Our work on the use of the existing gas storage and pipeline system for the synthesis gas has centered on the interaction of the synthesis gas with current pipeline materials, a preliminary view of compressor characteristics, and synthesis gas storage techniques, both above and below ground. In dealing with pipeline materials, we have been primarily concerned with hydrogen embrittlement, corrosion, and the potential for metal carbonyl formation. We are also evaluating the use and required conversion of existing natural gas pipelines to transport synthesis gas. In this regard, we have found a great diversity in pipeline capacity, number and diameter of parallel pipelines, pressures, and distances between compressor stations. Our goal is to arrive at some means of determining which natural gas systems may be used for our design.

D. Methanation

We are in the process of reviewing over 400 references on methanation systems, 12 commercial methanation process schemes, and most of the available methanation catalysts, of which four have been identified for further study. We plan to design methanator systems to the stage for which reasonable cost information is attainable. Our work on the quality of the water produced during methanation has centered on the formation of by-product impurities, such as acetone and methanol. Proper choice of operating conditions and catalyst should eliminate or minimize this potential problem.

E. SNG Interchangeability

Using in-house computer programs, we can predict the interchangeability (i.e., suitability for use in existing appliances without modification) of the product SNG with the natural gas types currently distributed. Natural gas composition varies with location, and exact interchangeability limits will depend on which natural gas is being supplemented or replaced.

F. Institutional, Safety, and Environmental Problems

We have reviewed the applicable Federal pipeline regulations on corrosion and odorization. Our synthesis gas pipelines will probably require corrosion monitoring, but may not require odorization, because the pipelines will probably traverse areas where it is not required.

The problem of water supply for the coal gasification plant is enormous. Water removal from the Great Lakes is regulated on a total-gallon-per-year basis; groundwater (subject to annual runoff) and water removed from rivers are subject to the Common Law of Water Rights. Since the methanator (where water is produced) may be far removed from where the process water is consumed, there is no assurance that water taken from any source will be returned to its original system.

V. Future Activities

In addition to the completion of the aforementioned areas of study, we will complete an analysis of the product energy and SNG end uses. In particular, we will be looking at time and location energy-use profiles for hot water, steam, process heat, and electricity generation in various applications.

The final task of this study will be to synthesize designs for the two specific cases, i.e., the near- and mid-term, including the pipelines, methanators, and end-use applications and products. These two designs will represent promising applications of the open-loop chemical energy pipeline. We will also evaluate the costs of such a system and assess, in a preliminary fashion, the expected environmental impact. We are anticipating that the final report will be issued in February.

References

1. General Atomic, "Process Heat Engineering Design Study for Very High Temperature Reactors," Report No. GA-A13801, July 1976.
2. Ingersol-Rand, private communication of August 1977.
3. Ralph M. Parsons Co., private communication of August 1977.

PROJECT SUMMARY

ORGANIZATION: Lawrence Berkeley Laboratory

ADDRESS: University of California, Berkeley, CA 94720

PROJECT TITLE: The Chemical Storage of Thermal Energy

PRINCIPAL INVESTIGATORS:	Alan S. Foss Scott Lynn	TELEPHONE NO.	415-642-4526 415-642-1634
CONTRACT NUMBER:	CS-EG-2184 ERDA	CONTRACT PERIOD:	10/1/76 - 9/30/77
CONTRACT AMOUNT:	$88,000		

PROJECT GOALS:

Processes that employ a heat-absorbing, heat-releasing reversible chemical reaction are being investigated for the storage of heat from high temperature nuclear power reactors and solar central receivers. Two chemical reactions of potential promise now under study are:

$$2\ SO_3 \rightleftharpoons 2\ SO_2 + O_2, \quad \Delta H = 47.0\ \text{kcal}$$

$$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2, \quad \Delta H = 49.4\ \text{kcal}$$

Heat absorption at about 800°C is necessary to drive both reactions to the right; heat liberation occurs for both by reaction to the left at 400°-600°C, a temperature range suitable as a heat source for modern steam cycle power generation.

The major objective of this work is to synthesize and evaluate technically feasible flowsheets for heat-storage processes employing these two reactions. The synthesis effort seeks process configurations that promise high energy efficiency. The evaluations to be carried out involve complete material and heat balances, equipment sizing and cost estimation, comparisons between the two chemical systems and comparisons between chemical storage and sensible or latent heat storage.

PROJECT STATUS:

An initial study of the sulfur oxide system applied to energy storage for a nuclear reactor has been completed--

> Bhakta, Mukund L. "Chemical Storage of Thermal Energy using the SO_3-SO_2-O_2 System" M.S. Thesis, U.C. Berkeley (1976)

A similar study of the methane system is nearing completion. The adaptation of the sulfur oxide system to a central solar receiver was discussed in a recent paper--

> Dayan, J., A.S. Foss and S. Lynn, "Evaluation of a Chemical Heat Storage System for a Solar Steam Power Plant", presented at 12th Annual IECEC Meeting, Washington, D.C., August 31, 1977.

The study of the comparison between chemical storage systems and sensible and latent heat systems is continuing.

I. PURPOSE:

Solar electric power plants will need some means of heat storage to permit operation during momentary interruptions in sunlight and during night hours. Perhaps the simplest storage device utilizes sensible heat, as when a checkerwork of brick is alternately heated and cooled. More complicated is the use of the latent heat of fusion of an appropriate substance that melts and solidifies in the temperature range of interest. The use of a reversible chemical reaction is potentially attractive because of the high energy per unit mass that can be stored and because storage is at ambient temperature so that no energy dissipation occurs. On the other hand, chemical systems suffer from the disadvantages that relatively complex reaction systems must be used and that one or more of the reaction constituents is usually a noncondensible gas. Evaluation of suitable candidate systems necessitates a fairly detailed engineering and economic analysis of each of the candidates before one or more can be shown to have clear cut advantages relative to the others. A major objective of this work is the synthesis of a process configuration by means of which a chemical storage system can be efficiently integrated with the central receiver and with the steam power cycle as well. The development here shows that, to achieve effective utilization of heat, the storage system must be coordinated with a solar steam power cycle operating in parallel. Major questions thus involve the relative sizes (capacities) of the steam and storage systems and the overall plant efficiency that can be expected under various process configurations and operating conditions.

II. BACKGROUND INFORMATION:

The use of reversible chemical reactions as a means for thermal storage and energy transmission has been suggested by Chubb [1], Kugeler [2], Vakil and Kosky [3], and other workers. The sulfur oxide reaction has been proposed by Schmidt and Lowe [4] for heat storage in a solar electric power plant using gas turbines in a Brayton cycle, in contrast to the use of conventional steam turbines suggested in the present study.

The central receiver in which heat is to be absorbed by the sulfur oxide system was assumed to be essentially identical to the design proposed by the Boeing Company for a closed helium cycle power plant [5,6]. This receiver is equipped with banks of tubes 9.5 m long and is designed to absorb 230 MW_t.

The means of electric power generation was chosen to be a conventional high pressure (167 bar, 540°C or 2400 psig, 1000°F) steam turbine plant of the type used in commercial fossil-fuel power plants. Ambient conditions important to the operation of the steam cycle were assumed to be typical of those in a desert location.

During the day steam is generated in ERDA central receiver solar power plant [7]. At night steam is produced from heat liberated by the catalytic oxidation of SO_2 in a process similar to the one used for commercial sulfuric acid production.

The choices of standard equipment and conditions were made with the intent of minimizing effort needed for the development of new technologies.

III. PROJECT DESCRIPTION:

Technically feasible flowsheets are being developed in which each of the energy storage systems mentioned above is incorporated in turn. Although no rigorous optimization is being attempted, in each case an attempt is being made to maximize the energy efficiency of the process. These flowsheets will be compared on the basis of cost and energy efficiency at the conclusion of the project. By making all duties and design bases essentially identical, an accurate comparison of the relative merits of the different systems is expected.

IV. RESULTS

Process flowsheets for both the sulfur oxide and methane systems have been investigated for heat storage in nuclear-fueled power plants (HTGR). Application of the sulfur-oxide storage system to central-receiver solar power plants has also been studied. This work has concentrated on the development of storage process configurations and their integration with the steam cycle in a manner that maximizes the overall heat efficiencies.

A "first-law" efficiency in the HTGR case of about 75% can be achieved by a sulfur-oxide system coordinated with a conventional steam power plant if the ratio of heat inputs is: steam plant/storage system = 2/1. An even higher ratio (∿4/1) is necessary to maximize the use of low-temperature heat from the storage system in preheating of boiler feed in the steam cycle. Further integration of the storage and power generation systems involves the use of a 200-psi steam bleed from the intermediate-pressure turbine to vaporize the SO_3. The efficiency of a similar but uncoordinated sulfur-oxide storage system is substantially lower, about 50%. A 24-hour average "second-law" efficiency may be obtained by running the electrical energy output over off-peak, peak, and normal periods and comparing with the total thermal energy input. For the coordinated system, for which the three operating periods were 8 hours each, this efficiency was about 42% and the ratio of peak power to off-peak power output was about 2.4.

A simplified sketch of a flowsheet for this coordinated system is given in Figure 1. Major features include operation of the heat-absorption step at 40 atmospheres and operation of the heat-release step at 10 atmospheres. These conditions enhance heat economy, help reduce equipment size, and allow the pumping of liquids only. The coordination involves SO_3 vaporization by 200-psi steam and the preheating of boiler feed water in both the heat-absorption and heat-release steps. Estimation of the equipment costs for such a system is still in progress.

A sulfur-oxide storage system for a solar power plant needs about a 3/1 ratio of steam plant/storage system charge rate to effectively recover the low-temperature heat by preheating boiler feed water. The overall plant "second-law" efficiency (electrical output/unit thermal input) is about 35% in that case. The efficiency is lower in solar plants than in nuclear plants because in the former the heat source is operative only one-third of the day and the turbine exhaust temperatures are much higher due to the high ambient temperature in the desert.

In preliminary studies of the methane system applied to a HTGR, only a 2.7/1 ratio of steam plant/storage charge rate is found necessary. This improvement results from the fact that a smaller quantity of low-temperature heat is involved in this chemical system. The 24-hour "second-law" efficiency for this system is about 43%.

In all these evaluations, steam generation conditions have been taken to be 1000°F and 3000 psi; these permit turbine operation at the standard value of 2400 psi. One stage of reheat to 1000°F has also been incorporated.

V. FUTURE ACTIVITIES:

Comparison of Storage Systems for Solar Electric Power Plants.

The work to date has concentrated on the process design and operating details of each of two chemical storage systems (the sulfur-oxide and methane systems). One major effort for the coming year will be the comparison of the technical features and economics of these two systems for solar heat storage. Points for comparison include the ease of incorporation of the endothermic reactors into the central receiver system, integration of the exothermic reactors with the steam generation system, degrees of interdependence or independence of the storage system on power plants operating in parallel with storage systems, efficiency differences related to the intrinsic chemical and thermodynamic properties of the chemical reactions, ease of storage of the gases and liquids, materials problems, and strengths and weaknesses of the systems when operating under diurnal cycles.

Because sensible heat storage systems seem to be a strong competitor of chemical storage systems for solar power plants, it is desirable to compare system costs of the two. It is essential that this be done on a common basis, else the conclusions concerning the merits of one system relative to the other become clouded. Use of a system evaluation made by one study group for comparison with the evaluation of another system made by a second group is risky owing to inevitable differences in assumptions, factors considered, and cost estimations. We therefore plan to make this comparison for the two types of systems using identical process conditions and estimating methods.

The cost estimates for the sensible heat system can be made with essentially no new basic investigation of such systems. The recent study of the Boeing Co. (Report EY-76-C-03-1300) proposes what appears to be an applicable process, and it will be adopted as the basic process for the comparison. However, it is necessary to interface the Boeing design for sensible heat storage with a steam-cycle power generation system so that it can be compared with the chemical energy storage system, which also employs steam generation.

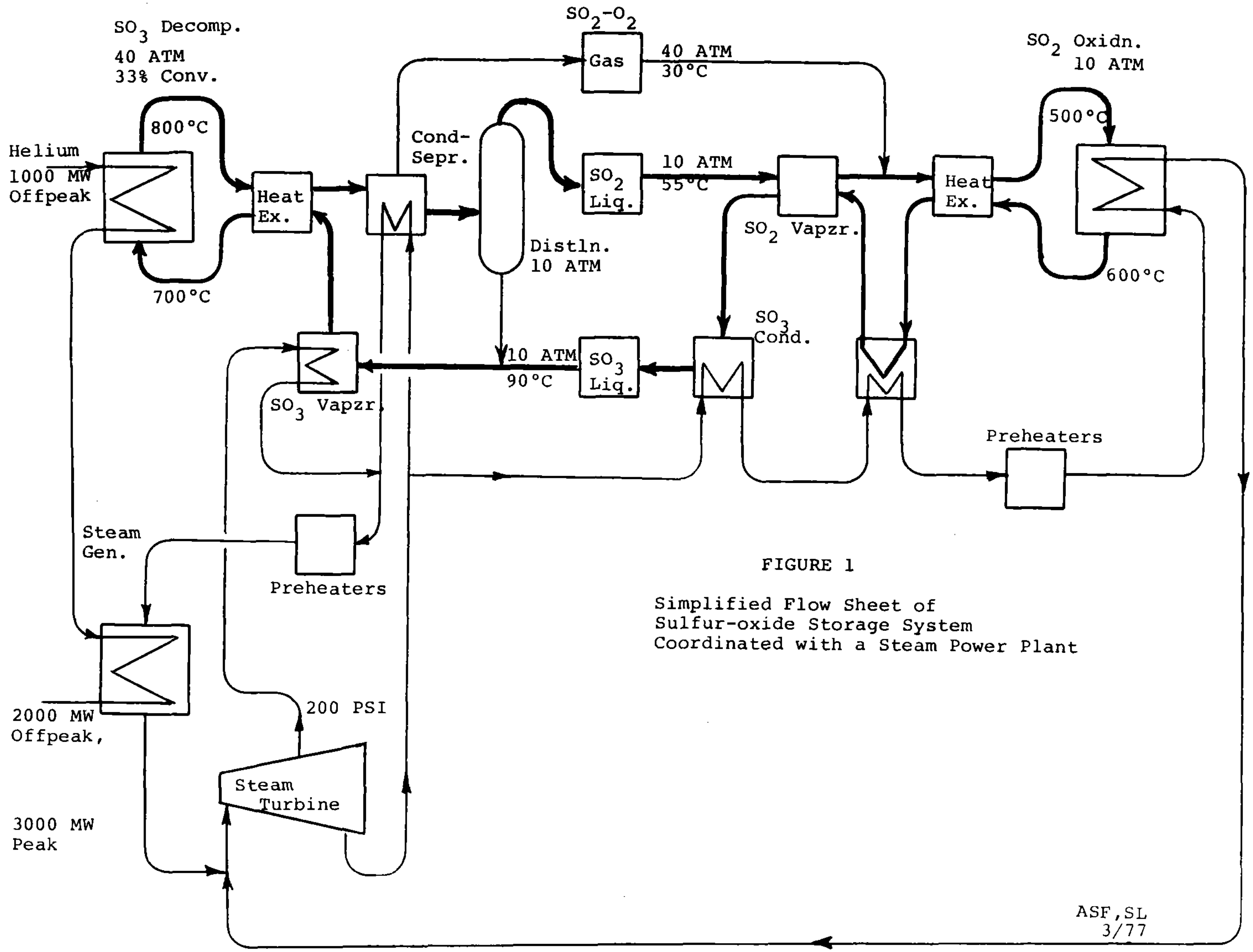


FIGURE 1

Simplified Flow Sheet of
Sulfur-oxide Storage System
Coordinated with a Steam Power Plant

ASF,SL
3/77

Literature Cited

1. Chubb, T.A., "Analysis of Gas Dissociation Solar Thermal Power System," Solar Energy 17, 129-136 (1975).

2. Kugeler, K., Kugeler, M., Niessen, H.F. and Hammelmann, K.H., "Steam Reformers Heated by Helium From High Temperature Reactors," Nuc. Eng. & Des. 34 No. 1, 129 (1975).

3. Vakil, H.B. and Kosky, P.G., "Design Analysis of a Methane Based Chemical Heat Pipe," Proc. Eleventh IECE Conf., 659-664, South Lake Tahoe, Sept. 12-17, 1976.

4. Schmidt, E.W. and Lowe, P.A., "Thermochemical Energy Storage Systems," ibid, 665-672.

5. Gintz, J.R., "Closed Cycle, High-Temperature Central Receiver Concept for Solar Electric Power," Boeing Eng. & Cons. Report for EPRI, NTIS PB-254-399, 1976.

6. Gintz, J.R. and J.E. Cummings, ibid, Electric Power Research Inst. (EPRI) Report No. SY 32, Feb. 1976.

7. Martin Marietta Co., "Central Receiver Solar Thermal Power System, Phase 1," Report for ERDA, 1976.

PROJECT SUMMARY

Organization: Martin Marietta Corporation
Denver Division

Address: P. O. Box 179
Denver, Colorado 80201

Project Title: Thermochemical Energy Storage Systems

Principal Investigator: F. A. Jaeger (303) 979-7000

Technical Director: M. T. Howerton

Contract No.: EY-76-C-03-1229

Contract Period: February through September 1977

Contract Amount: ERDA $243,824

Project Goals:

a. To demonstrate the technical feasibility of using paired, ammoniated salts for energy storage systems.

b. To obtain kinetic and physical properties data on various ammoniated salts.

c. To demonstrate reversibility and repeatability of the reactions over a number of cycles.

d. To develop a computer simulation of an ammoniated salt reactor.

e. To compare the cost of an ammoniated salt storage system with more conventional systems in a power plant application.

Project Status:

All effort on the present contract has been completed. The final report is being reviewed.

I. PURPOSE

The main objective of this program is to investigate the technical and economic feasibility of using paired, ammoniated salts for thermal energy storage.

II. BACKGROUND

This energy storage system is based on a pair of reversible ammoniated salt reactions; one reaction operates at an elevated temperature and the other reaction operates at a lower temperature which could be near-ambient. During operation the two reactions are at essentially the same pressure in the range between 0.5 and 3 atmospheres. Because this reversible system always operates close to equilibrium and has no moving parts, it has all of the characteristics of a reversible heat pump and possesses an efficiency close to that of the theoretical Carnot cycle.

In the charge mode, the high-temperature reaction accepts Q1 units of thermal energy at an elevated temperature T1 which endothermically decomposes the ammoniated salt and transfers ammonia gas to the low-temperature reactor where it reacts at near-ambient temperature T2 and generates a quantity of thermal energy Q2. Because the reactions are operating close to equilibrium conditions the Carnot cycle relation $Q2/Q1 = T2/T1$ is followed.

In the discharge mode, Q2 units of thermal energy are added to the low-temperature reactor which decomposes the ammoniated salt and transfers ammonia gas back to the high-temperature reactor where it reacts exothermically to regenerate the original Q1 units of high-temperature energy at the original temperature T1.

The difference between Q1 and Q2 is stored as chemical energy in the system which is equivalent to the work produced by a reversible heat engine or absorbed by a reversible heat pump. Because the stored chemical energy is temperature-independent and because no thermal energy is stored at elevated temperatures, thermal losses to the environment can be made negligible.

III. PROJECT DESCRIPTION

The program is divided into three major areas; analyses, chemical and physical property tests, and laboratory-scale system tests.

A. Analyses - Analyses included a computerized analytical model of a fixed-bed reactor and an economic evaluation of alternate bed designs for a power plant application. The analytical model of a fixed-bed reactor required the development of a new computer technique for solving a set of stiff differential equations under transient conditions. The economic analyses compared the cost of a large-scale ammoniated salt reaction storage system with an oil-based sensible heat storage system for application to feedwater heating in an electrical power plant.

