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# Thermochemical Energy Storage and Transport Program Progress Report (October 1977 - December 1978)

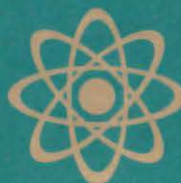
T. T. Bramlette

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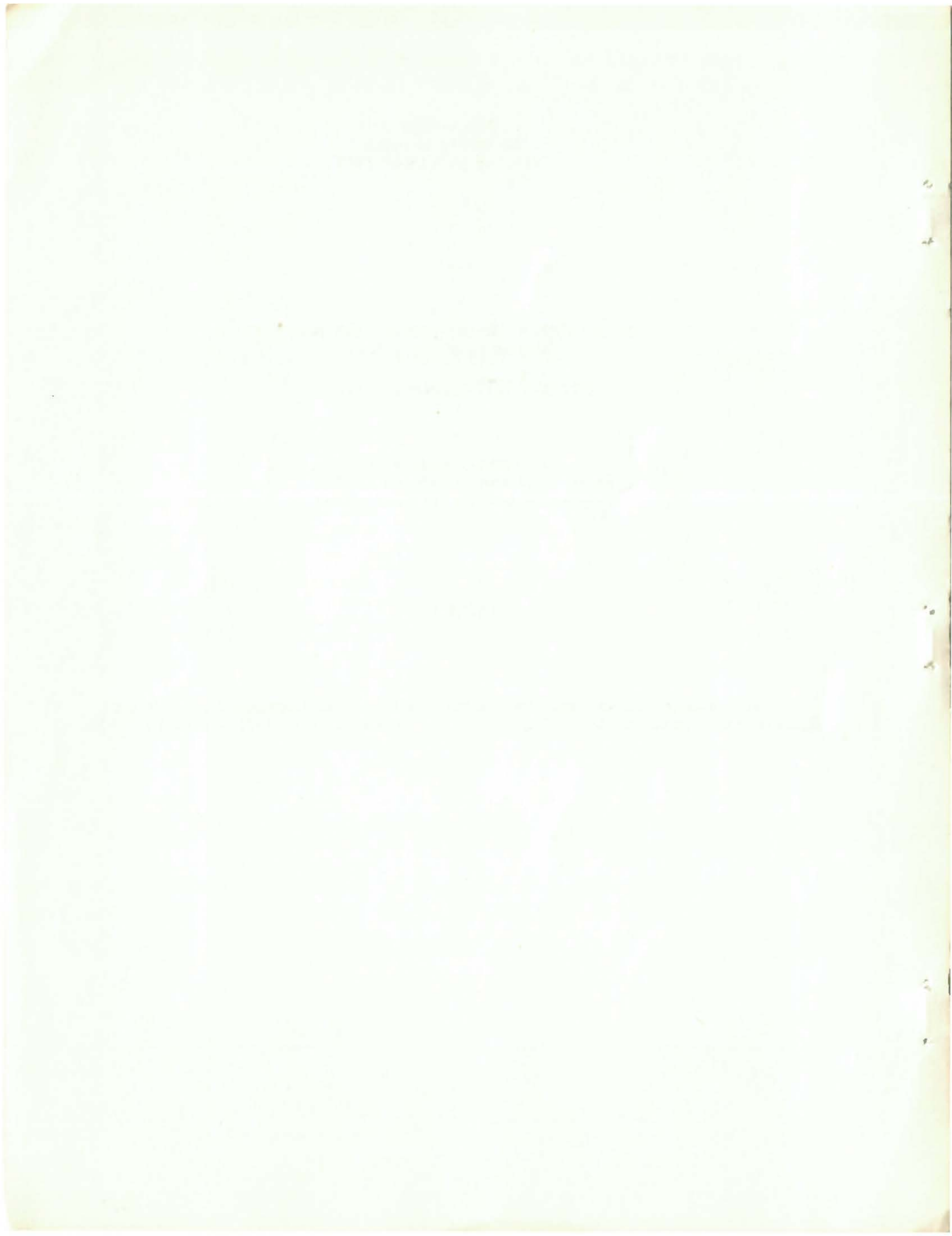
THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT  
PROGRAM PROGRESS REPORT

(October 1977 - December 1978)

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ABSTRACT

This document summarizes the progress made by the Thermochemical Energy Storage and Transport (TEST) Program in the period October 1977 - December 1978.