B. Chemical and Physical Properties - Chemical and physical properties were measured on $CaCl_2$ ammoniates and $MgCl_2$ ammoniates after a specified number of decomposition and recombination cycles. Properties measured included particle density, bulk density, particle size distribution, and effective surface area. Additional measurements included the effect of moisture and nonaqueous impurities on the reaction kinetics plus a direct determination of the heat of reaction.

C. Laboratory-Scale System Tests - On the basis of chemical reaction rate data obtained previously, five reactions were selected for further study;

one reaction of $CaCl_2$ and two reactions each of $MgCl_2$ and $MnCl_2$. Any one of these reactions can be paired with any other one of the reactions. A particular reaction pair is selected on the basis of the source and sink temperatures in a given application.

Figure 1 presents the thermodynamic data for the five reactions selected. In all cases, Reaction 1 served as the low or ambient temperature reaction. In the example for Reaction 3, it is assumed that thermal energy is available at 570K and that it is transferred to the salt bed through a 5K temperature differential. The operating reaction bed temperature is then 565K and the reactor pressure is 1.5 atmospheres. The ammonia gas which is evolved from the $MgCl_2 \cdot 2NH_3$ is transferred to the low-temperature reactor through a slight pressure differential where it reacts at 315K according to Reaction 1 to produce thermal energy. The thermal energy is transferred through a 5K temperature differential to a sink at 310K.

In reverse, a fluid to be heated is circulated through the high-temperature reactor, which lowers its temperature to 545K and its pressure to 0.9 atmospheres. The pressure reduction causes ammonia gas to flow from the low-temperature reactor back to the high-temperature reactor. The resulting endothermic reaction in the low-temperature reactor lowers its temperature to 305K and its pressure to 0.9 atmospheres. In order to maintain this temperature and pressure, low-temperature energy at 310K is transferred from the sink to the reactor. The exothermic reaction in the high-temperature reactor at 545K generates the original thermal energy which is used to maintain the circulating fluid at 540K.

The other reaction pairs operate in a similar manner. In the example shown for Reaction 2, the source temperature is assumed to be at 425K and the absorbed thermal energy is regenerated at 400K. With Reaction 4, the source temperature is assumed to be at 382K and the thermal energy is regenerated at 359K. With Reaction 5, the source temperature is assumed to be 540K and the thermal energy is regenerated at 510K. The sink temperature is assumed to be 310K in all cases.

Each of these reactions was verified by actual operation of a system according to the schematic shown in Figure 2. The system consisted essentially of a reactor heat exchanger, an external heat exchanger and a fluid heat transfer loop for both the high-temperature and the low-temperature reactions. Each reactor consisted of a shell and tube exchanger 6" in diameter and 1 foot long containing 31, 1/2-inch tubes on 1-inch triangular centers. A heat transfer fluid flowed inside the tubes and the salt bed was packed around the outside of the tubes. A positive displacement pump circulated water through the low-temperature reactor and its associated external, water-cooled exchanger. A second positive displacement pump circulated a heat transfer oil through the high-temperature reactor and its associated external, air-cooled heat exchanger. An electric heater in each of the external heat exchangers permitted controlled heat addition to each of the reactors upon demand.

During the charge mode, heat was added to the fluid circulating through the high-temperature exchanger by means of the electric heater and thermal energy was removed from the low-temperature fluid in the cooling water flowing through the low-temperature exchanger. During the discharge mode, thermal energy was added to the fluid flowing through the low-temperature exchanger by means of an electric heater and high-temperature thermal energy was removed from the high-temperature fluid in air flowing through the high-temperature exchanger.

The ammonia gas pressures in the manifold between the two reactors was measured by PG1 and PG2, and the ammonia transfer rate was measured by the central flowmeter. The ammonia transfer line was manifolded so that ammonia flow was always up through the flowmeter regardless of flow direction.

Temperature measurements throughout the system were made by thermocouples and a multipoint recorder. Coolant flow rates of air and water were measured with tapered glass flowmeters and flow rates of the circulating fluids were measured by calibration of the positive displacement pumps.

IV. RESULTS

A. Analyses - One steady-state analytical model and two transient models of a fixed-bed reactor were constructed. The steady-state model offered no technical problems and is operational on the Martin Interactive Thermal Analyzer System (MITAS). A transient model generates a set of stiff differential equations which required the development of a new computer technique for network solution. A technique was developed for a simplified transient model which contained only reacting nodes and boundary type nodes. This program is also operational on MITAS. A second, more comprehensive transient model of a fixed-bed reactor contained both reacting and non-reacting nodes, a two-dimensional conduction network plus unidirectional fluid-flow paths. This model required the development of a still more sophisticated analytical technique for network solution. Although the model has been constructed and the solution technique has been checked out with the simplified transient model, the complete program is not as yet operational on MITAS.

Economic analyses consisted of comparing the cost of an ammoniated-salt reaction storage system with an oil-based sensible heat storage system for the same application to feedwater heating in a power plant. In this analysis, it was assumed that the total system cost was a linear combination of the power-related costs and the storage-related costs.

For the fixed-bed reactor, the power-related costs are probably high because of the low heat transfer coefficient and the small temperature differential between the bed and the heat transfer fluid. The power-related costs can be reduced by incorporating forced ammonia flow through the bed and they can be reduced to a minimum by using a sufficient ammonia recirculation rate to fluidize the salt bed.

Container costs can be minimized by considering large diameter spherical containers for the salts. When costs are based on these conceptual designs, they are less for the ammoniated salt storage system than comparable costs for an oil-based sensible heat storage system.

B. Chemical and Physical Properties

Particle density was measured by the pynometer method after determination that the X-ray diffraction patterns of $CaCl_2$ and $MgCl_2$ ammoniates were too complex to interpret within the time span of this contract. The particle density ranged from 2.15 for anhydrous $CaCl_2$ to 1.58 for $CaCl_2 \cdot 4NH_4$. The physical properties of the octammoniate could not be determined because the high vapor pressure of the salt at room temperature caused it to decompose to the quadrammoniate during the measurement. The particle density ranged from 2.32 for anhydrous $MgCl_2$ to 1.41 for the hexammoniate.

Bulk density of a particle bed was measured after 1, 5, 10, 20, 50 and 100 decomposition/recombination cycles. Results indicate that the bulk density is not strongly influenced by either the number of cycles or the degree of ammoniation. The bulk density of $CaCl_2$ ammoniates was in the range of 0.5 to 0.6 grams/cc for the majority of measurements. The bulk density of $MgCl_2$ ammoniates was in the range of 0.2 to 0.3 for the majority of measurements.

Surface area measurements of $CaCl_2$ ammoniates, as determined by the BET Argon adsorption method (except the octammoniate, which could not be accurately determined under the experimental conditions), were in the range of 2000 to 4000 cm^2 per gram of ammoniate. The surface area of the $MgCl_2$ ammoniates were an order of magnitude higher in the range of 20,000 to 40,000 cm^2/gram. These areas were essentially independent of the number of cycles and the degree of ammoniation.

Particle size distribution measurements were attempted first by Coulter Electronics Particle Counting Laboratory in Hialeah, Florida. However, humidity in the laboratory caused particle agglomeration of the samples and voided the results. Finally, a conventional, visible light microscope with 35X magnification was used to categorize particle sizes in the 0-100 micron, 100-300 micron and 300-3000 micron ranges. A typical distribution for the $CaCl_2$ ammoniates was 5, 10 and 85% in each of the 3 ranges. A typical distribution for the $MgCl_2$ ammoniates was 70, 20 and 10% in each of the three ranges. The particle size distribution was not strongly influenced by either the degree of ammoniation or the number of cycles.

The influence of small concentrations of moisture was determined by preconditioning the anhydrous salts of $CaCl_2$ and $MgCl_2$ with 1, 2, 4 and 6% moisture in a Mettler TA-Thermoanalyzer. After preconditioning, the salt was exposed to ammonia vapor and the association/dissociation cycles were carried out. During the first few cycles, the reaction rate gradually increased and approached the rates determined previously for the anhydrous salts. Apparently within the range of moisture concentrations covered, the initial moisture is preferentially replaced by ammonia and does not interfere with the reactions after the first few cycles.

The effect of non-aqueous impurities on the reactor rate were measured in a similar manner. One percent calcium sulfate in the calcium chloride, 3% calcium chloride in magnesium chloride and up to 2% air in the ammonia vapor had no significant effect on the measured reaction rates.

Finally, the heats of reaction were remeasured and compared both with previously measured values and with heats of reaction obtained from the literature. The remeasured heats of reaction were in good agreement with previously measured values and in reasonable agreement with values reported in the literature.

C. Laboratory System Tests - The system shown in Figure 2 was operated for a total of 128 cycles with the $CaCl_2$ ammoniated salt in the low-temperature reactor. A cycle consisted of 1 hour steady-state operation in the discharge mode followed by a 1 hour operation in the discharge mode. During the discharge mode, heat was added to the low-temperature (LT) reactor and heat was removed from the high-temperature (HT) reactor with the air-cooled external exchanger. During the charge mode, heat was added to the HT reactor and heat was removed from the LT reactor with the water-cooled external exchanger.

The reaction $MgCl_2 \cdot 6NH_3 \rightleftharpoons MgCl_2 \cdot 2NH_3 + 4NH_3$ was conducted in the HT reactor for the first 20 cycles. A typical steady-state energy balance for each reactor is given in Figure 3. During the discharge mode, the ammonia flow rate was 55.9 grams/hour and during the charge mode it was 50.3 grams/hour. Ideally in steady-state, the heat of reaction, the heat transferred in the reactor and the heat transferred in the exchanger (or the heater power) should all be the same. Any discrepancy is attributed to heat loss, non-attainment of steady-state conditions and to small errors in measurement of temperatures and flow rates. The loss term includes all unaccounted for conduction losses to the environment plus changes in the sensible heat inventory in the system. It is noted that the loss is greater when the electric heater is operational than when the external exchanger is used.

The ammonia flow rate for both the charge and discharge modes is shown as a function of cycle number in Figure 4. No obvious trend in ammonia flow rate (reaction rate) is noted over this period.

The reaction $MgCl_2 \cdot 2NH_3 \rightleftharpoons MgCl_2 \cdot NH_3 + NH_3$ was conducted in the HT reactor during the next 38 cycles. Similar results were obtained except that a continuous decline in ammonia flow rate was noted. After 38 cycles, the reaction was terminated and the HT reactor was unloaded. No observable change in the salt structure was apparent. However, a solid plug of entrained $MgCl_2$ powder was found in the ammonia transfer line immediately adjacent to the HT reactor. On the basis of existing evidence, no clear distinction can be made between chemical degradation of the $MgCl_2$ salt and mechanical blockage of the ammonia transfer line as a cause for the decline in ammonia flow rate. Only additional data will resolve this question.

The HT reactor was reloaded with $MnCl_2$ and the reaction $MnCl_2 \cdot 6NH_3 \rightleftharpoons MnCl_2 \cdot 2NH_3 + 4NH_3$ was conducted for 20 cycles. The results verified the reaction conditions defined in Figure 1 and no significant trend in ammonia flow rate was noted during this period.

The reaction $MnCl_2 \cdot 2NH_3 \rightleftharpoons MnCl_2 \cdot NH_3 + NH_3$ was then conducted in the HT reactor for the next 20 cycles. Again, the reaction conditions defined in Figure 1 were verified and no significant trend was noted in the ammonia flow rate.

Finally, the HT reactor was reloaded with $MgCl_2$ and additional data were obtained on the reaction $MgCl_2 \cdot 2NH_3 \rightleftharpoons MgCl_2 \cdot NH_3 + NH_3$ for another 30 cycles. During this period the ammonia flow rate was reasonably constant and did not decline to the extremely low rates observed previously.

V. FUTURE ACTIVITIES

A. The energy storage-heat pump system studied in this contract will be applied to space heating and cooling under a separate ERDA contract. A residential-sized prototype system will be constructed and tested.

B. A continuation of the present contract will study reactions in support of the heat-pump cooling application. A liquid-phase reaction operating below ambient temperature has been proposed for experimental investigation in a laboratory-sized system.

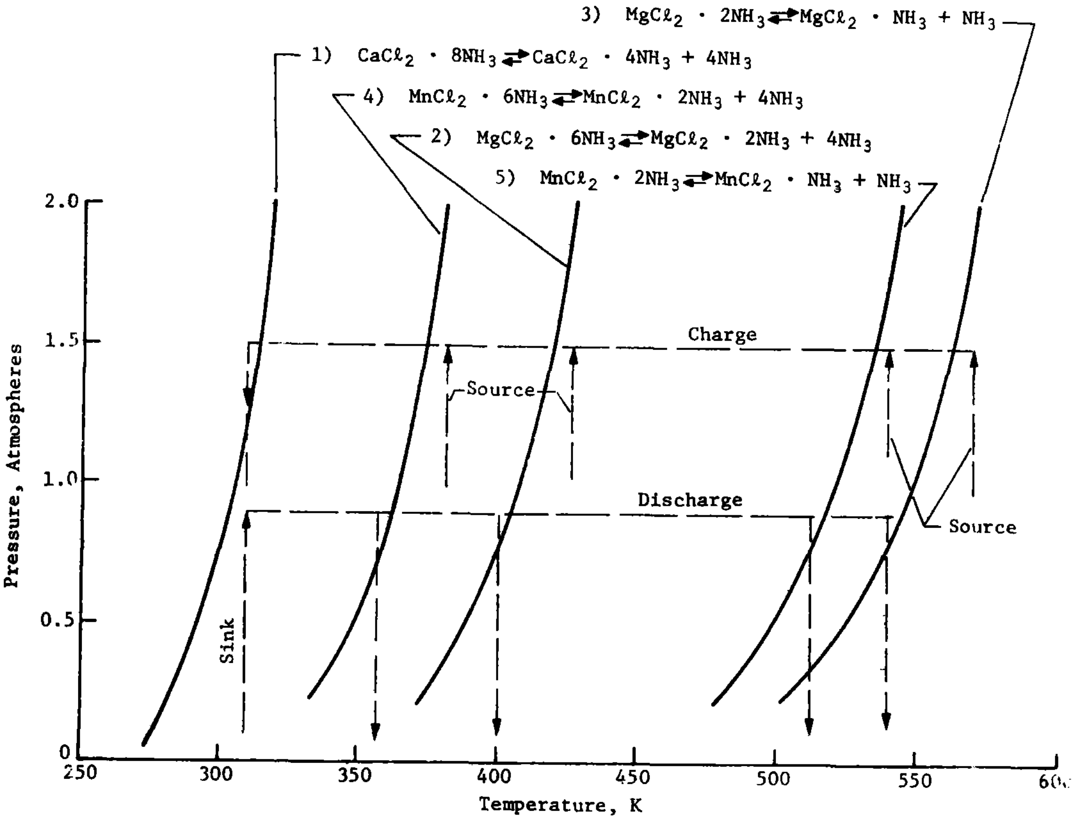


Figure 1 Examples of Operating Conditions

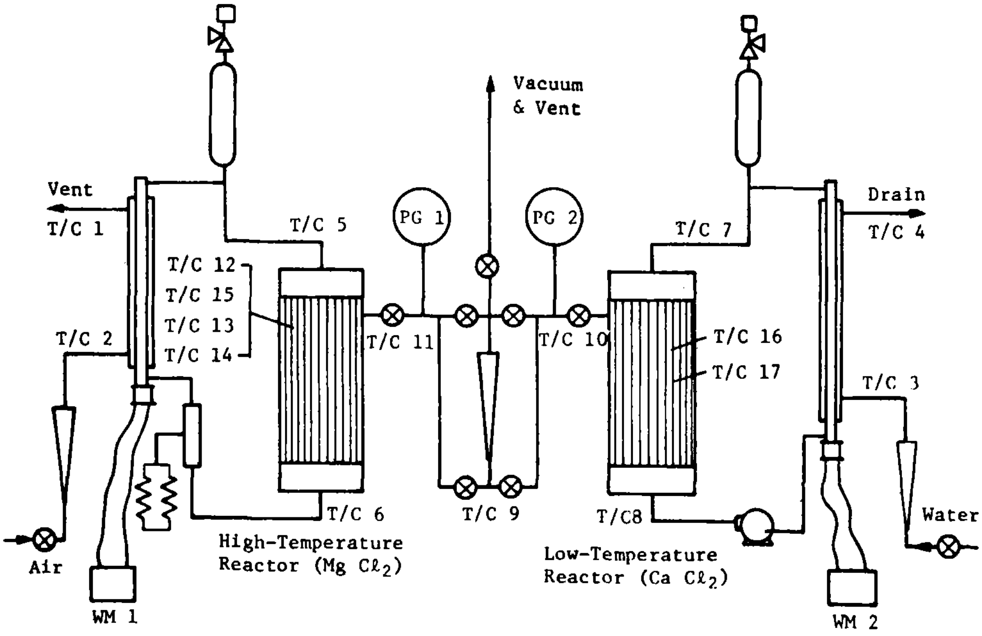


Figure 2 Lab Scale Schematic

	Discharge		Charge	
NH_3 Flow Rate, gms/hr	55.9		50.3	
	HT	LT	HT	LT
Heat of Reaction	47.2	37.6	42.5	33.8
Heat Transfer in Reactor	(34.6)	(37.2)	(56.9)	(22.3)
Heat Transfer in Exchanger	36.7	----	----	24.8
Heat to Ammonia	4.3	----	3.8	----
Heater Power	----	80.0	190.0	----
Loss	6.2	42.4	143.7	9.0

Figure 3. Steady State Energy Balance, Watts, Cycle 10

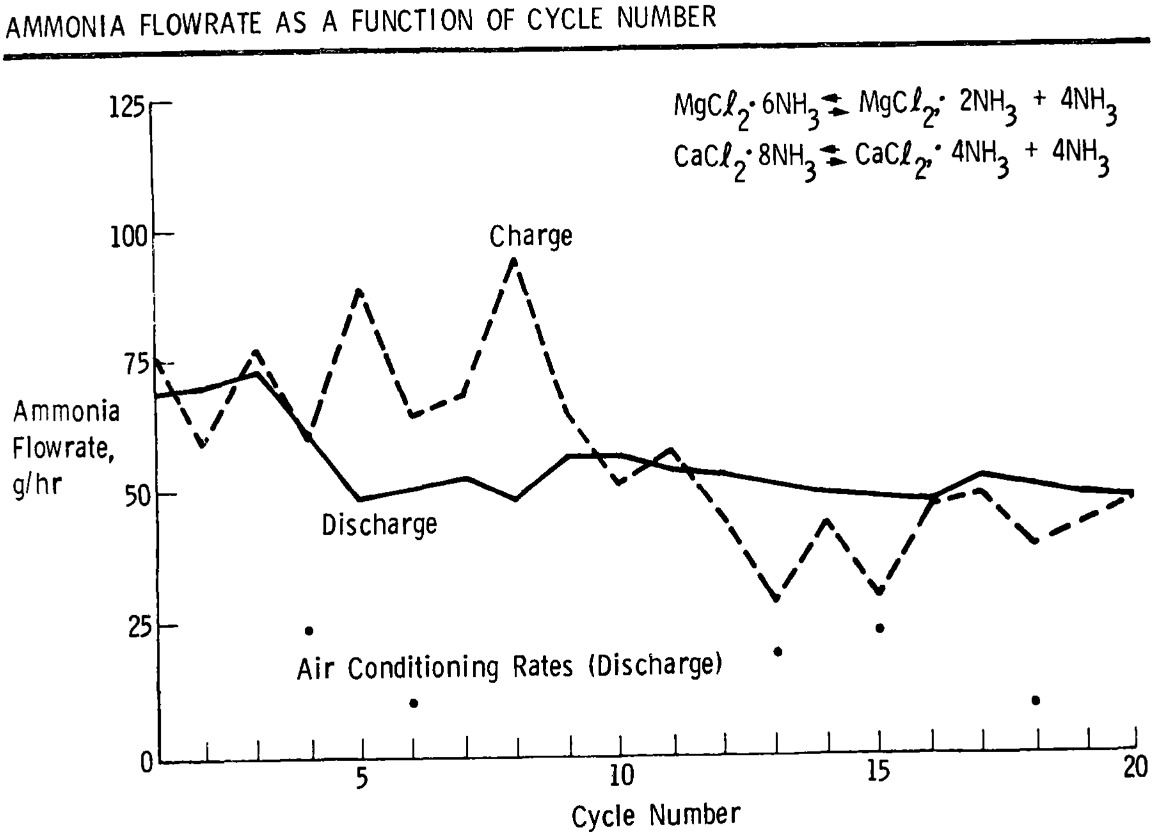


Figure 4

PROJECT SUMMARY

ORGANIZATION: Rocket Research Company

ADDRESS: York Center
Redmond, Washington

PROJECT TITLE: Chemical Energy Storage for Solar-Thermal Conversion

PRINCIPAL INVESTIGATORS: Dr. D. R. Poole
Dr. R. D. Smith

TELEPHONE NO.: 206 885-5000

CONTRACT PERIOD: 7/76 – 10/78

CONTRACT NO.: AER 75-22176

CONTRACT AMOUNT: NSF $120,000
ERDA $150,000

PROJECT GOALS:

The overall objective of this program is to evaluate the concept of chemical storage of solar energy on a total system basis. Technical considerations include selection of reactions or reaction sequences which may be useful in reversible-chemical-reaction (RCR) energy storage, evaluation of selected reactions on theromodynamic and kinetic bases, and preliminary design and modeling of energy storage subsystems based on these reactions. By means of a computer model of a solar-thermal, power generation facility (including various RCR energy storage subsystems), the technical and economic feasibility of extending the solar-thermal conversion (STC) concept to include baseload power generation is being studied.

PROJECT STATUS:

Selection of promising chemical reactions is complete, as well as tabulation of physical, thermodynamic, and kinetic properties for these reactions. At present, 24 potentially useful reactions have been identified for further study, and preliminary estimates of applicable temperature range, storage density, and storage round-trip efficiency for each reaction have been made.

Simplified performance and cost models, on a subsystem basis, of each of three types of solar-thermal power generation facility have been generated. Insolation and demand-load models have been generated, on an hourly basis, for each of four locations in the continental United States. At present, these performance and insolation/demand models can be used to predict the required size and performance of a solar-thermal conversion facility for a specified location, plant type, load profile, and storage round-trip efficiency.

I. Purpose

Again, the overall objective of the present research effort is to evaluate the concept of chemical storage of solar energy on a *total system* basis. Central to such an evaluation is the identification of promising chemical reactions and consideration of the technical, environmental, and safety problems associated with the use of these reactions for energy storage. In addition, it is intended to determine the economic impact of extension of STC plants from intermediate to load-following baseload capability, and to provide operational and design requirements which are compatible with facilities under active investigation by the solar division of ERDA.

II. Background Information

Approximately 2 years have passed since the proposals were submitted in response to program solicitation NSF 75-16 which initiated this effort. During this time, changes have taken place in the concept of utilization of RCR energy storage in solar-thermal conversion applications.

In the past, STC electric power plants have been tied to a short-term (nominally 6 hours) energy storage system. This design constraint results in an intermediate load power plant, i.e., energy is available when nature provides adequate insolation and not necessarily at the time of demand by the customer.

The short-term storage capacity in current STC programs was determined on the basis of economic considerations using sensible and/or latent heat storage systems. These systems typically increase linearly in cost with storage capacity, thus large systems become extremely expensive. Chemical energy storage, a technique of storing energy as the heat of reaction in reversible chemical reactions is, on the other hand, unique since the cost per kilowatt-hour decreases substantially as the total store increases in capacity. This reduction in cost occurs because increasing the capacity of an RCR energy storage facility requires only the addition of inexpensive chemicals and storage containers, while the expensive components such as heat exchangers, chemical reactors, etc., are essentially constant in size (and cost) as the store is increased, being dependent only on the power plant generating capacity.

Results of preliminary in-house investigations at Rocket Research Company (RRC) indicate that the energy costs for an intermediate facility extended to load-following baseload capability using an RCR energy storage subsystem can be competitive with present intermediate load facilities. Other factors that provide incentive to increase systems capability to baseload include the ability to provide power on demand while not being limited by Nature's weather patterns and the elimination of full-sized, fossil-fueled backup facilities. Finally, by maintaining power generation on a 24-hour basis, the life shortening thermal transients on the turbine and other components when exposed to daily startup thermal gradients are eliminated.

Because of the promise offered by these preliminary studies, the scope of this program has been expanded to include a detailed analysis of extending STC plants, by means of RCR energy storage, to baseload capability.

III. Project Description

The overall program is depicted schematically in Figure 1, which shows the integration of the supplementary program (Subtasks I–VI, ERDA funded, contract number to be assigned) with the original NSF program (NSF Grant No. AER 75-22176). Task I 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. Tasks II (low temperature) and III (high temperature) then run in parallel, and consist of thermodynamic and kinetic analyses of reactions selected in Task I, followed by engineering studies of the most promising reactions in the low-temperature and high-temperature categories.

As noted above, RCR energy storage appears most economical for storage times that exceed the 6-hours usually specified for the STC concepts presently being studied by the solar division of ERDA. The economics of extending these STC concepts to baseload capability have not previously been studied in depth, and Subtasks I–IV represent such a study. The result should be a generalized computer model of a solar-thermal, power generation facility, with a subroutine for modeling RCR energy storage subsystems (as part of the total plant) based on appropriate chemical reactions selected during the Task I effort.

Program inputs will include plant type (distributed, central receiver, etc), location, load profile, and the particular chemical reaction on which the storage subsystem is based. Program outputs will be plant size, plant cost, a plant performance map, and an estimated busbar energy cost (BBEC) for electricity generated by the plant specified by the program inputs. Optimization on the BBEC, with respect to each of the above inputs, will be performed, thus accomplishing the dual task of critical examination of the extension of STC facilities to baseload capability, as well as the ranking of the reactions selected under Task I on an economic basis. Subtask III of the supplementary program represents a joint effort for information exchange by RRC and the Systems Studies Division of Sandia, Livermore, with Sandia providing RRC with guidance on modeling various STC plant subsystems, and RRC providing Sandia with storage subsystem performance data for use in their optimization studies of solar/fossil fuel, hybrid power generation facilities.

Using the above model, the most promising low- and high-temperature reactions will be selected for further study in the concluding segments of Tasks II and III. Results of this concluding effort will be a review and description of storage subsystems based on these two reactions, including interface drawings, system diagrams, and site drawings.

IV. Results

Reaction Selection and Evaluation:

All of Task I and the thermodynamic and kinetic analyses of Tasks II and III are complete. The periodic table of the elements served as the starting point for the process of generating and selecting chemical reactions for energy storage applications. After eliminating numerous elements due to their high cost, toxicity, or lack of availability, all known chemical compounds of the remaining elements were considered. In this way, a list of approximately 750 compounds was generated. Methane and methanol are the only organic compounds which were retained, since most organic reactions of larger molecules tend to be nonstoichiometric.

Chemical reactions were then listed using the selected elements and compounds, resulting in a list of approximately 550 reactions. Based on the following criteria, 85 candidate reactions were identified:

1. Reaction appears to be reversible
2. $\Delta H_R \geqslant 110$ kcal/kg
3. $|\Delta G_{298^oK}|$ or $|\Delta G_{800^oK}| \leqslant 10$ kcal/mole
4. Approximate equilibrium temperature $T = \Delta H/\Delta S$ in the range of 400^oK to $1{,}300^oK$.

It was found that nearly all of the 85 reactions could logically be classified into 14 categories based on the reaction or chemical type. These categories are listed in Figure 2. The final selection of the 24 reactions listed in Figure 3 is the result of trying to select the highest rated reactions from each category while also including reactions which were known to be under investigation by other workers. A data book has been assembled which includes, for each of the 24 selected reactions, such information as theoretical energy content, endothermic and exothermic reaction temperature, physical state and density of reactants and products at 298^oK, estimated storage round-trip efficiency, and a simplified process flow sheet for a storage subsystem.

Completion of Tasks II and III of the original program will be delayed pending completion of the six subtasks of the supplementary effort.

Extended Storage Model:

Three solar thermal-electric power plant systems have been selected for modeling and extension to baseload capability. They include:

1. Central receiver collection, Rankine cycle power generation (783°K)
2. Central receiver collection, open-Brayton cycle power generation (1,310°K)
3. Distributed collection, Rankine cycle power generation (588°K).

Each of these systems has been broken down into subsystems, and each subsystem has been modeled with respect to energy efficiency and capital cost as a function of size.

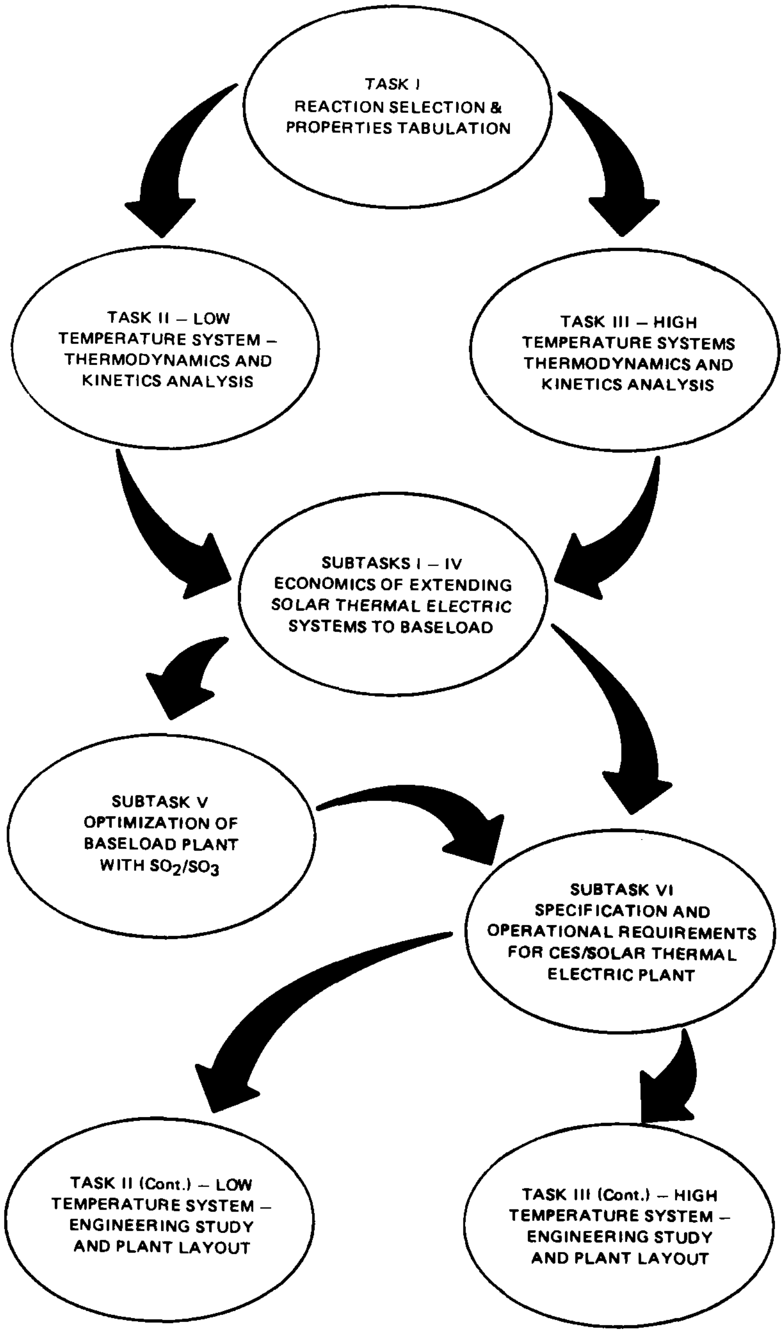
Four sites have been selected for hypothetical location of a STC power plant, including Miami, Florida (SE), Milwaukee, Wisconsin (NC), Albuquerque, New Mexico (SW), and New York, New York (NE). Hourly profiles of direct-normal insolation and electrical grid load have been obtained for each location for at least one representative year.

A system-sizing computer program has been written as a first step toward the overall computer model described under "Project Description". This program utilizes the subsystem models and insolation/demand data described above, and, by means of an iterative, hour-by-hour energy balance over the course of a year, computes the required size of each subsystem for specified load profile (baseload, baseload plus intermediate, or grid independent) and storage round-trip efficiency, η_{RT}. Some preliminary results of the sizing of a high-temperature, Brayton cycle STC system for 100 MW_e baseload service are shown in Figure 4. The results shown here are plotted as required collector area as a function of storage system round-trip efficiency. The most surprising results of this preliminary analysis are the near identical collector areas required at locations NC and SE for all values of η_{RT}. The same sizing analysis shows that location NC requires almost four times the storage capacity of system SE at all values of η_{RT}. Since collectors are by far the most expensive component of a solar power generation facility, accounting for up to half the total plant cost in most current designs, it appears that inclusion of extended storage capability may lessen considerably the effects of latitude and extended bad weather on the feasibility of baseload solar-thermal power generation. It should be emphasized that these results are preliminary, however, and further conclusions must await development of the complete cost and performance model.

V. Future Activities

During the next fiscal year, work will be directed toward completion of Subtasks IV through VI of the supplementary program, and the remainder of Tasks II and III of the original NSF program. Completion of the overall effort is scheduled for October 1978.

INTEGRATION OF SUPPLEMENTAL PROGRAM WITH THE ORIGINAL PROGRAM



29007-36

Figure 1

CHEMICAL ENERGY STORAGE REACTION CATEGORIES

- METAL OXIDES/HYDROXIDES
- METAL SULFATES
- PEROXIDES/SUPEROXIDES
- CARBONATES
- AMMONIA REACTIONS
- NO_2 REACTION WITH OXIDES, HYDROXIDES, CARBONATES
- CARBON DISULFIDE
- FLUORINE/FLUORIDES
- SULFUR TRIOXIDE
- CHLORINE/CHLORIDES
- HYDRIDES
- ORGANIC REACTIONS
- NITROGEN OXIDES
- MISCELLANEOUS

Figure 2

CES REACTIONS RANKED IN ORDER OF DECREASING ENDOTHERMIC REACTION TEMPERATURE

Reaction	$T_{\text{Endothermic}}$ °K	$T_{\text{Exothermic}}$ °K
$Ca + H_2 = CaH_2$	1,350	1,150
$K_2O_2 + O_2 = 2KO_2$	1,300	900
$K_2O_2 + O_2(AIR) = 2KO_2$	1,300	750
$C_2H_4 + H_2 = C_2H_6$	1,200	1,000
$NH_3 + H_2O + SO_3 = NH_4HSO_4$	1,200	700
$ZnO + SO_3 = ZnSO_4$	1,175	1,060
$CaO + CO_2 = CaCO_3$	1,125	1,000
$2SO_2 + O_2 = 2SO_3$	1,100	800
$CO + 3H_2 = CH_4 + H_2O$	1,100	700
$4HCl + O_2 = 2H_2O + 2Cl_2$	900	700
$CaO + H_2O = Ca(OH)_2$	800	675
$CS_2 = C + 2S$	800	600
$C + 2Cl_2 = CCl_4$	750	550
$HF + KF = KHF_2$	725	600
$MgO + CO_2 = MgCO_3$	700	600
$2Na + H_2 = 2NaH$	700	600
$MgCl_2 + NH_3 = MgCl_2 \cdot NH_3$	640	540
$N_2 + 3H_2 = 2NH_3$	600	800
$C_6H_6 + 3H_2 = C_6H_{12}$	590	670
$MgO + H_2O = Mg(OH)_2$	550	450
$FeCl_2 \cdot NH_3 + NH_3 = FeCl_2 \cdot 2NH_3$	550	450
$Li_2O + SO_3 = Li_2SO_4$	*	*
$Na_2O + 2NO_2 + 1/2O_2 = 2NaNO_3$	*	*
$NH_3 + HCl = NH_4Cl$	*	*

*Not established

Figure 3

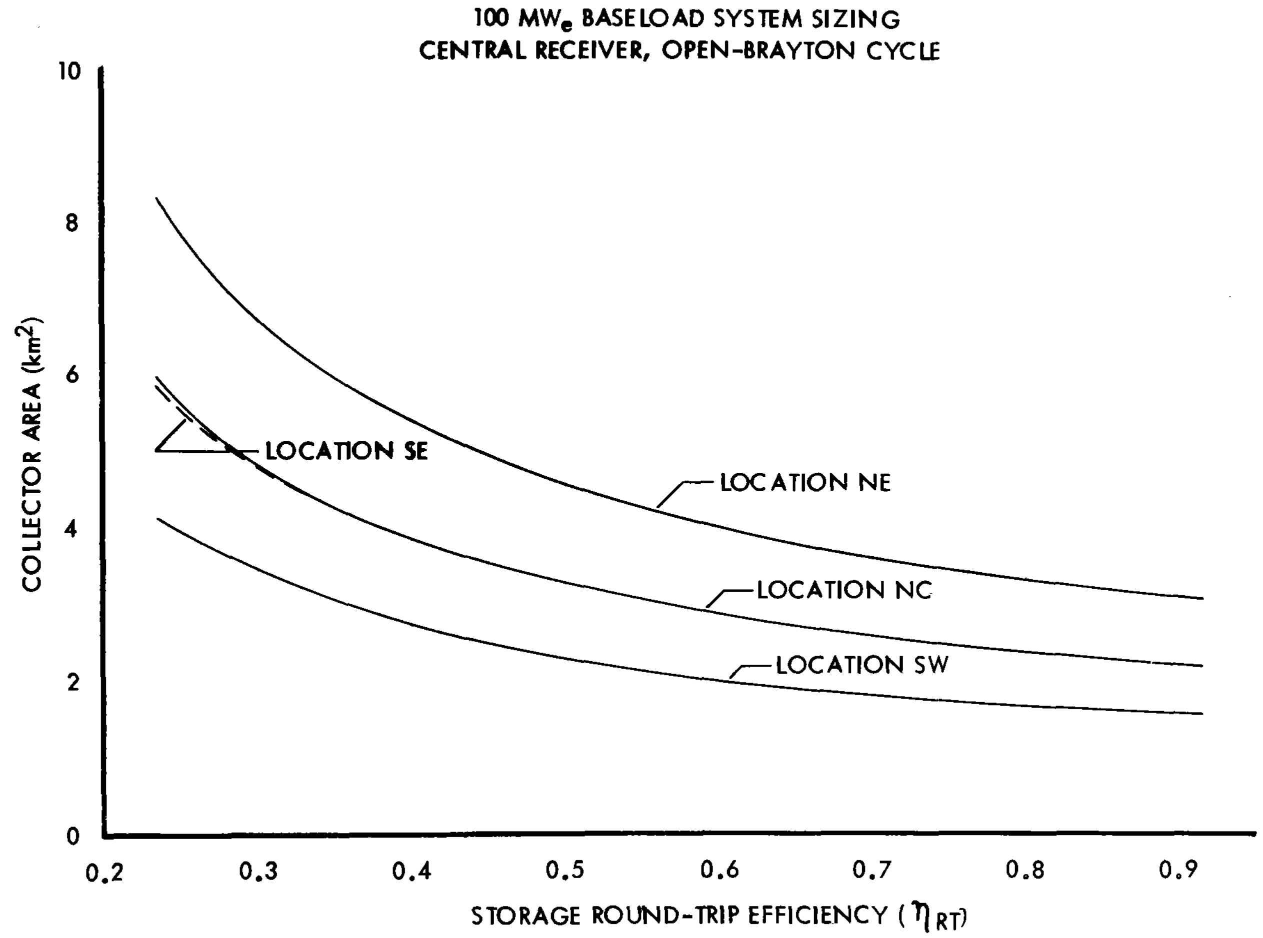

100 MW$_e$ BASELOAD SYSTEM SIZING
CENTRAL RECEIVER, OPEN-BRAYTON CYCLE
COLLECTOR AREA (km^2)
10
8
6
4
2
0
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
STORAGE ROUND-TRIP EFFICIENCY (η_{RT})
LOCATION SE
LOCATION NE
LOCATION NC
LOCATION SW