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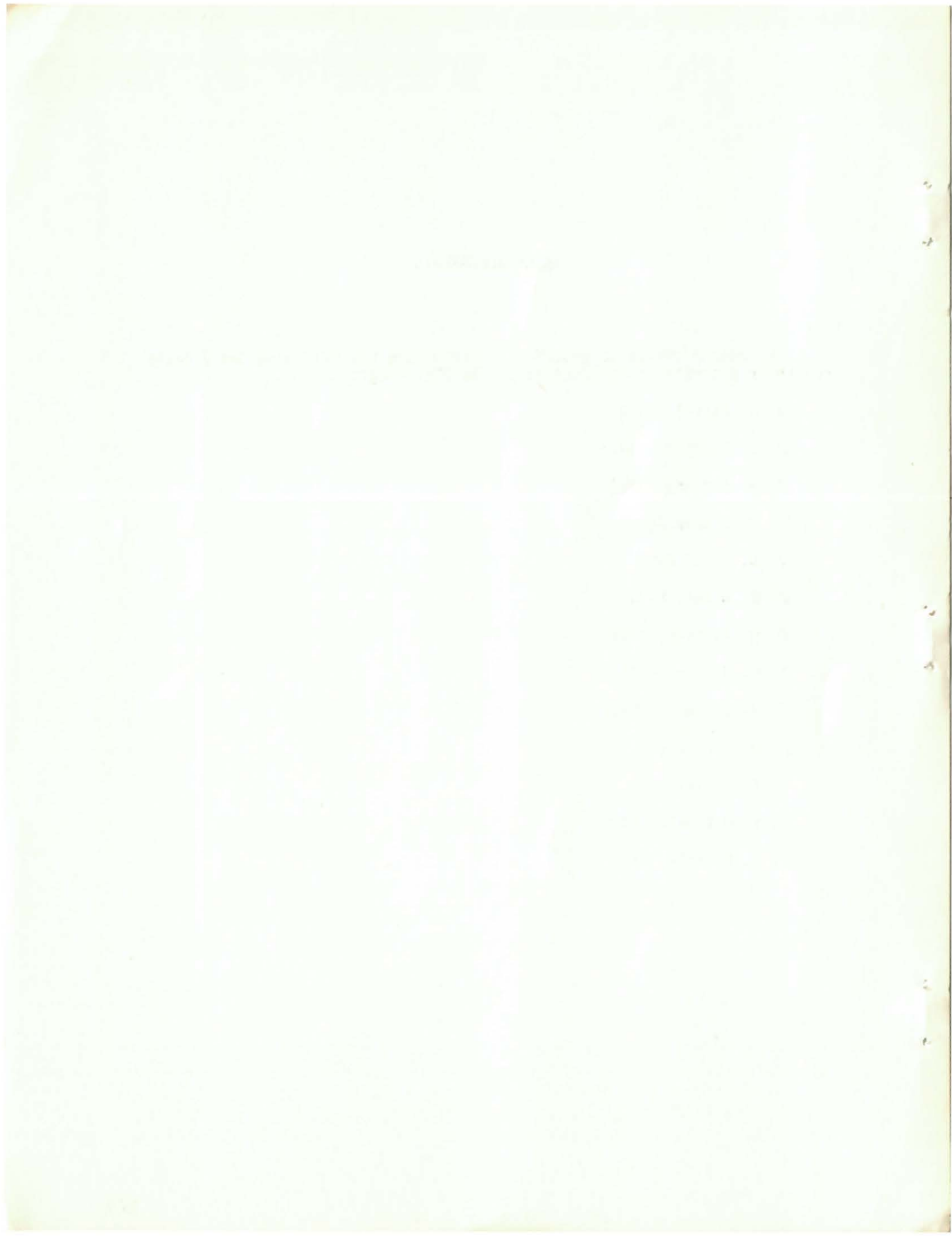
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