Figure 4

DEVELOPMENT OF A LONG-LIFE HIGH-TEMPERATURE CATALYST FOR THE SO_2/SO_3 ENERGY STORAGE SYSTEM

CONTRACTING AGENCY:	SANDIA LABORATORIES, LIVERMORE, FOR ERDA
CONTRACT NUMBER:	SAND 87-9119
SANDIA TECHNICAL PROJECT MANAGER:	DR. BERNICE MILLS
CONTRACTOR:	ROCKET RESEARCH COMPANY, REDMOND, WA.
RRC PROGRAM MANAGER:	DR. ECKART W. SCHMIDT
FUNDING PERIOD:	APRIL 25, 1977 THROUGH SEPTEMBER 1979

V02844

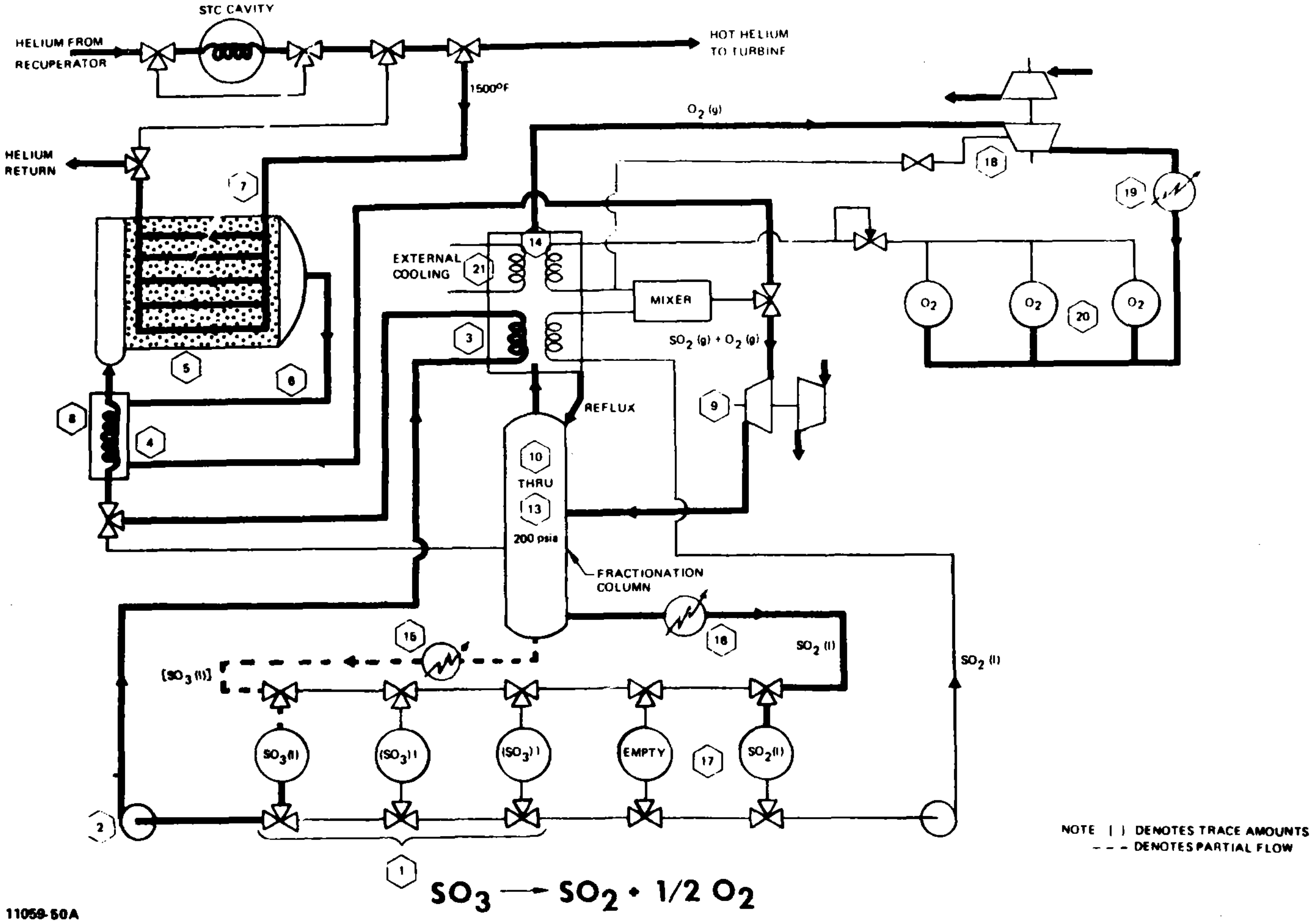
RRC 77-H-169

ENERGY CONTENT AND OPERATING TEMPERATURE RANGE OF CES REACTIONS

REACTION	ENERGY J/g	TEMPERATURE, ^{0}K		
		10%	90%	$\Delta H/\Delta S$
$CO(G) + 3H_2(G) \rightleftharpoons CH_4(G) + H_2O(G)$	6,053	754	1,466	961
$N_2(G) + 3H_2(G) \rightleftharpoons 2NH_3(G)$	2,695	346	528	463
$SO_2(G) + 1/2\ O_2(G) \rightleftharpoons SO_3(G)$	1,235	792	1,235	1,053

V02645

CHEMICAL ENERGY STORAGE SYSTEM – REACTANT GENERATION CYCLE



11059-50A

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	AIR/SO_2	O_2/SO_2
SPACE VELOCITY	2,000 h^{-1}	10,000 h^{-1}
CATALYST LIFE	2 TO 10 YEARS	30 YEARS (DESIRABLE)

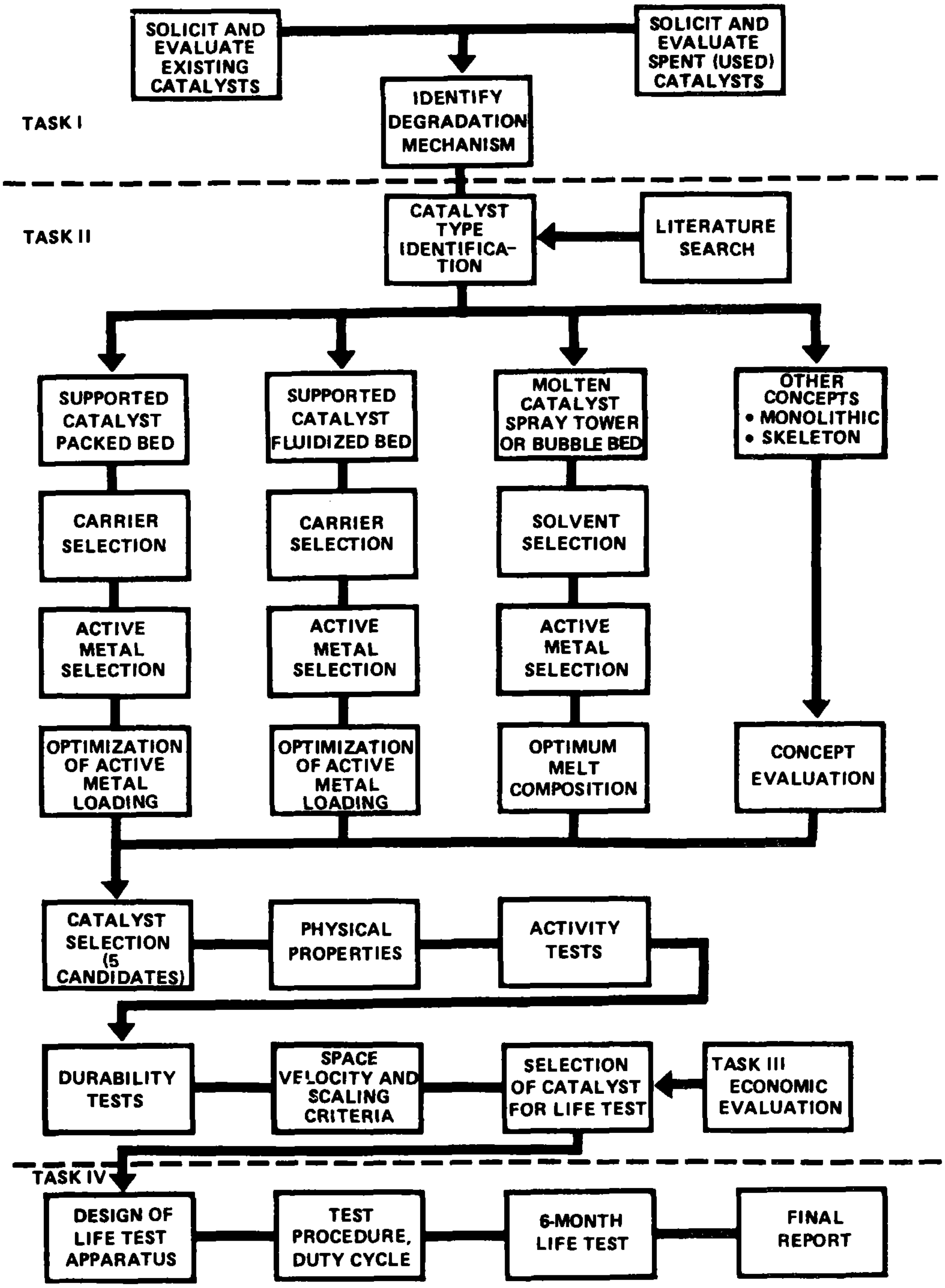
V02843

SO_x CATALYST DEVELOPMENT

- OBJECTIVES
    - EVALUATION OF COMMERCIAL CATALYSTS
    - CATALYST DEVELOPMENT
    - ECONOMIC EVALUATION
    - ACCELERATED LIFE TEST
- GOALS
    - LOW COST, DURABLE CATALYST CAPABLE OF SUSTAINING FAST RATES OF REACTION IN EXOTHERMIC AND ENDOTHERMIC MODES
    - 30 YEAR USEFUL LIFETIME

V02845-1

SULFUR OXIDE CONVERSION CATALYST DEVELOPMENT – PROGRAM FLOW CHART



29006-78

SO_x CATALYST DEVELOPMENT

- PROGRAM STATUS AS OF SEPTEMBER 1977
  - 21 FRESH AND 10 USED CATALYST SAMPLES RECEIVED FOR ANALYSIS
  - CATALYST ACTIVITY TEST APPARATUS UNDER CONSTRUCTION
  - MELT COMPOSITIONS FOR MOLTEN CATALYST CONCEPT IDENTIFIED

V02845-2

SO_x CATALYST DEVELOPMENT

FUTURE PLANS

- COMPLETION OF CURRENT CONTRACT
  - GFY 1978: CONTINUE DEVELOPMENT OF NEW CATALYSTS.
    EVALUATE ACTIVITY OF NEW CATALYSTS.
  - GFY 1979: ACCELERATED LIFE TEST
- PROPOSED FOLLOW-ON ACTIVITIES (NOT YET FUNDED)
  - BENCH SCALE PILOT REACTOR
  - CLOSED CYCLE TESTS
  - MATERIALS EXPOSURE TEST

V02845-3

SO_x CATALYST DEVELOPMENT

- RELATED DEVELOPMENTS USING CATALYSTS
  - WESTINGHOUSE WATER SPLITTING CYCLE FOR PRODUCTION OF HYDROGEN
  - GENERAL ATOMICS WATER SPLITTING CYCLE FOR PRODUCTION OF HYDROGEN
  - UNIVERSITY OF CALIFORNIA AT BERKELEY/LAWRENCE BERKELEY LABORATORIES ENERGY TRANSMISSION AND STORAGE SYSTEM
- OTHER APPLICATIONS
  - RECOVERY OF HIGH-GRADE ENERGY IN PRODUCTION OF SULFURIC ACID
  - SO_x REMOVAL FROM STACK GASES

V02845-4

PROJECT SUMMARY

ORGANIZATION: Rocket Research Company

ADDRESS: York Center
Redmond, Washington 98052

PROJECT TITLE: Sulfuric Acid/Water Integrated Chemical Energy Storage System

PRINCIPAL INVESTIGATOR: E. Charles Clark TELEPHONE NO.: (206) 885-5000

CONTRACT NO.: EY-76-C-03-1185 CONTRACT PERIOD: 12/19/75 – 11/30/77

CONTRACT AMOUNT: ERDA $51,924 Phase I
$290,000 Phase II
OTHER None

PROJECT GOALS:

This program is divided into three phases. The goals of the completed initial phase were to determine the feasibility of using sulfuric acid and water as a chemical energy storage media, generate basic design concepts, and estimate the respective system costs.

The second phase objectives are to select a concept for detailed sizing and scaling analysis, design and construct a subscale (~100,000 Btu) closed loop demonstration system, conduct operational tests to verify system performance and efficiency, and provide recommendations for the third phase full-scale pilot plant design. Additionally, as an intermediate follow-on to Phase II, component optimization testing will be conducted using the subscale system and the economic and environmental impact for commercialization of the sulfuric acid system will be assessed.

PROJECT STATUS:

All of the tasks in Phase I have been completed and were reported during the previous contractors meeting in September 1976. During the initial Phase II effort starting in October 1976, the sulfuric acid heat pump concept with storage densities in excess of 600 Btu/lbm of dilute acid was identified. Currently, the Phase II sizing and scaling analysis has been completed as well as the design and procurement of the subscale system components. Initial evaluation tests are scheduled to start in October 1977.

I. Purpose

This paper presents a summary of the technical progress of the Energy Research and Development Administration (ERDA) three phase contract, EY-76-C-03-1185, entitled "Sulfuric Acid/Water Integrated Chemical Energy Storage System." It covers the work conducted to date since the previous contractors meeting in September 1976, plus the anticipated activities for the future.

II. Background

Thermal energy storage is expected to play an important role in the effective utilization of solar energy and conservation of existing energy sources. The sulfuric acid-water system was one of the first chemical systems to be considered as a thermal storage media. At the present time, sulfuric acid is of great interest because it has excellent energy storage capabilities (in excess of 600 Btu/lbm of dilute solution) when utilized as a heat pump and also because it is an inexpensive chemical ($0.022/lbm). It is produced in very large quantities and has an extensive background of handling data and chemical/physical properties. By considerable margin, more sulfuric acid is produced than any other chemical. Liquid chemicals are preferred over solid substances because they are easier to store, pump and meter, and usually have superior mass and heat transfer properties.

The sulfuric acid heat pump utilizes the heat of condensation of water as part of the stored energy. Energy densities in excess of 600 Btu/lbm of dilute acid are possible with separation temperatures of 400°F. The system consists of two liquid containers (Reference Figure 1) connected by a duct with an interlocking valve. Initially, the system is evacuated and the pressure in the tanks is dependent on the concentration of the acid and the respective temperatures in each tank. To store energy (charge the system), the dilute acid (left) is heated by an external source (e.g. solar heat), water vapor is driven off and condenses in the water tank (right), which removes the heat of condensation by means of a constant temperature source (e.g. air, ground, or water). Higher and higher temperatures are required as the system approaches the fully-charged state (concentrated acid), at which time the valve is closed until heat is needed. To discharge the system (remove stored energy), the acid is cooled, thereby developing a pressure differential between the acid tank and water tank. This pressure difference is sufficient to boil the stored water. The valve is opened and water vapor is then condensed into the acid tank, diluting the acid, and reclaiming the heat of vaporization of water plus the heat of acid dilution. The boiling water is prevented from freezing by energy transferred from the constant temperature source. In summary, heat is pumped using water vapor from a high-temperature reservoir to a low-temperature reservoir during the charging process. During the discharge process, heat is again pumped (using water vapor) from a low-temperature reservoir to a high-temperature reservoir.

III. Project Description

Phase II of the subject contract is divided into four tasks. During Task 1, a system application was selected and a detailed sizing and scaling analysis was conducted. Component testing for both the charge mode (acid/water separation) and discharge mode (acid dilution) using laboratory scale equipment was conducted during Task 2, as well as the detailed design of the subscale closed loop demonstration system. A subscale system is being fabricated and assembled during Task 3. The final task for Phase II will consist of a series of closed loop demonstration tests to evaluate the system performance and efficiencies. Performance predictions made during the sizing and scaling analysis will be compared to test data.

IV. Results

To date, Tasks 1 and 2 have been completed. A detailed computer model of the heat pump system has been completed as part of the sizing and scaling analysis. The model utilizes the thermochemical data generated during the Phase I program. The primary input and output parameters are summarized in Table 1.

Table 1
PRIMARY INPUT AND OUTPUT PARAMETERS FOR THE SULFURIC ACID HEAT PUMP COMPUTER MODEL

Input Parameters	Output Parameters
Storage capacity	Acid tank size
Charge time	Water tank size
Discharge time	Duct size
Percent acid carryover	Heat exchanger sizes
Maximum acid concentration	Storage efficiency
Minimum acid concentration	Storage density
Thermal source temperature	Parasitic pump power
Constant temperature source temperature	The following functions versus time:
Minimum storage output temperature	Heat input rate
Heat exchanger temperature differentials	Accumulated heat input
Shell and tube heat exchanger criteria	Heat output rate
	Accumulated heat output
	Vapor flow rate
	Acid concentration, pressure, temperature
	Water concentration, pressure, temperature
	Heat exchanger temperatures

The computer program is capable of sizing full-scale systems and was used to provide the design criteria for the subscale demonstration system being fabricated under this contract. The resulting system storage densities are shown plotted in Figure 2 as a function of thermal source temperature. This data represents a system design for use with a space heating application. The minimum acid temperature is 90°F when fully discharged. The maximum acid temperature will be 5 degrees lower than the thermal source temperature. A constant temperature source of 52°F has been assumed in Figure 2. Figure 3 presents a plot of storage density as a function of a constant temperature source temperature.

To conduct preliminary economic analyses, the computer program was used to size a full-scale space heating system located in the eastern United States using a seasonal 100% solar system. Based on the sizes provided by the model, the following costs are estimated for a large seasonal storage system:

Sulfuric acid storage media	\$33/M Btu
Acid tank (lined)	\$90/M Btu
Water tank (lined)	\$65/M Btu
Heat exchangers	\$58/M Btu
Miscellaneous components and controls	\$23/M Btu

The cost of the storage system is \$269 per million Btu. It is again emphasized that this cost is for a total seasonal solar heating system with no fossil fuel backup system.

During Task 2, a series of tests were performed to determine the design criteria for both the acid separation and recombination modes (acid concentration and acid dilution respectively).

The results of the separation tests indicate that two separation techniques are possible: continuous and batch. Continuous separation is a steady flow process where dilute acid is pumped to one end of a fractionating column and concentrated acid is removed at the other end. This process allows for a constant temperature drop across a solar collector system. However, it does impose a more complex storage requirement since both dilute and concentrated acid must be stored simultaneously. In the batch separation process, the entire bulk acid is concentrated within the acid tank in a similar manner to a distillation process. The batch process was selected for demonstration because it is by far the simplest and most cost-effective technique. The results of the batch separation test yielded demonstrated concentrations from 50% H_2SO_4 (by weight) to 98% H_2SO_4, which yields a storage density of 641 Btu/lbm of dilute acid. The batch tests were very repeatable, and verification of heat transfer coefficients assumed in the computer model was obtained. Acid carryover in the water vapor was minimized to a value of 0.05% H_2SO_4 using Raschig rings in the reflux column.

The test goals of the recombination studies were to achieve repeatable recombination without interferences from noncondensibles and provide the design criteria for the total integrated system. Of the many approaches tested, the absorption column was clearly the best. Acid is pumped to the top of the reflux column (Reference Figure 1), where it is allowed to cascade down the Raschig rings. The large surface area provides ample reaction area for the condensation and absorption of water vapor. The tests were extremely repeatable and recombination was successfully demonstrated at acid concentrations as low as 50% H_2SO_4. The parasitic power required is less than 0.5% of the total stored energy.

The detailed design of the demonstration system has been completed as well as procurement of all components. The system is presently undergoing final assembly with the demonstration testing starting in October 1977. The acid tank is constructed from glass column components, with allowances in the design made for future optimization testing. The water tank is fabricated from 316 stainless steel, and uses copper tubing for the water condensor and boiler heat exchangers. A glass tube and shell heat exchanger is used for heating and cooling the acid. The charge and discharge rates have been sized for 25,000 Btu/hr, with a total capacity of 100,000 Btu's.

V. Future Activities

As mentioned previously, the demonstration testing will be started in October 1977. During this testing, the subscale system will be operated at thermal source temperatures of 150, 300, and 400°F. Round-trip efficiency and storage density will be calculated from the resulting data. Additionally, cycle tests will be conducted to determine the effects of acid carryover in the water vapor. The objectives of the next phase are to conduct an economic analysis of the system, including integration of various types of collector and building heating systems. The influence of geographical location and storage requirements such as weekly, monthly, and seasonal will be studied. Tests will be conducted with the subscale system for optimization of components to increase cost effectiveness. Additionally, an assessment of the environmental impact of using sulfuric acid as a storage media will be conducted. Building codes and institutional barriers will be studied. The Phase II-A studies are planned to begin in December 1977, and conclude in September 1978. The Phase III program, to design and test a pilot plant, is planned for initiation at the beginning of the fiscal year 1979.

Figure 1

H_2SO_4/H_2O CHEMICAL HEAT PUMP

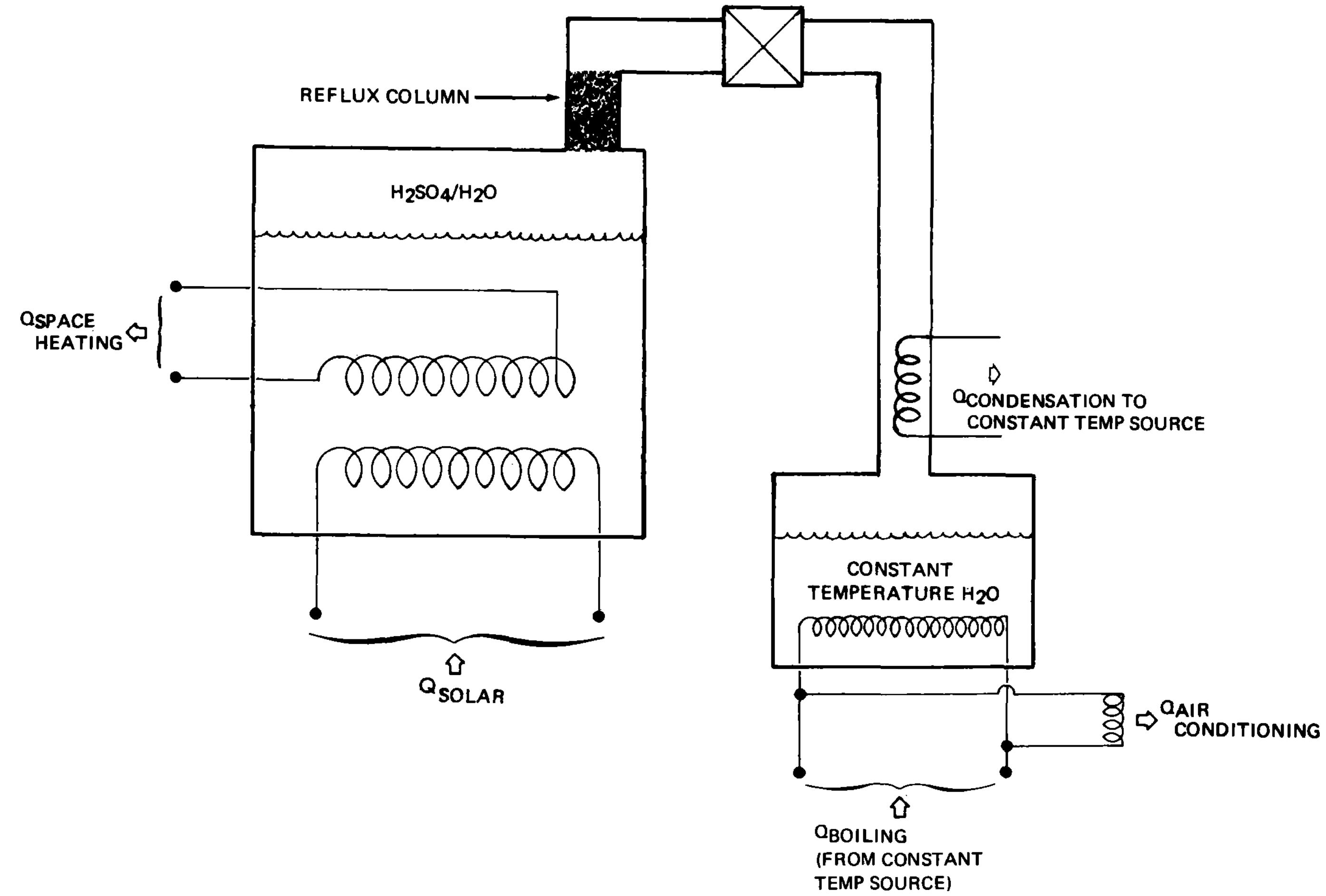


Figure 2
STORAGE DENSITY SULFURIC ACID HEAT PUMP
MINIMUM ACID CONCENTRATION = 53%
CONSTANT TEMPERATURE SOURCE = 52°F

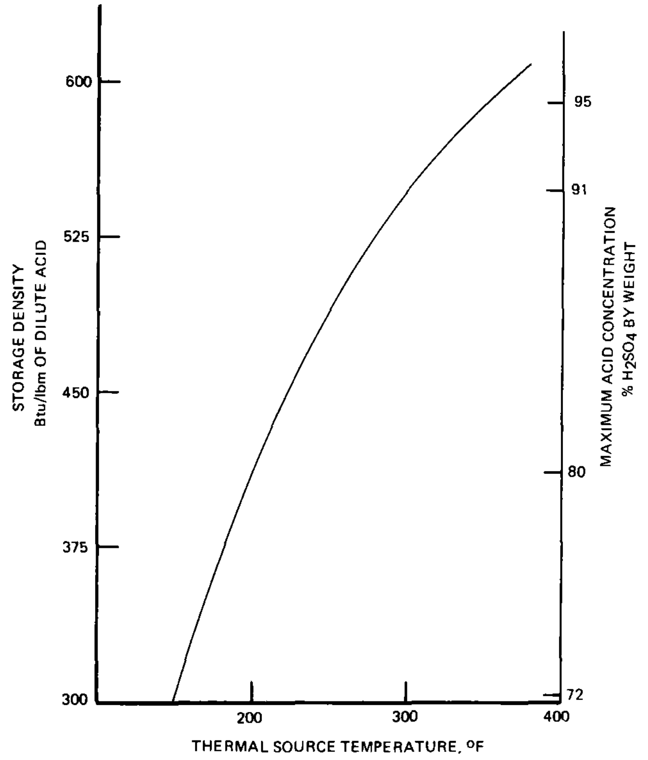
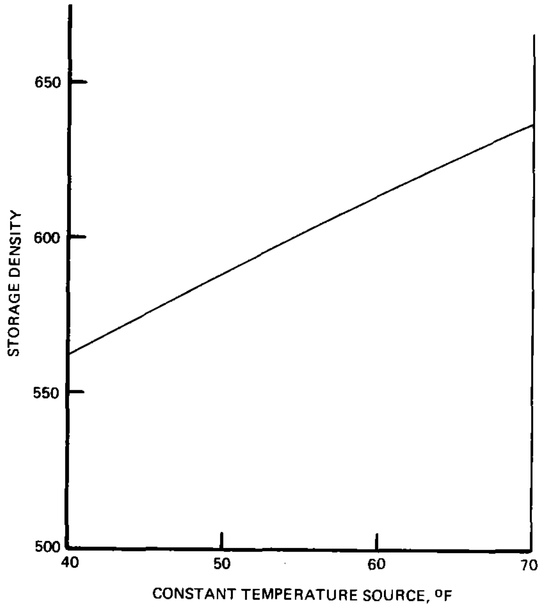


Figure 3
STORAGE DENSITY
SULFURIC ACID HEAT PUMP
THERMAL SOURCE TEMPERATURE = 350°F



PROJECT SUMMARY

ORGANIZATION: University of Houston

ADDRESS: 4800 Calhoun, Houston, Texas 77004

PROJECT TITLE: Cyclic Catalytic Solar Energy Storage Systems

PRINCIPAL INVESTIGATOR: Dr. W. W. Wendlandt TELEPHONE NO: 713/749-2614

CONTRACT NO: EG-77-C-04-3974 (Task III) CONTRACT PERIOD: 5/1/77-4/30/78

CONTRACT AMOUNT: $25,000

PROJECT GOALS:

The goal of this preliminary study will be to optimize the process stages of the EVA-ADAM concept of energy storage and transmission and to determine the process parameters at the steam reforming - liquid sodium receiver end. This will provide not only an indication of the feasibility of the system but also establish the range of temperatures, pressures and composition to be encountered by the reforming catalyst.

PROJECT STATUS:

The project is now entering its fifth month and all tasks are on schedule.

I. PURPOSE

The purpose of this preliminary work will be to optimize the process stages and determine the process parameters at the steam reforming-liquid sodium receiver end. This will provide not only an indication of the feasibility of the scheme but also establish the range of temperatures, pressures and composition to be encountered by the reforming catalyst.

II. BACKGROUND INFORMATION

The EVA-ADAM concept of energy storage and transmission will be interfaced with the proposed liquid sodium receiver system. The former is a potential method for solar energy utilization in which the steam reforming reaction of methane is carried out at high temperatures with the resultant transmission of the "synthesis gas" to a demand center and then methanation to produce heat. Due to the question of cyclic heat supply at the solar tower collector, the reforming reactor will be interfaced to a liquid sodium receiver which will contain a thermal storage unit and a heliostat subsystem optimized for this receiver. The liquid sodium offers three advantages: (a) higher efficiencies due to possible higher temperatures; (b) equal nighttime (thermal storage) and daytime cycle efficiencies; and (c) smaller, lighter and less expensive receiver.

III. PROJECT DESCRIPTION

1. Computer programs will be developed modelling each of the steps in the overall process. These include: (a) Steam reforming at the liquid sodium - reforming reactor; (b) Cooling and water removal; (c) Carbon dioxide removal; (c) Transmission from the reactor to the demand center; (e) Storage; (f) Shift reactions; (g) Methanation and heat removal; (h) Carbon dioxide removal; (i) Transmission back to the reforming reactor. For each of the stages, equilibrium compositions will be calculated as a function of pressure, reactor temperature, and quantity of heat supplied.
2. Two possible cases will be considered: (a) Single pass operation, i.e., methane supply to the collector and heat/methane extracted

at the demand center. (b) Equilibrium operation, i.e., a steady-state closed loop system. Carbon and energy efficiencies will be calculated for both cases. Reactor temperature will be the principal parameter but process configuration, such as the removal of CO_2, etc., will also be considered.

3. Isothermal operation in (2) will be compared with cyclic operation to be expected from current designs for: (a) The liquid sodium receiver; (b) Direct heat exchange at the solar tower collector; (c) Utilization of other heat storage systems.
4. Comparison of these variations will be made; including a preliminary estimate of the economic factors involved.
5. The process configuration, operating ranges, etc., will be determined for the optimum case. Comparison of vessel sizes, etc., will be made using existing catalyst information.
6. A list of catalyst performance requirements will be made together with a plan for future research and development to meet these needs.

IV. RESULTS

A computer model of the proposed cyclic CO/CH_4 solar storage process has been prepared. This model identifies two major stages (solar plant heat input and demand plant heat output), required interstage processes (heat exchangers to heat or cool the input and output streams at each plant), steam generation and water removal, compression and pipeline transport), and optional operations (carbon dioxide removal, carbon monoxide shift, sulfur removal). The model, as developed to date, gives equilibrium compositions for all streams as a function of process operating conditions (temperature, pressure, steam-hydrocarbon ratios). Necessary heat inputs and diverted heat outputs are also calculated. The model may be run at a number of different modes, i.e.:

(1) Isothermal at all stages.

(2) Single pass or recycle for the methane feed.

(e) Non-isothermal - cyclic at the solar plant and/or adiabatic at the demand plant.

(4) With or without interstage processes.

These capabilities will be used to assess:

(1) Optimum configuration.

(2) Optimum operating conditions.

(3) Overall efficiencies.

V. FUTURE ACTIVITIES

Further work will continue on the computer model of the proposed cyclic H_2-CO/CH_4-H_2O solar storage system, using the ideas discussed under Part III, Project Description.

PROJECT SUMMARY

ORGANIZATION: University of Houston

ADDRESS: Cullen Boulevard, Houston, Texas 77004

PROJECT TITLE: Development of Operational Chemical Cycles for the Storage of Energy

PRINCIPAL INVESTIGATOR: Wayne E. Wentworth TELEPHONE NO.: 713-749-2627

CONTRACT NO.: EG-77-C-04-3974 (Task I) CONTRACT PERIOD: May 1, 1977 - April 30, 1978

CONTRACT AMOUNT: ERDA $227,283
OTHER

PROJECT GOALS:

The overall objective of this program is to find, develop, and demonstrate a chemical reaction cycle which can be used for solar energy storage and regeneration in conjunction with electrical power generation systems which operate within the temperature range 450-500°C. In particular, the thermal decomposition of ammonium hydrogen sulfate (NH_4HSO_4) into ammonia (NH_3), water (H_2O), and sulfur trioxide (SO_3) is being investigated for the energy storage step:

$$NH_4HSO_4 \rightarrow NH_3 + H_2O + SO_3 \qquad \text{Energy Storage}$$

and the reverse recombination reaction:

$$NH_3 + H_2O + SO_3 \rightarrow NH_4HSO_4 \qquad \text{Energy Regeneration}$$

for the energy regeneration step. The overall cycle has high energy storage density and should be operable at the desired temperature. The program includes the efforts of three research groups (identified as phase IA, IB, and IC) which work separately but coordinate their efforts and planning through bi-weekly meetings.

PROJECT STATUS:

The project is now entering its 5th month and all tasks are on schedule at this time. Providing there are no unforeseen delays in ordering equipment and chemicals we expect the project to remain on schedule.

I. Purpose

The purpose of this project is to develop operational chemical cycles which can be used to store energy for subsequent use in electrical power generation. The cycle will be demonstrated using concentrating solar energy from a parabolic dish. The reaction which will be given most serious consideration is the thermal decomposition of ammonium hydrogen sulfate (AHS):

$$NH_4HSO_4 \rightarrow NH_3 + H_2O + SO_3 \qquad (1)\ \text{Energy Storage}$$

and the reverse recombination reaction:

$$NH_3 + H_2O + SO_3 \rightarrow NH_4HSO_4 \qquad (2)\ \text{Energy Regeneration}$$

for the energy regeneration reaction. Since these reactions are uncatalyzed a satisfactory separation scheme must be worked out for reaction (1). Also the proper conditions for the reverse reaction must be established so that heat in the desired range 450-500°C can be regenerated. The process and engineering configurations will be developed for the operational chemical cycle selected. In addition the solar energy input configuration from a parabolic collector will be integrated into the system to demonstrate the storage of solar energy for power generation.

II. Background Information

The decomposition of ammonium hydrogen sulfate into NH_3, H_2O, and SO_3 is well documented in the literature and several patents are related to the process. This information is helpful in this project; however, in order to use the reaction for energy storage the reactions must have very high yields so that the process can be cycled many times without excessive loss of ammonium hydrogen sulfate. Furthermore, the process must be carried out conserving energy so that a high thermal efficiency can be attained for the process. The use of chemical reactions for energy storage have unique requirements that must be addressed in the research program.

III. Project Description

A. Phase IA Chemical Reaction Fundamentals

Various reaction mechanisms will be screened (literature and experiment) in search of net reaction cycles which are equivalent to reactions (1) and (2) and which allow satisfactory separation of SO_3 from NH_3 and H_2O at high temperature. The use of metal sulfates to form intermediate pyrosulfates:

$$NH_4HSO_{4(sol)} + M_2SO_{4(sol)} \xrightarrow{T_{1a}} NH_{3(g)} + H_2O_{(g)} + M_2S_2O_{7(sol)} \qquad (1a)$$

$$M_2S_2O_{7(\ell)} \xrightarrow{T_{1b}} M_2SO_{4(s)} + SO_{3(g)} \qquad (1b)$$

where M is any group IA metal, and the use of metal oxides to form intermediate sulfates:

$$NH_4HSO_{4(s)} + MO_{(s)} \xrightarrow{T_{1c}} NH_{3(g)} + H_2O_{(g)} + MSO_{4(s)} \qquad (1c)$$

$$MSO_{4(s)} \xrightarrow{T_{1d}} MO_{(s)} + SO_{3(g)} \qquad (1d)$$

where M is a metal, will be studied as possible mechanisms for accomplishing reaction (1). Physical methods of separation will also be considered. Promising reaction mechanisms will be analyzed experimentally to identify any detrimental side reactions.

After suitable reaction mechanisms (including separation procedure) are identified, appropriate kinetic and thermodynamic measurements will be made on the decomposition and recombination steps of each. These will be used to establish the best reaction conditions for each mechanism. Finally a high pressure reactor will be designed to study the individual mechanisms under operational conditions and to test long-term reversibility.

B. Phase IB Process and Engineering Configurations

The most suitable chemical reaction cycle selected through the work of phase IA will be investigated in a flow mode. Transport and thermal data will be obtained from the literature on the reactants and products. Design equations will be developed and used to design a flow mode bench scale reaction unit. The flow reaction kinetics and heat transfer characteristics will be studied for each reaction step in the cycle. These results will then be used to design and specify a pilot unit. The economics and technical feasibility will be under constant consideration.

C. Phase IC Solar Energy Input Configuration

Solar input configuration studies will be conducted simultaneously with the work of phases IA and IB. These will involve location and evaluation of parabolic solar concentration systems, establishment of specifications, procurement of suitable concentrator, and preliminary heat transfer studies. Materials suitable for a solar heated reactor will be identified. Throughout the project, high temperature receiver design studies at other research facilities will be followed, and from these a conceptual design for a full scale demonstration plant including storage will be developed. The basic cost estimates of the chemical storage portion of a solar tower electrical system will be developed for inclusion in the annual report. The chemical modification cost estimate will be updated upon completion of the conceptual design.