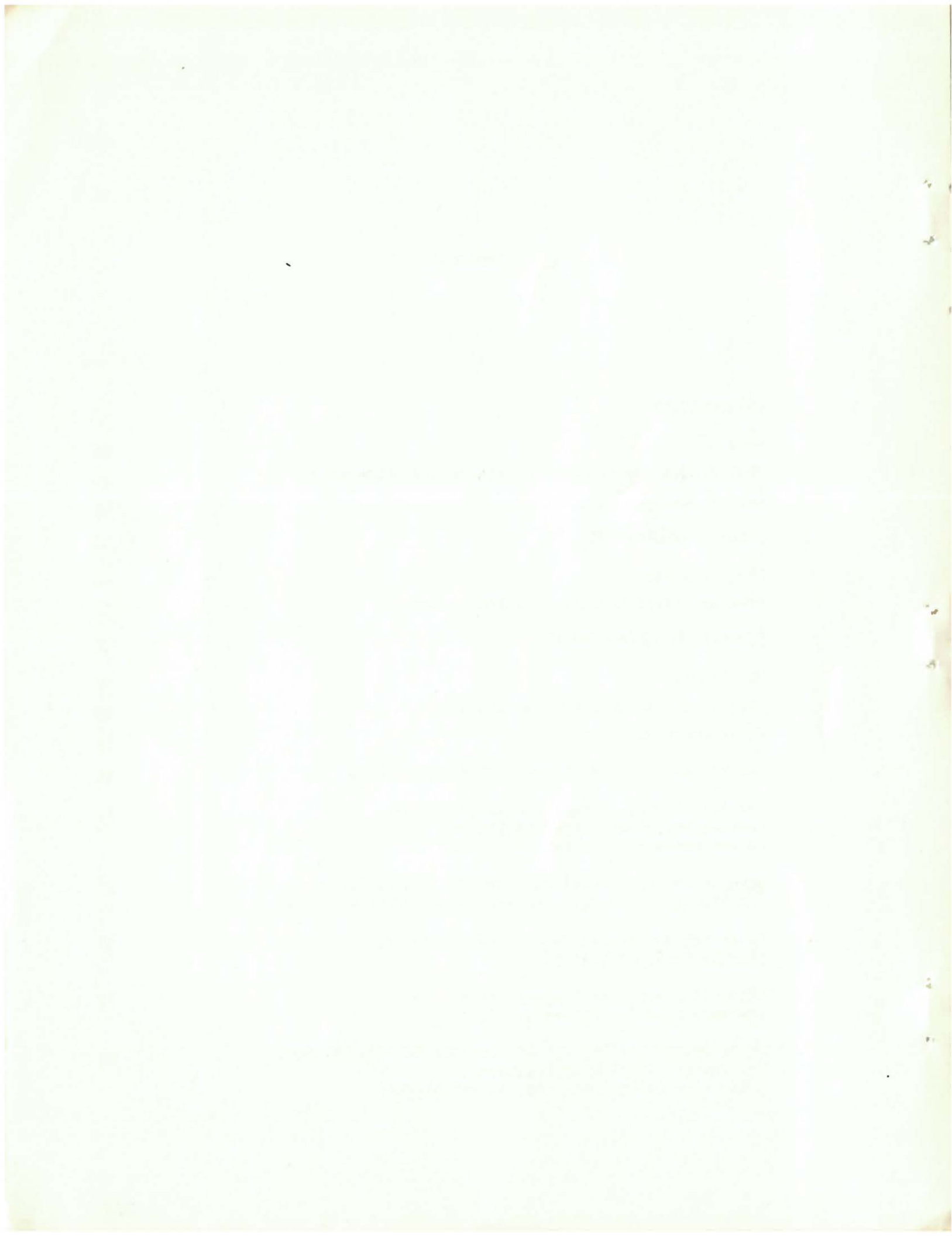
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## I. INTRODUCTION