IV. Results

A. Phase IA Chemical Reaction Fundamentals

The principal objective in the early stages of Phase IA is to find a workable mechanism for accomplishing reaction 1 (energy storage) with a high product (NH_3,H_2O, SO_3) yield and in a way which allows separation of these products at the temperature under which this yield is realized. Two mechanisms (reactions 1a + 1b, or reactions 1c + 1d) are being investigated.

Reactions 1a and 1b require different temperatures for measurable yields. The separation of $NH_{3(g)}$ and $H_2O_{(g)}$ from $SO_{3(g)}$ is facilitated if reaction 1a can be run to completion at some temperature T_{1a} which is less than the temperature T_{1b} required to drive reaction 1b to completion. For this separation process is to be workable, T_{1a} must be sufficiently lower than T_{1b} so that the yield of $SO3(g)$ from reaction 1b is negligibly small at T_{1a}.

The literature data for many specific examples of reactions 1a and 1b has been analyzed and the group IA metal sulfates have been selected as the most promising choices for M_2SO_4, but other metal sulfates are also being considered.

A laboratory apparatus has been constructed for studying these reactions experimentally. Briefly the experiments involve placing weighed amounts of NH_4HSO_4 and M_2SO_4 in a fixed mole ratio inside a quartz reaction tube and heating the mixture. The reaction tube is connected to a vacuum manifold. The internal volume of the manifold plus reactor is calibrated and the pressure generated in the vacuum system is measured as a function of the reaction mixture temperature. The manifold includes a trap cooled to zero °C in which most of the water evolved is condensed. At slow heating rates (~ 1°C/min) the partial pressures of the gases in the vacuum manifold are assumed to be those in equilibrium with the reaction mixture at a given temperature. Reaction 1a is assumed to proceed through a continuous series of equilibrium conditions as the temperature is increased until the amount of NH_4HSO_4 is insufficient to produce the equilibrium $H_2O_{(g)}$ and $NH_{3(g)}$ partial pressures at a given temperature. At this temperature (T_{1a}) the reaction goes essentially to completion and the pressure increase stops. From such curves the experimental value of T_{1a} was measured for a variety of reaction mixtures. Since the equilibrium pressure approaches the maximum asymptotically, it is difficult to determine T_{1a} quantitatively. For this reason the results are not particularly consistent for a given M_2SO_4. This inconsistency in T_{1a} may also reflect a lack of consistency in heating rate. The furnace used in these experiments does not have adequate controls to allow a constant and reproducible heating rate to be maintained over the experimental temperature range.

The most significant conclusion from these experiments is drawn not from T_{1a} itself but from the temperature at which there is a sharp rise in pressure for the different reaction mixtures. Qualitatively this temperature is highest for the NH_4HSO_4 + Li_2SO_4 system and decreases as the metal sulfate is changed according to the following order:

$$Rb_2SO_4 < K_2SO_4 < Na_2SO_4 < LiSO_4$$

The reaction of Cs_2SO_4 + NH_4HSO_4 has not been run under precisely the same conditions but from other results appears to be similar to the reaction with Rb_2SO_4. From this we conclude that the heavier metal sulfates will give a higher yield of NH_3 at a given temperature than the lighter metal sulfates, and for reasons of material cost and supply we are focusing on K_2SO_4 or Rb_2SO_4 as the most promising choices for use in reaction 1a.

Several metal oxides have been investigated for the separation described in Reactions 1c and 1d. Zinc oxide appears to be the most promising candidate examined thus far in the research. Reaction 1c occurs at ≃ 362°C and reaction 1d at ≃ 880°C.

In order to run the reactions at higher pressures we will need to use metal reactors. Since the reaction mixtures being considered are potentially very corrosive, we have initiated a systematic study of the corrosion of the metal. Thus far only K_2SO_4 + NH_4HSO_4 mixtures have been run at 450°C containing various metal coupons. The metal showing the least amount of corrosion is Rene 41 which gave a weight loss of 0.0030 g/cm^2 over a 24 hour period.

B. Phase IB Process and Engineering Configurations

Work has begun on compilation of information from the literature into an engineering data book where key properties of reactants and products will be presented as functions of temperature and pressure. A preliminary mathematical model has been developed for the design of tubular flow reactors to predict heat transfer, conversion, and pressure drop down the tube. This model has been applied to sample calculations of three arbitrarily selected reactor capacities to get a feel for its use and a preview of possible difficulties. A preliminary bench scale design has been completed for the flow system, initial reaction step, in which inert gas pressure forces the molten salt feed through electrically heated coiled tube preheater and similar reactor. Temperature is monitored through the system, which is maintained at the appropriate pressure by back pressure control. The gaseous products are collected for measurement and analysis. Procurement has begun for supplies and equipment to modify an existing bench scale flow reaction unit for this service and set up of the facility is under way. A study has been completed of the off-axis effects in a Cassegrainian solar concentrator, including prediction of the size of the hyperbolic reflector, the size of the solar image as reflected from the hyperboloid in terms of the point of first reflection from the parabolic surface, and how much energy will be accepted by a hole into a solar furnace which is smaller than the largest solar image. Work is under way to determine the incident concentrated solar flux intensity inside short cylindrical, long cylindrical, and conical furnaces heated by a Cassegrainian concentrator. Proper selection of furnace configuration can give a constant flux intensity distribution or zones of high and low flux intensity distribution inside the furnace. Samples of high temperature alloys are procured and cut into corrosion test coupons.

C. Phase IC Solar Energy Configuration

For a parabolic solar concentrator of a design based on a tracking microwave antenna with an optically reflective coating on the dish, a survey was completed of sources of parabolic concentrators. Specifications for a parabolic concentrator were set and prospective vendors were selected. A survey was completed for high temperature materials and it was concluded that a nickel-chromium alloy would be required for reactor tubing; a half dozen were selected for corrosion testing. Work is under way to determine incident flux intensity inside of solar furnace configurations heated by a simple parabolic concentrator. Plans have been made for a heat transfer study during steam generation in a solar furnace heated by a parabolic concentrator.

V. Future Activities

A. Phase IA Chemical Reaction Fundamentals

Evaluation of separations using M_2SO_4 and MO (Reactions 1a to 1d) will be continued and the yields of the reactions will be determined. The high pressure reactor will be built and the reactions carried out at high pressure. Analysis of trace components will be carried out using gas chromatography and mass spectrometry. Solubility measurements of M_2SO_4 and MO in NH_4HSO_4 will be carried out on the most likely candidates for the separation procedure. Corrosion studies will continue with a comparison of electron micrographs of the metals before and after the reaction.

B. Phase IB Process and Engineering Configurations

The flow reaction study of the initial decomposition step will be followed by a heat transfer study for the same step. Flow reaction and heat transfer studies will be done for the second reaction step. A flow unit for the recombination step will be designed, fabricated and operated for flow reaction and for heat transfer studies. A pilot scale unit will be designed, and the process economics will be evaluated.

C. Phase IC Solar Energy Input Configuration

Some variation on a parabolic solar concentrator will be purchased and installed. Prototype receivers/furnaces will be designed, fabricated, and tested with the parabolic concentrator. Heat transfer experiments will be run while generating steam with the various dish-furnace combinations. Receiver specifications will be developed for a final design. A conceptual design will be developed for a full scale demonstration plant.

During the fourth and fifth years, we expect to fabricate and operate a complete, small scale pilot unit, with parabolic heating, to demonstrate the success of chemical storage of energy, and to obtain information for the design of a full scale prototype unit.

IV. COORDINATE PROGRAMS

THERMAL ENERGY STORAGE R&D PROGRAM FOR SOLAR HEATING AND COOLING

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Solar Heating & Cooling
R&D Branch, DSE, ERDA

INTRODUCTION

U. S. Government support for the development of solar energy technologies was initiated primarily through National Science Foundation grants for research on solar energy materials, components and systems. Many of these programs were continued by ERDA, after its creation, and were augmented by additional R&D projects selected from the large number of unsolicited proposals submitted to ERDA.

This resulted in a fairly substantial program which has produced a great many significant advances both in the basic understanding of solar energy processes and in the practical engineering technology of solar energy devices. However, built upon a base of relatively random unsolicited proposals, this program was inevitably uneven, being very strong in some technological areas and weak or lacking in others. Recognizing this uneveness in the program, specifically in the area of solar heating and cooling, the R&D Branch of the Division of Solar Energy initiated a general assessment of solar heating and cooling technologies and, based on this assessment, the formulation of an overall R&D plan for the directed development of these technologies to the level required for successful and widespread commercialization of solar heating and cooling systems. The lead role in the formulation of the technical assessment and R&D plan was given to Los Alamos Scientific Laboratory, which was assisted in its work by five other national laboratories. Each of the national laboratories was also given the responsibility for technical monitoring of a specific area of solar heating and cooling technology.

As a final step in moving to a fully planned and directed R&D program, the R&D Branch is presently conducting a large series of proposal solicitations to fill in the weak or missing areas in the existing program.

THERMAL ENERGY STORAGE AND HEAT EXCHANGE

The basic characteristics of solar energy (its low energy density, intermittency, and the lack of coincidence between the times of greatest availability and the energy load demand pattern) make energy storage an absolutely essential factor for its successful utilization. The Thermal Energy Storage (TES) program of the Solar Heating and Cooling R&D Branch has evolved in much the same manner as the other technical areas. However, because of the many non-solar applications of energy storage, the bulk of the Governments' R&D program in Energy Storage was centered in the Conservation Administration's Division of Energy Storage Systems (STOR). Specifically, the Chemical and Thermal Storage Branch of STOR is supporting a wide range of R&D projects in TES, including many with potential or specific solar energy heating and cooling applications. A close liaison has been maintained between the TES programs of the two branches, and a delineation of responsibility has been defined. In general, the R&D Branch sponsors those projects characterized by fairly mature storage technologies, where the emphasis is on utilizing the technology for specific solar applications. In addition, it also assumes responsibility for the application of more advanced technologies whenever these reach a level of maturity sufficient for practical integration into a solar system. For solar heating and cooling applications, there is a further limitation in that the maximum storage temperature should not exceed 350°F.

The general objectives of the R&D program in thermal energy storage and heat exchange are to develop TES subsystems which, compared to existing systems, have reduced initial and life cycle costs, improved heat exchange and volumetric storage capacity, and a greater retrofit capacity. The technical assessment revealed a large number of specific problems and R&D needs in seven technical areas, which needed to be dealt with in order to meet these overall objectives. These specific technical problems and needs are summarized in Table I.

TABLE I. Thermal Energy Storage and Heat Exchange - Status, Problems, and Needs in Various Technical Areas

A. Systems Performance and Modeling

System computer codes with TES subroutines, and separate TES codes exist. Steady-state modeling is adequate; transient poor. No adequate models for phase change materials. Insufficient well-instrumented systems. Need development, standardization, and documentation of codes. Need comprehensive user-oriented TES handbooks.

B. Heat Transfer and Exchange

Need lower cost, improved performance and durability heat transfer fluids, heat exchangers, piping and duct work, insulation, and heat circulation and control systems. Need improved system design and packaging, and integrated TES-HE systems, to reduce manufacturing and installation costs.

C. Water Tank Thermal Energy Storage

Present technology is metal, anticorrosion coated, insulated tanks at cost of 50 to 75¢/gallon. Need lower cost and increased durability tanks, waterproof insulation, and auxiliary heat devices; improved retrofit application through new designs and/or materials; investigation of temperature stratification, multiple tanks, hybrid systems, large tanks for annual storage, heat pump input, and passive storage.

D. Rockbed Thermal Energy Storage

Technology well developed and relatively low cost. Need to investigate higher and lower temperature, cooling and heat pump applications, health hazards, and retrofit. Adequate models need to be developed.

E. Phase Change Materials (PCM) Thermal Energy Storage

Many PCM for TES under study; few well understood or tested. Additional research required, particularly in 195 to 300°F range. Encapsulation of PCM needs reduced cost, better durability, and increased heat transfer rate and storage density. Need to develop detailed PCM models.

F. Chemical Reactions Thermal Energy Storage

Has greatest potential for high-density, long-term TES. Few chemical systems known or adequately studied in applicable range. Additional research required. Development of models required.

G. Tests and Standards

ASHRAE/ANSI TES performance consensus standard adopted. Need evaluation and improvement in this standard. Need standards for testing durability and safety of TES devices.

The R&D plan encompasses these specific problems and needs by defining a set of fifty-one R&D tasks in the seven TES technical areas as follows:

There are ten tasks defined in Storage System Studies, which include complete TES subsystem analysis, modelling and validation testing, handbook preparation, passive TES, annual storage systems, and the preparation of R&D guidelines for advanced TES studies. In the Heat Transfer and Exchange area there are nine tasks covering piping, ducting and heat exchanger cost and performance analysis and development, as well as a study of self pumping systems; while in the Water Tank Storage area, thirteen R&D tasks are specified to develop lower cost and higher performance and durability water storage tanks and to design and develop components and systems specifically for retrofit, passive storage, and air conditioning applications. Five R&D tasks are described in Rockbed Storage, chiefly for heat pump and cooling applications. In Phase Change Materials Storage nine tasks are defined for further research on newer materials and for the engineering development of prototype storage components, utilizing the better understood materials, for hot water and space heating and cooling applications. In the area of Chemical Reaction Thermal Energy Storage, there are three R&D tasks for continuing the investigation of known suitable reactions, and for the uncovering of additional suitable chemical reactions and materials. Finally, two tasks are defined for the improvement of existing, and the development of new Test Procedure Standards for TES components.

ACCOMPLISHMENTS AND FUTURE PLANS OF CURRENTLY FUNDED PROGRAMS IN TES

A number of the problems identified in the technical assessment, and the related tasks defined in the R&D plan are already being addressed in the currently funded program of the R&D Branch. At present there are eight ongoing projects in four different areas. These eight projects and their major accomplishments and future plans are listed below:

HEAT TRANSPORT AND EXCHANGE

Conventional Heat Exchangers - Altas Corp.

1. Completed data compilation and analysis on commercially available heat exchangers and on properties of heat transfer fluids.
2. Developed computer simulation programs for a two-fluid, counterflow heat exchanger into a water tank, and for a jacketed (externally bonded heat exchanger tubes) water tank.
3. Developed a computer program for optimizing the design parameters of counterflow and jacketed tank heat exchangers.
4. Planning future evaluation and development of double wall, buffered heat exchangers.

Direct Contact, Liquid-Liquid Heat Exchanger-Colorado State Univ.

1. Completed general survey of potential heat transfer fluids for this device, and a toxicological evaluation of the top 34 candidate fluids. Completed detailed property analyses on three of the thermally superior and least toxic liquids.
2. Successfully completed pilot plant tests of liquid-liquid heat exchanger design with each of the three liquids.
3. Completed design, construction, and installation in a mobile trailer of a full-scale (1000 gal) steel, liquid-liquid heat exchanger.
4. Completed thermal performance analyses and preliminary cost estimates. Costs expected to be lower than standard heat exchanger systems.
5. Future planned activities include:
    a. Testing of the full-scale device, using simulated heat source and heat load to determine overall heat transfer characteristics and best mechanism for extracting heat from the tank to the load.
    b. Connecting the full-scale unit to either Solar House I or III and conducting a full winter season operation to determine system performance characteristics and efficiency.

ANNUAL STORAGE WITH WATER AS THE STORAGE MEDIUM

Large, Well-insulated Underground Water Tanks-Univ. of Toronto

1. Developed and validated a computer simulation program for an annual storage vertical cylindrical water tank system. This includes a sizing optimization program and a system economics calculation.

2. Completed simulation runs for several years performance, based on Ontario's Provident House parameters, and 10 year average weather data. The model predicts that 100% solar heating can be provided for these conditions. Short-term insolation fluctuations have no effect on the system performance due to large thermal mass of storage tank.

3. Computed cost projections for large annual storage tank systems. In the 10^5 to 10^6 gal range (for multi-unit residences, or large apartment houses or commercial buildings), estimated construction costs vary from 16¢/gal down to 8¢/gal.

4. Developed a noncomputer algorithm for optimization of annual storage solar heating systems on a life cycle cost basis. Optimum sizing falls slightly below the capacity required for 100% of heat requirements for the average year (based on 10 year weather data).

5. Future planned activities include:

   a. Further development of the simulation model to include square cornered tanks and soil layering.

   b. Validation of the model against data from last year and a full year's operation in the coming year, for Provident House.

   c. Calculation and tabulation of a full set of values of the annual storage tank heat loss parameters for the complete range of likely tank and soil configurations. Based on this, a noncomputer algorithm will be developed which will allow simple calculation of the optimum configuration annual storage solar heating system for a given set of parameters (heat demand, ambient temperatures, etc.).

Large Capacity, Low Cost Heat Storage Pool - University of Virginia

1. Completed construction of and filled an annual solar energy collection and storage pool (capacity 27,400 gal). This consists of a plastic lined, uninsulated sloping earth wall pool covered by floating styrofoam beads and a near horizontal solar energy trickle collector (surface area 576 ft^2), with a vertical reflector.

2. Successfully completed five months of operation, in the energy collection mode only. Temperatures in the pool have reached stratified values of 133°F at the top of the pool and 113°F at the bottom.

3. Future planned activities include:

   a. Continued operation of system in heat collection mode, until October when heat extraction into a simulated load will begin.

   b. Make design modifications in the trickle collector and the pool heat input and output procedures based on performance data and simulation predictions.

   c. Analog and computer digital simulation models which are under development will be validated against measured pool performance and then used for prediction of pool performance under various conditions and for the design of improved system components.

   d. A general cost analysis will be made.

PHASE CHANGE THERMAL ENERGY STORAGE WITH PARAFFIN AS THE STORAGE MEDIUM

Macroencapsulated Paraffin - North Carolina State University

1. Determined the physical and thermal properties of ten commercial waxes considered as potential candidates for this application.

2. Completed construction and thermal performance and cycling tests on reduced scale paraffin thermal energy storage devices of three different heat exchanger container designs including: a honeycomb structure; a tube and fin; and a corrugated plate. Both commercial and pure

paraffin was used and in all cases, heat transfer rates were reasonable and no performance problems were encountered.

3. Planning to complete a relative cost analysis of the different device designs.

Microencapsulated Paraffin - General Electric

1. Small samples of encapsulated paraffin pellets of satisfactory size, wall uniformity, and durability were developed and delivered by Pennwalt Corp.
2. Completed successful cycling tests on a small laboratory scale sample.
3. Future planned activities include:
   a. Obtaining a satisfactory, pilot plant scale encapsulated pellet sample and conducting packed bed cyclic tests on it.
   b. Preparing a detailed cost analysis of this TES concept.

MISCELLANEOUS

Test Procedures and Standards - National Bureau of Standards

1. Adoption by ASHRAE of Standard 94-77 for performance testing of TES devices. Also adopted as ANSI Standard B199.1-1977.
2. Completed construction and testing (in accordance with 94-77 test procedures) of a 500 gal water tank and a 64 ft^3 pebble bed. Air leakage and moisture transfer were found to seriously affect the reproducibility and validity of the air fluid-pebble bed tests.
3. Participated on ASTM and ASME Standards committees, and prepared test methods and procedures for TES devices with respect to safety, durability, etc., for interim performance criteria.
4. Future planned activities include.
   a. One or more phase change TES devices and one encapsulated water TES device will be tested in accordance with ASHRAE Standard 94-77.
   b. Improvements and modifications in ASHRAE 94-77 will be suggested based on test experiences in the past and upcoming year.
   c. Establishment of consensus standards on TES device testing with respect to safety, and general reliability and durability of materials and components.