### General

The Chemical and Thermal Storage Branch of the United States Department of Energy (DOE), Office of Energy Technology, Division of Energy Storage Systems has implemented a National Thermal Energy Storage (TES) Program. The objective of this National Program is to develop and disseminate thermal and thermochemical energy storage and transport technology which offers the potential for energy conservation or fuel substitution (nuclear, coal, or solar for petroleum). The National Program consists of three subprograms:

- Low-Temperature Thermal Energy Storage Program (managed by Oak Ridge National Laboratories), with the objective to develop sensible and latent heat technologies for low-temperature ( $\leq 250^{\circ}\text{C}$ ) applications.
- High-Temperature Thermal Energy Storage Program (managed by NASA Lewis Research Center), with the objective to develop sensible and latent heat technologies for high-temperature ( $> 250^{\circ}\text{C}$ ) applications.
- Thermochemical Energy Storage and Transport (TEST) Program (managed by Sandia Laboratories, Livermore), with the objective to develop reversible chemical reaction technologies for thermal energy storage and transport applications.

Of the three subprograms, the technology is least advanced for thermochemical energy storage and transport. Without exception, no one reaction is understood well enough to allow a commercial scale system to be designed and fabricated. Thus, the current phase of the TEST program is concerned with the development of a technology base from which such systems could be evolved.

The motivation for conducting this research is that thermochemical reactions offer some unique characteristics when compared with sensible or latent heat systems. These include:

- High Energy Densities - Thermochemical storage systems have energy storage densities (based on mass or volume) ranging from about a factor of two to more than an order of magnitude greater than is possible with sensible and latent systems.



- Ambient Storage - Energy storage at ambient temperatures is possible for thermochemical systems, i.e., chemical reactants and products can be cooled to and stored at ambient temperatures.
- Long-Term Storage - With ambient storage, long-term storage with little or no degradation is possible, which makes seasonal or extended storage applications feasible.
- Transportability - Chemical reactions can be selected such that the products and reactants are easily transported, e.g., as gases in a pipeline. Therefore, the endothermic and exothermic reactors can be physically separated by long distances.
- Heat Pumping - Proper selection of chemical reactions allows one to construct a single device capable of heating, cooling, and energy storage. Heating COP's in the range 1.5 - 2.0 are possible.
- Low Capacity Costs - The cost of an energy storage system can generally be divided into two categories: power costs and capacity costs. The power related costs are those associated with reactors, heat exchangers, etc.; capacity related costs are associated with raw materials costs, storage tank costs, etc., and are generally low for thermochemical systems.

While these characteristics may be considered advantages for many applications, they must be weighed against the following potential drawbacks:

- Furthest From State-of-the-Art - Thermochemical technologies are the least developed, and considerable amounts of time, money, and effort are required to develop thermochemical systems to commercialization.
- System Complexity - Thermochemical systems probably will be quite complex when compared to sensible and latent heat systems. Not only will individual components be complex, but interactions between various components will be needed to achieve acceptable total system efficiencies.

#### TEST Program Development Procedure and Organization

To exploit the potential advantages and quantify the disadvantages of thermochemical reactions for energy storage and transport applications, the program has been structured initially to explore a wide range of chemical reactions and applications. In general, the development procedure consists of:

- Identification and evaluation of preferred current and future users of reversible chemical reactions for energy storage and transport.
- Identification of specification requirements and evaluation of available technology and technology needs for selected storage and transport systems.



- Formulation and evaluation of energy storage and transport concepts which meet the requirements established above.
- Definition and development of the required technology.
- Comparison of thermochemical storage and transport concepts with competing technologies, and assessment of their conservation potential.
- Development of the most promising concepts and systems to the point of demonstration on a scale commensurate with commercial application.

It should be emphasized that before a concept is allowed to proceed to the last state of development, the need for and value of the concept must be established clearly.

As illustrated in Figure 1, the program has been divided into four technology elements according to a Technology Breakdown Structure. The four Technology Breakdown Structure (TBS) elements are:

- Thermal Energy Storage (TBS 1.0)
- Thermochemical Pipelines (TBS 2.0)
- Chemical Heat Pump Storage (TBS 3.0)
- Generic Research (TBS 4.0)

Each major element has been further divided into subelements which represent specific concepts or applications being pursued. The activities to date in each of these TBS elements are summarized below.

Thermochemical energy storage technology (TBS 1.0) is being considered for both solar and nonsolar electric utility applications. Activities include systems studies to establish the technical and economic viability of proposed concepts, and parallel laboratory investigations of promising reactions.

Emphasis for the thermochemical pipelines portion of the program (TBS 2.0) has been on systems studies and component development. Studies of both open-loop and closed-loop pipelines have been conducted for a variety of energy sources including nuclear, fossil energy and solar. Promising reactions have been identified, and applications requiring additional study have been noted. In one case where the reaction technology was well understood, a major hardware development activity was initiated.

Following a preliminary analysis of the potential of chemical heat pump storage systems (TBS 3.0), experimental investigations of several attractive concepts were initiated. Closed-loop operation of a prototype configuration was demonstrated for one concept, and laboratory results to date suggest the other concepts are viable alternatives.