Thermal Energy Storage and Heat Exchange Handbooks - Argonne

1. Completed a preliminary survey on commercially available water tanks, plumbing, insulation, heat exchangers, etc, as well as associated installation, cost, maintenance, and other related factors.
2. Prepared and tested a computer program for calculating rockbed pressure drop, heat transfer, and thermal stratification as a function of rock size, bed dimensions, and air velocity. Currently generating a series of parameter combination curves for rockbed design guidance.
3. Completed a survey of a selected sample of the solar manufacturing and installation industry, with respect to information needs and desired format in the thermal energy storage area.
4. Future planned activities include:
   a. Preparation of the first draft of a design and installation manual for use by small residential and commercial builders and HVAC contractors. This manual is scheduled for several cycles of review by potential users, and subsequent revisions before finalization.
   b. Preparation of the first draft of a state of the art review and analysis of advanced thermal energy storage systems for solar heating and cooling applications, currently available or under development.
   c. Preliminary studies aimed at preparation of a TES design handbook for passive and hybrid solar heating and cooling systems.

NEW PROJECTS INITIATED THROUGH RFP & PRDA SOLICITATIONS

A total of 18 new R&D projects in six technical areas of TES have been initiated by awards made under the RFP & PRDA solicitations. A brief description of these projects is given below:

1. HEAT TRANSFER AND EXCHANGE

a. Self-controlling, Self-pumping Heat Circulation System Study - The Franklin Institute Research Laboratories: Review and evaluation of the technical and economic feasibility of all known methods for circulating and regulating heat flow without the use of active mechanical pumps and controls.

2. SHORT-TERM STORAGE IN WATER TANKS

a. Modeling and Measurement of Thermal Stratification in Water Tanks - University of Alabama: Development of computer programs, with experimental validation, for predicting thermal stratification in water tanks of varying configuration, and the effect of various degrees of thermal stratification on solar system performance.

b. Hybrid Thermal Storage with Water - Rockwell International Corp., Atomics International Division: Review and evaluation of the technical and economic feasibility of a TES system combining water tank with additional storage media.

c. Gas Backup Heater - Altas Corp: Development, fabrication, and testing of a novel, automatic backup heater for a solar heated domestic water system.

d. Fiberglass Reinforced Plastic Sandwich Wall Water Tank - Independent Living, Inc: Development, fabrication, and testing of a fiberglass water tank, with insulation and strength provided by a sandwich construction between a waterproof plastic liner and the outer fiberglass shell.

e. Flexible Fabric Water Tank Storage - University of Nebraska: Development, fabrication, and testing of cost effective, flexible fabric water storage containers, supported on an insulated frame.

f. Modular Insulating Concrete Water Tanks - Westinghouse Advanced Energy Systems: Design, fabrication, and testing of several light-weight concrete water storage tanks constructed of prefabricated modular sections of water impermeable insulating concrete.

3. ROCKBED STORAGE

a. Rockbed Storage for Cooling - Dynatech R&D Company: Evaluation, on a regional basis, of the technical and economic feasibility of using a rockbed, chilled by night air or evaporatively cooled air, for space cooling applications.

b. Rockbed - Heat Pump Analysis - California State U at Fullerton: A systems analysis of various heat pump series-parallel arrangements in a rockbed thermal energy storage unit.

c. Optimum Matching of a Heat Pump with a Rockbed - ZIA Associates: Determination of the feasibility of matching a heat pump to a rockbed thermal storage unit, and examination of the configurations and control strategies which provide optimum performance at lowest cost.

4. PHASE CHANGE STORAGE FOR SOLAR HEATING

a. Thermocrete Central TES System - Suntek: Development, construction, and testing of a central TES system constructed of "Thermocrete" (coated, phase change material permeated, foamed concrete) blocks.

b. Rolling Cylinder, Phase Change Material TES System - GE: Design, construction, and testing of a rolling cylinder TES device filled with phase change material.

c. Salt Hydrate-Eutectic TES Systems - CALMAC: An existing CALMAC TES device, with a synthetic elastomer mat as an integral heat exchanger, and two different phase change material formulations for the storage medium, will undergo development, testing, and a scale-up in size. The device will contain, in one case, a eutectic of sodium sulfate decahydrate, sodium chloride and ammonium chloride, which melts at 55°F, and, in the other case, sodium thiosulfate pentahydrate plus 2% sodium sulfate, which melts at 115°F.

5. THERMAL ENERGY STORAGE FOR SOLAR DRIVEN AIR CONDITIONERS

a. Paired-Ammoniated Chemical Reactions TES System - Martin Marietta Aerospace: Development of a TES system, based on two ammoniated chemical reactions, which accepts and delivers energy at a high temperature, but stores it at near ambient temperature.

b. Isothermal, Higher Temperature TES Systems - Univ. of Delaware: Investigation and development of isothermal TES systems in the 195 to 350°F transition temperature range. Prime candidates under consideration are ferrous sulfate heptahydrate, and pressurized boiling water.

c. Magnesium Chloride Hexahydrate TES System - CALMAC: This utilizes the same basic CALMAC TES device previously described. In this higher temperature application, the device will contain magnesium chloride hexahydrate, which melts at 240°F.

6. GENERAL TES MODELING AND GUIDELINES

a. Development and Upgrading of Solar System TES Simulation Models - Boeing Computer Services: Existing TES simulation models will be acquired, evaluated, and standardized as compatible system library modules in a general linkage program, based on an existing ERDA funded storage linkage program. These TES models will be upgraded and validated against operational data. Streamlined TES models will also be developed, utilizing the more detailed models for validation.

b. Advanced TES Guidelines - EIC Corp: Determination, through systems analysis, of the optimum role which advanced TES subsystems can play in solar heating and cooling applications. This project will provide guidelines for the direction of R&D in advanced TES subsystems.

A visual summary of the entire R&D Branch program in thermal energy storage and heat exchange is given in Figure 1, which indicates the specific projects, both current and new, in each TES technical area.

SOLAR HEATING & COOLING
RESEARCH AND DEVELOPMENT PROGRAMS

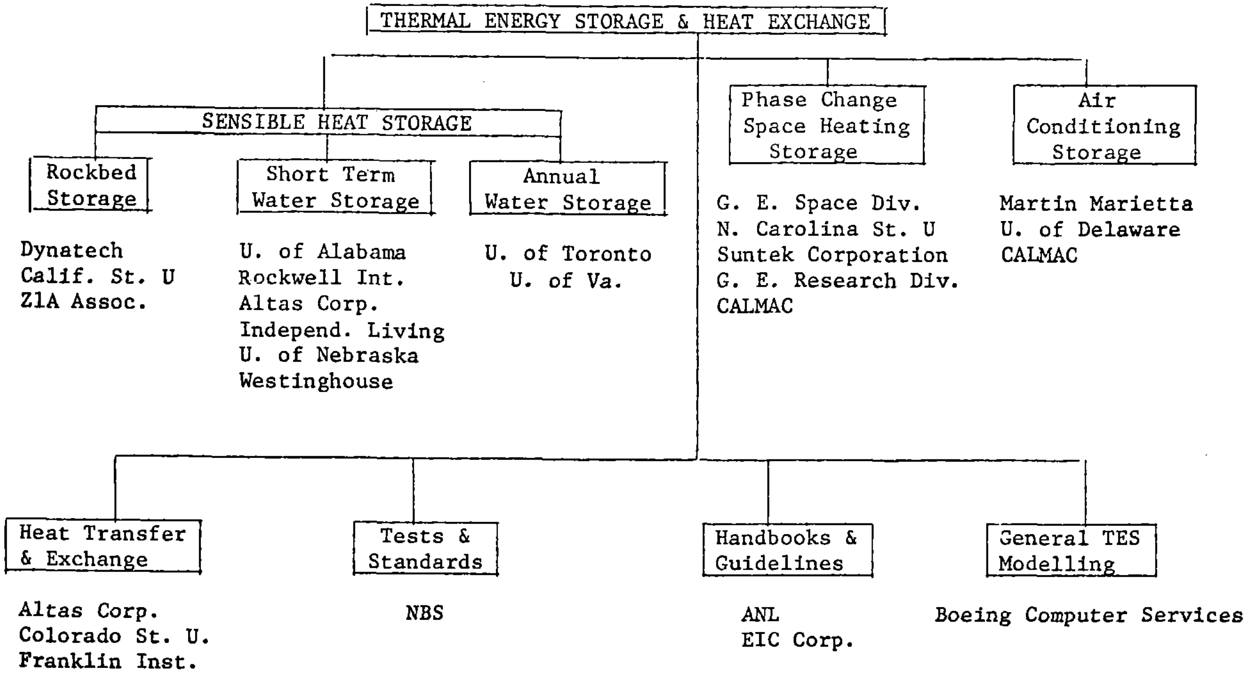

FIGURE 1

PROJECT SUMMARY

ORGANIZATION:	Argonne National Laboratory Special Projects Group
ADDRESS:	9700 South Cass Avenue Argonne, Illinois 60439
PROJECT TITLE:	Thermal Energy Storage - Space Heating Technical Validation
PRINCIPAL INVESTIGATOR:	R.M. Wolosewicz Telephone No. 312-739-7711 X5489

PROJECT GOALS: Using Operating TES System Data:

1. Establish TES Heating/Cooling Viability under U.S. operating conditions;
2. Develop realistic sizing criteria;
3. Develop R&D recommendations for new/improved systems;
4. Establish TES testing facility and develop TES standards;
5. Develop electric utility rate recommendations.

I. PURPOSE

The European experience with electric storage heating and systems studies of storage heating and cooling for application in the United States indicate that these technologies offer substantial energy conservation potential. Currently there is a pressing need to acquire and evaluate thermal energy storage (TES) cost and performance data under actual U.S. operating conditions. The proposed program will: acquire and evaluate TES heating baseline operating data; develop recommendations for improved TES heating system design; specify R & D needs; establish a facility for testing and evaluating conventional and prototype systems; and work to establish TES system standards.

II. BACKGROUND

Electric storage heating was rapidly commercialized in several European countries during the 1960's.* In West Germany, for example, installed capacity increased from 200 MW_e in 1960 to 19,000 MW_e in 1970. Today, installed storage heating capacity is approximately 40% of the West German peak power load.

The rapid growth of summer air conditioning peaks during the 1960's limited the U.S. market for storage space-heating. However, a continuation of the present rapid growth of electric space-heating loads will shift the former summer peak into a winter peak. In these peak-shifting utility areas, it will be advantageous to reduce the winter-peak growth by encouraging the installation of currently available TES space-heating systems.

There is currently a need to evaluate alternative TES system design and performance characteristics under U.S. operating conditions. The proposed program will establish baseline TES operating data, will develop recommendations for improved system design and operation, will specify R & D needs, and will work to establish U.S. TES heating/cooling standards.

III. PROJECT DESCRIPTION

The proposed program will experimentally evaluate in several utility service areas residential TES space-heating systems. The systems to be evaluated will include the available commercial (central and dispersed) electrical resistance storage units and heat pumps combined either with electrical resistance storage units or with an oil/gas auxiliary furnace.

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*See: *Electric Storage Heating: The Experience in England and Wales and in the Federal Republic of Germany*, ANL/ES-50 (April 1976).

The electrical resistance storage systems will be in-place for the 1977-78 heating season and the storage-heat pump systems will be installed for the 1978 heating season. Each TES system will be evaluated over two heating seasons.

In future work, cold storage applications in residential and in commercial buildings will be investigated.

As currently envisioned, the space-heating TES program will consist of the projects presented in the following table.

Table 1. TES Experimental Space Heating Projects

Project	TES Application	No. of Installations*	Instrumentation Cost Installed**	TES Installation Cost
1	Residential Storage Heating	35	140K	15K
2	Residential Storage + Heat Pump†	15	60K	40K

*Includes new, existing, and retrofit installations; does not include an equal number of control installations.

**Residential instrumentation costs include monitoring/recording equipment for experimental TES and for approximately the same number of control dwellings.

†Ten heat pumps with storage and up to five heat pump installations with auxiliary oil/gas furnaces.

Each project will be carried out by a local research team. ANL will select the project manager, while retaining overall program management control.

The program is divided into the following phases and tasks.

Phase I. Design of Experimental Evaluation Program.

- A. Define Program Objectives.
- B. Select Project Participants.
- C. Design Individual Projects.
- D. Establish Funding and Contractual Arrangements.

Phase II. Performance of Experimental Evaluation Program.

- A. Installation of TES and Monitoring Equipment.
- B. Acquisition of Data.
- C. Evaluation of Data.
- D. Documentation and Dissemination of Program Findings.

Phase III. R & D Recommendation.

Phase IV. TES Testing Facility.

PROJECT SUMMARY

ORGANIZATION:	Data Management Group Lawrence Livermore Laboratory P.O. Box 808, Livermore, California 94550
PROJECT TITLE:	Research Leading to the Production and Early Use of Numeric Data Banks of Material Properties and System Analyses
PRINCIPAL INVESTIGATOR(S):	Viktor E. Hampel and Terrence M. Quick
PHONE NO.: (1)	(415) 447-1100,X-4061,4995 (2) FTS: 457-4061, 457-4995
CONTRACT NO.:	E(49-1)3835 PERIOD: Ongoing
PROJECT GOALS:	(1) Creation of bibliographic and evaluated materials properties data bases for energy storage systems. (2) Creation of storage technology characterization data bases. (3) Remote access to energy storage data bases for comparative analysis and decision making.
PROJECT STATUS:	(1) Flywheel and molten salts/TES bibliographic data bases are being completed. (2) Molten salts/TES material properties data base under development. (3) PDP-11/70 computer system being set up to allow remote access to data bases.

TECHNOLOGICAL DATA BASES FOR ENERGY STORAGE

Terrence M. Quick
Lawrence Livermore Laboratory
University of California
Livermore, CA 94550

SUMMARY

The Data Management Group at the Lawrence Livermore Laboratory is conducting research leading to the creation of data bases for energy storage systems. These data bases are computer-based and will contain bibliographic information, material properties data, and data on essential criteria for energy storage systems. Access to these central files will be from remote terminals over computer networks and by telephone dial-up, in addition to the more conventional means of computer-generated reporting, and dissemination on magnetic tape.

To validate the material properties data, a working agreement has been established between the Lawrence Livermore Laboratory (LLL) and the National Bureau of Standards (NBS). The Office of Standard Reference Data at NBS coordinates and monitors data evaluations by recognized data evaluation centers. One data request, for molten salts and molten salts systems (battery and thermal energy storage materials), has been completed and the data is being entered into a thermal energy storage (TES) and molten salts data bank. Other data requests for selected properties of metals and metal alloys (flywheel materials), composite materials (flywheel materials), solid electrolyte materials (battery materials), and metallic hydrides (hydrogen storage materials) are currently being worked by several data evaluation centers. A bibliographic data base for flywheel energy storage has been created and is currently in the process of publication. In addition, a comprehensive bibliography for molten salts and TES materials is in preparation. Preliminary computer printouts which demonstrate interactive aspects of the molten salts/TES material properties data base are part of this report.

1. Introduction and Background

"Research Leading to the Production and Early Use of Numeric Data Banks of Material Properties and System Analysis" has been carried out since February, 1976, by the Data Management Group of the Lawrence Livermore Laboratory under contract to the U.S. Energy Research and Development Administration, and the Division of Energy Storage Systems (ERDA/STOR), under Contract Number E(49-1)-3835.

Many alternate energy storage systems are undergoing continued research and development: thermal, chemical, electro-chemical, battery, physical, etc. The technological efficiency of these systems, and their cost-effectiveness, often depend in large measure upon the properties of materials and substances in heretofore uncharted operational domains. Technical and economical feasibility is the central issue in the decision-making process. Basic data on material properties, and on characterizations of energy storage systems are required to provide a reliable foundation for these activities.

Data bases of this type are, therefore, being created. When completed, they will contain *evaluated* physical and chemical properties for materials used in energy storage systems, and information and data to characterize the validity domains of storage systems. The National Bureau of Standards and selected data evaluation centers are collaborating. These computerized data banks will be made available to industry and to universities. As such they will serve as a public resource for the scientific and technological research community. It is anticipated that data bases of this type will provide a solid and expanding basis for the accelerating research activities in energy storage. They should help to eliminate discrepancies and should be a valuable aid to channel work into promising directions.

A staff of up to five professionals are participating in the project. Their academic backgrounds and experience are in chemistry, metallurgy, and computer science. Dr. Terrence Quick, material scientist, is Project Leader.

Project activity during the last year has centered around the computerization of the molten salts/TES evaluated data received from NBS and the acquisition of a computer system on which energy-storage-related data will reside. Molten salts/TES data received during the year consists of up to 16 physical properties of 82 salt systems. This data has been combined with the inorganic salt data already computerized to create a molten salts/TES data bank, which is still under development. A PDP-11/70 computer system is being set up for the collection, manipulation, and dissemination of energy-storage-related data. Data of this type will be made available over the ARPAnet, a national computer network, and by telephone dial-up later in FY1978.

2. Technological Data Base Activities

During the past year we have made major progress in the creation of bibliographic and evaluated material properties data banks. We have also acquired a computer system that is being prepared to handle these data banks for ERDA's Division of Energy Storage Systems.

2.1 Bibliography on Flywheel Technology

A selected bibliography for flywheel energy storage and fiber composites is in the process of publication. It contains 382 citations on the properties and mechanics of fibers, fiber composites, matrix materials, and on flywheel energy storage systems. The materials and flywheel systems citations were derived from the world literature. The bibliography is machine produced and is generated in two parts: a concordance on keywords and phrases, and the chronological listing of all bibliographic citations.

2.2 Molten Salts/TES Bibliography

A comprehensive molten salts/TES bibliographic data base is being created in a similar way as the flywheel bibliography. Major sources of machine-readable citations have been received from Dr. George Janz of the Molten Salts Data Center at the Rensselaer Polytechnic Institute (approximately 4000 citations) and from Sandia Laboratories Fused Salt Bibliography (approximately 3000 citations). Sources of hardcopy citations include a M.S. thesis by L. S. Charnoff (approximately 4000 citations) and other citations from ongoing literature searches at LLL. These bibliographic sources (References 3-6) are being combined into a single data bank which will be completed during FY1978 for general use.

2.3 Molten Salts/TES Material Properties Data Base

A molten salts/TES material properties data base is being developed for interactive use on our dedicated PDP-11/70 computer system. In addition to the inorganic salts data already computerized (Reference 7-8), we have added the evaluated molten salts/TES material properties data received during the past year from Dr. George Janz. These data include values of up to 16 properties on 82 salt systems. An example of possible ways in which those data can be accessed in an interactive manner is presented in Section 3.

2.4 Computer System to Handle Storage Data

A PDP-11/70 computer system is being set up on the ARPAnet, a national computer network, for the storage, manipulation, and dissemination of energy-storage-related data. The basic computer system was procured and tested during the past year. In FY1978, additional capability will be installed to enable both technological data bases, and other energy-storage-related data bases, to be accessed directly over the ARPAnet or by telephone dial-up.

3. Examples

Sample printouts from our molten salts/TES data base of material properties are shown in Figures 1-4. The molten salts data was derived primarily from evaluated data received from the Molten Salts Data Center of RPI. The TES data was derived primarily from a report by the Borucka Research Company (Ref. 7). The data base currently resides on the LLL Time-Sharing System and is maintained under the MASTER CONTROL Data Base Management System. It will be transferred in FY1978 to the PDP-11/70 system and made available for general use with a similar interactive capability as that shown in the example.