Generic research (TBS 4.0) has consisted of catalyst development, heat transfer investigations, and laboratory investigations of promising reaction systems. Also included in this TBS is the Sandia in-house research program.

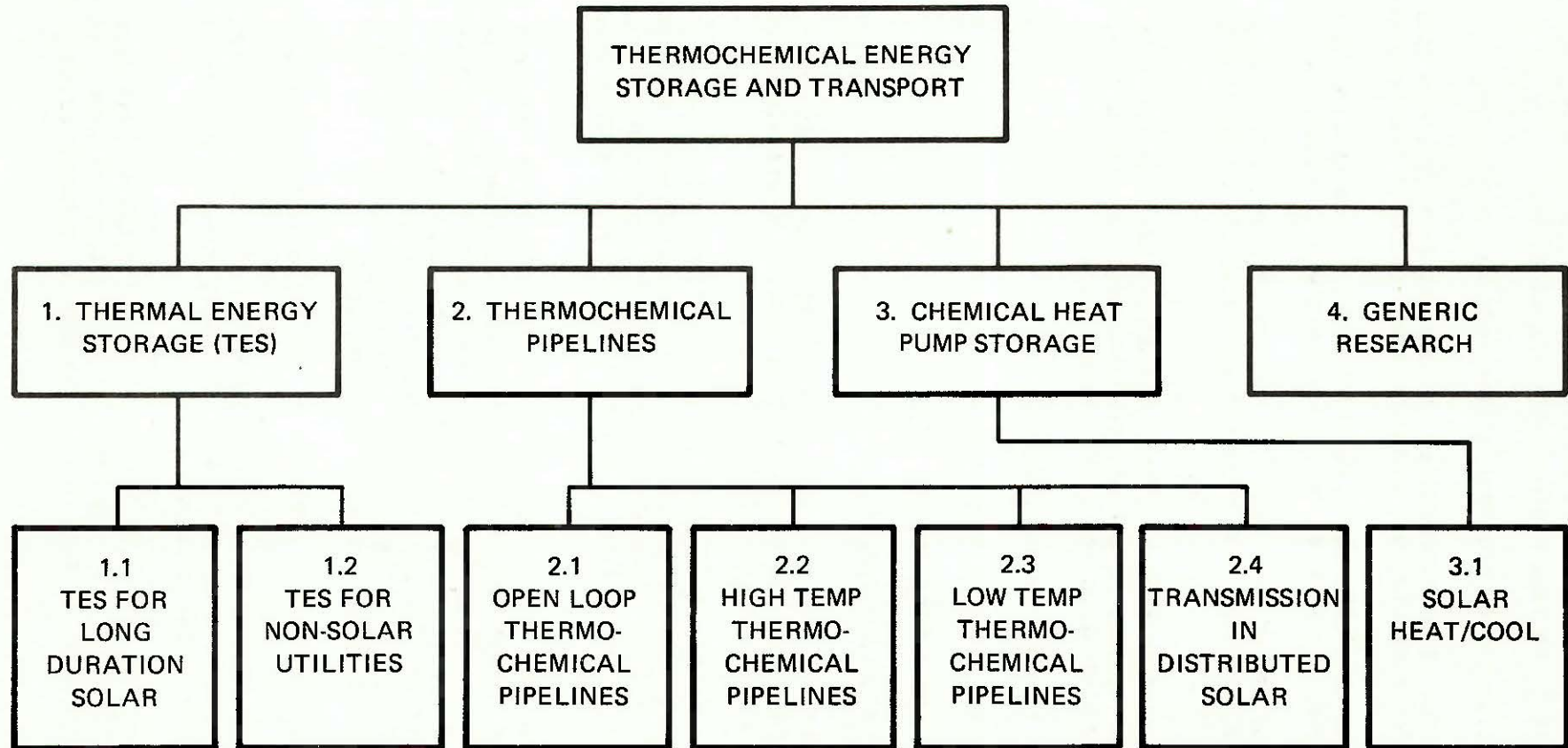


FIGURE 1. Technology Breakdown Structure for the TEST Program



## Report Outline

In the next section, the long-range program goals, milestones, and target dates selected for each of the TBS elements are presented. The topics discussed include a brief discussion of the five-year plan for the program, as well as a summary of the projects in progress during the present reporting period. Progress made in achieving TEST Program goals is summarized in Section III. Detailed discussions of current projects are presented in Section IV. The report concludes with a summary and recommendations in Section V.