There are numerous advantages to be derived from computerized materials property data as illustrated by the sample printouts. Aside from such obvious advantages as the selective identification of properties and classes of materials, it is readily possible to convert the up-to-data data and information available on any one of the materials. In the past, properties of materials would have to await the infrequent and often costly printing of a comprehensive compendium. The computer-based data base, however, lends itself, for selective, i.e., *dynamic* printing, reporting, and graphical representation.

EXAMPLE 1 List all the thermal energy storage salts in the data base, ordered alphabetically. Include density, melting point, and cost values for all salts and salt systems.

User command: [ALL-TES]

Data Output (partial):

```
[ALL-TES]
  EDIT        ON

 IDN    SALT OR SALT MIXTURE              DENSITY    AVERAGE     M. PT.    REL.
                                           GM/CC     DENSITY     DEG C     COST
                                          LIQUID     GM/CC                 CAL/$
                                                     LIQUID

   14  BA(NO3)2                              3.220                592.00   1241.
   31  BACL2                                 3.170                963.00   2424.
  514  BACL2 MGCL2                                      2.490     560.00   5602.
   11  CA(NO3)2                                                   561.00   2882.
   20  CABR2                                 3.110                730.00
   23  CACL2                                 2.070                772.00   5095.
  519  CACL2 MGCL2                                      1.890     614.00   7060.
   36  CACO3                                                     1339.00   8164.
   35  CAF2                                  2.540               1360.00  10690.
  530  CAF2 MGF2                                        2.490     944.00  18140.
   12  CDCL2                                 3.390                569.00    631.
   42  CDI
   40  CSBR
   38  CSCL                                                       645.00
   30  K2CO3                                 1.900                891.00   6719.
 1002  K2CO3 LI2CO3 NA2CO3                              1.900     397.00   6320.
 1010  K2CO3 NA2CO3 CACO3                                         700.00   7474.
   21  KBR                                   2.120                730.00   4309.
  505  KBR MGBR2                                        2.350     334.00   6597.
   24  KCL                                   1.500                776.00  11578.
 1009  KCL BACL2 CACL2                                  2.450     551.00   5384.
  518  KCL CACL2                                        1.690     600.00   9008.
  520  KCL CACL2                                        1.900     640.00   6988.
 1005  KCL CACL2 MGCL2                                  1.740     487.00   8770.
  508  KCL MGCL2                                        1.580     435.00   9250.
  510  KCL MGCL2                                        1.620     470.00   7730.
  517  KCL NA2CO3                                       1.740     587.00   9855.
  522  KCL NACL                                         1.530     658.00  16691.
 1008  KCL NACL BACL2                                   2.400     542.00   8844.
 1006  KCL NACL CACL2                                   1.900     504.00  10622.
 1000  KCL NACL CDCL2                                   2.650     375.00   5807.
 1001  KCL NACL MGCL2                                   1.630     385.00  12766.
 1007  KCL NACL SRCL2                                   2.340     504.00   6838.
  501  KCL ZNCL2                                        2.200     228.00   4581.
  502  KCL ZNCL2                                        2.340     262.00   3196.
  507  KCL ZNCL2                                        1.970     432.00   6890.
   27  KF                                    1.920                846.00  10324.
```

<u>EXAMPLE 2</u>   List those thermal energy storage salts whose melting points lie within the one or two temperature ranges specified and order by melting point.

User command: [RDMPT-TS] MIN 500. MAX 750. MIN 800. MAX 950. [ORMPT-TS]

Data Output (partial):

```
[RDMPT-TS] MIN 500. MAX 750. MIN 800. MAX 950. [ORMPT-TS]
  SEARCH      ON

    44 RECORD(S) FOUND DURING LINEAR SEARCH, 2.90E-01 SECONDS, LIST ?
NO
  EDIT        ON


 IDN     SALT OR SALT MIXTURE         M. PT.
                                      DEG C

    43   PBCL2                         500.00
   512   NACL CACL2                    500.00
  1006   KCL NACL CACL2                504.00
  1007   KCL NACL SRCL2                504.00
   513   MGCL2 SRCL2                   535.00
  1008   KCL NACL BACL2                542.00
    10   LIBR                          547.00
  1009   KCL BACL2 CACL2               551.00
   514   BACL2 MGCL2                   560.00
    11   CA(NO3)2                      561.00
   515   NACL SRCL2                    564.00
    12   CDCL2                         569.00
    13   SR(NO3)2                      570.00
   516   NACL NICL2                    574.00
   517   KCL NA2CO3                    587.00
    14   BA(NO3)2                      592.00
   518   KCL CACL2                     600.00
    15   LICL                          614.00
   519   CACL2 MGCL2                   614.00
   520   KCL CACL2                     640.00
    38   CSCL                          645.00
    16   MNCL2                         650.00
   521   LIF NAF                       652.00
   522   KCL NACL                      658.00
    17   MGBR2                         700.00
  1010   K2CO3 NA2CO3 CACO3            700.00
    18   MGCL2                         708.00
   523   NA2CO3 K2CO3                  710.00
   524   KF NAF                        710.00
  1011   KF LIF MGF2                   713.00
    37   RBCL                          722.00
    19   LI2CO3                        723.00
    20   CABR2                         730.00
    21   KBR                           730.00
```

EXAMPLE 3 — List those molten salts which include density equations that are valid within the specified temperature range. Order the salts by the minimum valid temperature value of the density equation.

User command: `[SRCH-MS] 950. [RDTMN-MS] 350. [ORTMN-MS]`

Data Output:

```
[SRCH-MS] 950. [RDTMN-MS] 350. [ORTMN-MS]
  SEARCH       ON

    20 RECORD(S) FOUND DURING LINEAR SEARCH, 2.91E-01 SECONDS, LIST ?
NO
  EDIT         ON


 IDN     SALT OR SALT MIXTURE            MIN TEMP   MAX TEMP
                                          DENSITY    DENSITY

  1541   SULFUR: S8                       394.30     713.20
  1505   ALCL3-NACL EUTECTIC, 36.8        397.00     610.00
          MOLE % NACL
  1562   ALCL3-NACL-KCL                   430.00     540.00
  1504   ALCL3-LICL EUTECTIC, 40.         448.00     498.00
         MOLE % LICL
  1518   ALCL3                            462.00     569.00
  1552   LINO3                            550.00     690.00
  1529   NA2S3.7                          563.00     669.00
  1515   NA2S2.9                          566.45     636.95
  1527   NA2S3.4                          570.00     640.00
  1531   NA2S3.88                         570.00     610.00
  1536   NA2S4.4                          571.00     680.00
  1533   NA2S4.8                          573.00     683.00
  1526   NA2S3.3                          576.00     689.00
  1510   NA2S3                            590.00     683.00
  1550   NANO3                            590.00     690.00
  1551   KNO3                             620.00     870.00
  1513   NA2S5                            623.20     723.20
  1524   N2S4                             623.20     723.20
  1553   KNO3-NANO3                       625.00     720.00
  1560   LII                              760.00     830.00
```

EXAMPLE 4 List all molten salts in the data base and order them by the minimum valid temperature value of the density equation.

User command: [ALL-MS]

Data Output (partial):

```
[ALL-MS]
  EDIT        ON

 IDN    SALT OR SALT MIXTURE          MIN TEMP  MAX TEMP
                                       DENSITY   DENSITY

  1501  KCL-LICL EUTECTIC 41.5 MO
        LE % KCL, 58.5 MOLE % LIC
        L
  1508  NA2S
  1509  NA2S2
  1511  NA2S4-NA2S5 EUTECTIC
  1512  NA2S2-NA2S4 EUTECTIC
  1514  NA2S2.1
  1516  NA2S3.1
  1519  LI2CO3
  1525  NA2S3.2
  1528  NA2S3.6
  1530  NA2S3.8
  1532  NA2S3.9
  1533  NA2S4.1
  1534  NA2S4.2
  1535  NA2S4.3
  1537  NA2S4.7
  1539  NA2S5.1
  1540  NA2S5.2
  1557  LI2SO4-NACL
  1563  CACL2-KCL-LICL
  1564  CACL2-KCL-LICL
  1565  KCL-LICL-NACL
  1566  LI2SO4-K2SO4-NA2SO4
  1567  KNO3-LINO3-NANO3
  1541  SULFUR: S8                    394.30    718.20
  1505  ALCL3-NACL EUTECTIC, 36.8     397.00    610.00
         MOLE % NACL
  1562  ALCL3-NACL-KCL                430.00    540.00
  1504  ALCL3-LICL EUTECTIC, 40.      448.00    498.00
        MOLE % LICL
  1542  ALCL3-KCL EUTECTIC, 33. M     461.00   1051.00
        OLE % KCL, 67. MOLE % ALC
        L3
```

GENERAL REFERENCES

1. T. M. Quick and E. A. Henry, "Research Leading to the Production and Early Use of Numeric Data Banks of Material Properties and System Analyses," Quarterly Progress Report, Lawrence Livermore Laboratory, Report UCRL-50038-76-3 (March, 1977). See also Second Quarterly Progress Report, UCRL-50038-76-2 (September, 1976) and First Quarterly Progress Report, UCRL-50038-76-1 (May, 1976).

2. E. A. Henry, K. W. Johnson, F. E. McMurphy, and T. M. Quick "Bibliography of Flywheel Energy Storage Systems, "Lawrence Livermore Laboratory (being published).

3. G. J. Janz, R. P. T. Tomkins, J. R. Downey, Jr., and C. B. Allen, Editors, "Molten Salts Awareness Bulletin, Annotated Bibliography," RPI, Troy New York (1975).

4. G. J. Janz, C. B. Allen, J. R. Downey, Jr., and R. P. T. Tomkins, "Eutectic Data: Safety, Hazards, Corrosion, Melting Points, Compositions and Bibliography," ERDA Division of Energy Storage Systems, TID-27163-P1 and -P2 (2 volumes), July, 1976.

5. M. Shalit, Editor, "Fused Salt Bibliography," Sandia Laboratories Report SLA-73-0053 (December, 1972).

6. L. S. Charnoff, "An Annotated Bibliography of Molten Salts," M. S. Thesis, New York University (1958), University Microfilms, Inc., Ann Arbor, Michigan.

7. A. Borucka, "Survey & Selection of Inorganic Salts for Application to Thermal Energy Storage," ERDA-59, June, 1975.

8. G. A. Lane, D. N. Glew, E. C. Clarke, S. W. Quigley, and H. E. Rossow, "Isothermal Solar Heat Storage Materials — Phase 1," Technical Report, ERDA-117 May, 1975.

APPENDIX

SECOND ANNUAL THERMAL ENERGY STORAGE CONTRACTORS' INFORMATION EXCHANGE MEETING

Mountain View Hotel and Motor Lodge
Gatlinburg, Tennessee
September 29 & 30, 1977

PROGRAM

Wednesday, September 28

8:00-10:00 p.m.	Registration

Thursday, September 29

8:00 a.m.-12:00 noon	Registration
9:00 a.m.	Call to Order - H. W. Hoffman, ORNL
9:05 a.m.	Welcoming Remarks
9:20 a.m.	TES Program - C. J. Swet, ERDA

Session I

Low-Temperature Thermal Energy Storage
Chairman - H. W. Hoffman, ORNL

9:45 a.m.	*Low-Temperature Thermal-Energy Storage Program Overview* H. W. Hoffman, ORNL
10: 00 a.m.	*Technical and Economic Feasibility of Earth Storage,* George Washington University
10:15 a.m.	*Modeling of Solid Sensible Heat Storage Systems,* Pennsylvania State University
10:30 a.m.	Coffee Break
11:00 a.m.	*Commercial Feasibility of Thermal Energy Storage,* Argonne National Laboratory
11:15 a.m.	*Form Stable Polyethylene,* Monsanto Research Corporation
11:30 a.m.	*Immiscible Fluid - Direct Contact Heat Storage Concept,* Clemson University

11:45 a.m.	*Heat of Solution for Thermal Energy Storage,* The Franklin Institute
12:00-1:30 p.m.	Lunch
1:30 p.m.	*Regenerated Desiccant Crop-Drying Concept,* Lockheed Missiles and Space Company
1:45 p.m.	*Macro-Encapsulation of Phase-Change Materials,* Dow Chemical Company
2:00 p.m.	*Energy Storage with Hydrated Salts,* University of Delaware
2:15 p.m.	*Thermocrete,* Suntek Research Associates
2:30 p.m.	*Mathematical Modeling of Moving Boundary Problems,* Oak Ridge National Laboratory
2:45 p.m.	Coffee Break
3:15 p.m.	*Solar R&D* Allan Michaels, ANL

Session II

High-Temperature Thermal Energy Storage
Chairman - Bill Masica, NASA-Lewis Research Center

3:45 p.m.	*High-Temperature Thermal Energy Storage Program Overview,* Bill Masica, NASA-LeRC
4:00 p.m.	*Molten Salt Thermal Energy Storage for Utility Peaking Loads,* Grumman Aerospace Corporation
4:15 p.m.	*Identification and Conceptual Design of Storage Systems for Solar Thermal Electric Power Systems,* Xerox Electro-Optical Systems
4:30 p.m.	*Molten Salt Thermal Energy Storage (Carbonates),* Institute of Gas Technology
4:45 p.m.	*Thermophysical Property Measurements of Metal Alloy Thermal Storage Media,* University of Delaware
5:00 p.m.	Adjourn

5:30 p.m.	Social
6:30 p.m.	Dinner
8:00-10:00 p.m.	Parallel Informal Discussions by Program Area Managers (Format at discretion of Area Manager)

Friday, September 30

9:00 a.m.	Call to Order
9:15 a.m.	*Laboratory Studies and Design of Sodium Hydroxide Storage System for Solar Total Energy System,* Comstock & Wescott, Inc.
9:30 a.m.	*Fabrication of NRL Energy Storage Boiler Tank,* Naval Research Laboratory
9:45 a.m.	*Rockbed Heat Accumulators for Seasonal Storage,* University of Minnesota
10:00 a.m.	*An Assessment of Incorporating an All-Solid Thermal Storage Unit with New Construction Base-Load Power Plants to Provide Load Following Capability,* JPL - California Institute of Technology
10:15 a.m.	*Thermal Energy Storage Using Prestressed Cast Iron Vessels (PCIV),* Graz University of Technology
10:30 a.m.	Coffee Break

Session III

Thermochemical Energy Storage and Transport
Chairman - Ray Mar, SLL

11:00 a.m.	*Thermochemical Energy Storage and Transport Overview,* Ray Mar, Sandia Laboratories - Livermore
11:15 a.m.	*Methanol-Based Heat Pumps,* EIC Corporation
11:30 a.m.	*Sulfuric Acid Heat Pump,* Rocket Research Corporation
11:45 a.m.	*Hydrated Salt Heat Pump,* Chemical Energy Specialists
12:00 noon	Lunch

1:30 p.m.	*Ammoniated Salt Storage Systems*, Martin-Marietta Corporation
1:45 p.m.	*Solar-Extended Storage Applications*, Rocket Research Corporation
2:00 p.m.	*Ammonium Hydrogen Sulfate Decomposition*, University of Houston
2:15 p.m.	*Heat Storage/Transmission Analysis*, Lawrence Berkeley Laboratory
2:30 p.m.	*Chemical Energy Storage and Transmission*, General Electric Company
2:45 p.m.	*Open-Loop Heat Pipe*, Institute of Gas Technology
3:00 p.m.	*Duplex Steam Reformer/Alternate Catalyst Development*, General Electric Corporation
3:15 p.m.	Closing Remarks and Adjournment
4:00 p.m.	Executive Review - TES Area Managers and Staff, ERDA Staff

Saturday, October 1

9:00 a.m.	TES Area Managers' Meeting - TES Area Managers and Staff, ERDA Staff

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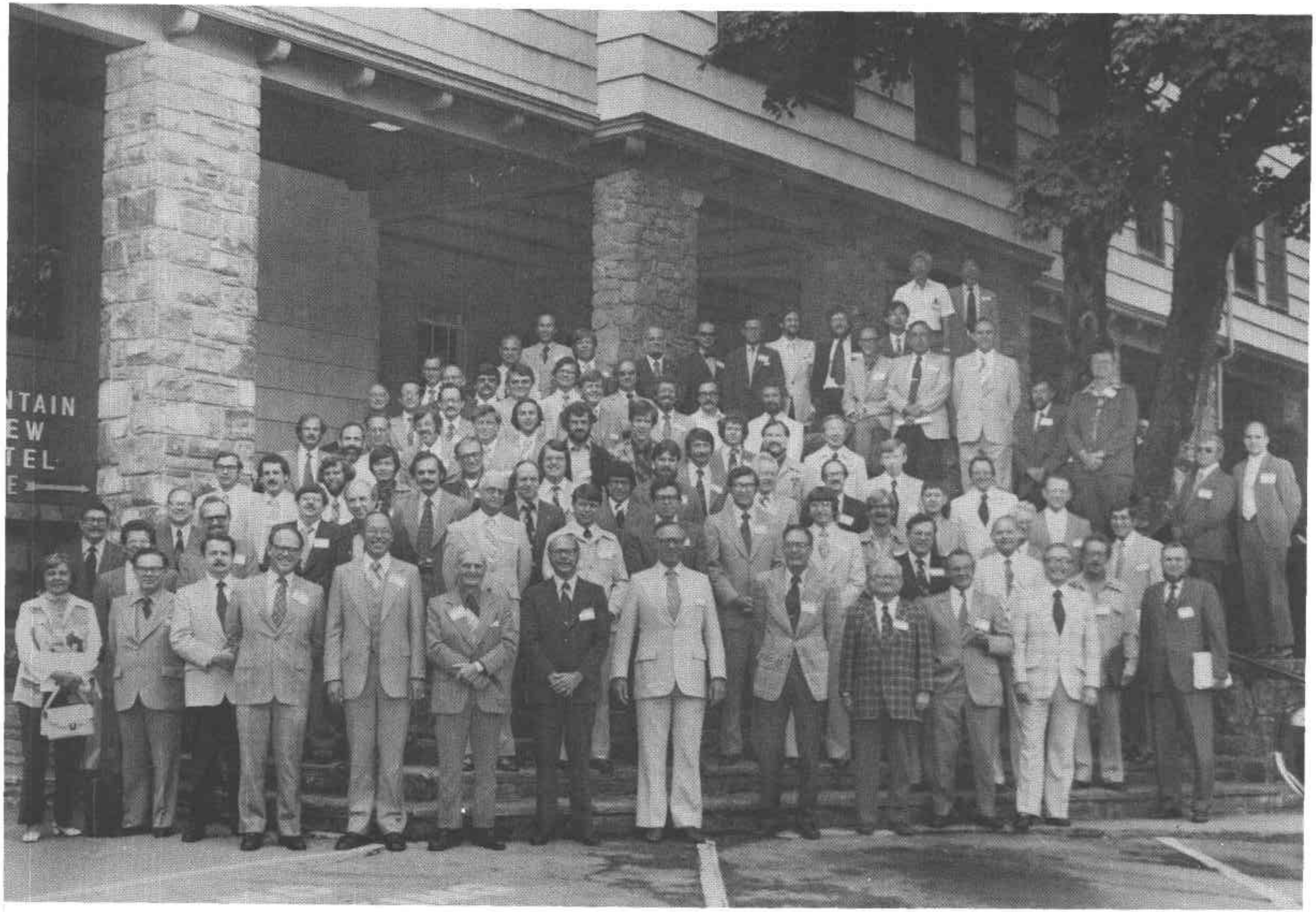

Attendees at 2nd Annual Thermal Energy Storage Contractors Information Exchange Meeting, Mountain View Motel, Gatlinburg, Tennessee, September 29–30, 1977.

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