## CURRENT PROGRAM GOALS

This section provides a brief narrative description of the five-year plan for the TEST Program, and presents a summary of the projects in progress during this reporting period.

### Five-Year Plan

In describing the five-year plan, the Technology Breakdown Structure of the program will be utilized. Since the intent is only to present the framework within which the current program fits, the discussion is brief.

#### Thermal Energy Storage for Solar Utilities (TBS 1.1)

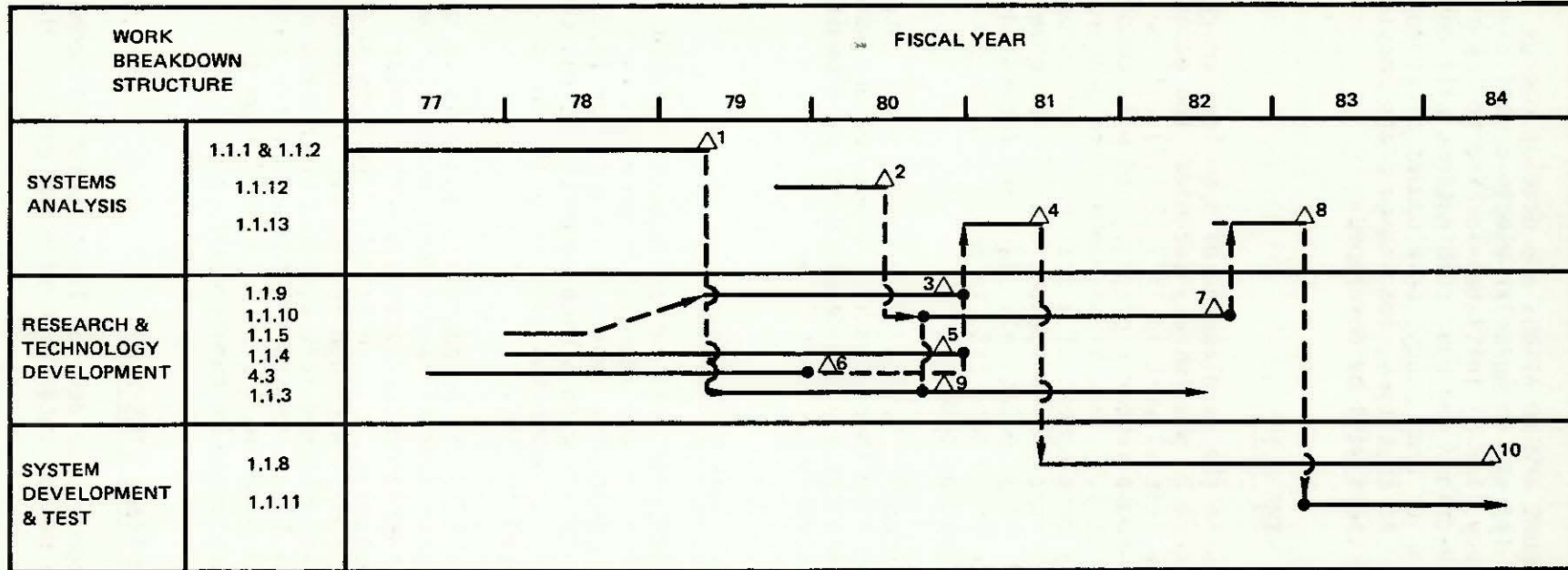
The objectives of this subelement are to assess and develop thermochemical storage technologies on a schedule compatible with the development schedules for solar thermal electric conversion systems. Because the solar thermal electric conversion systems actually chosen for large scale demonstration will depend upon the results of a number of ongoing solar programs, it is essential to carry on a number of parallel investigations of promising thermal energy storage concepts. The coordination, interaction, and anticipated results of these various activities are depicted in Figure 2.

The systems analysis (1.1.1)\* of selected solar thermal electric power plants and investigations of several first-generation chemical reactions (1.1.4, 4.3, and 1.1.9) which were initiated in FY77 and 78 will continue in FY79. New programs in FY79 are a systems analysis of more advanced solar thermal electric power plants (1.1.12) and initial laboratory investigations (1.1.3) of promising additional chemical reaction systems. Results from these two activities may lead to the initiation of a development activity for a second generation TES system (1.1.10) in mid FY80. In late FY80, results from 1.1.9, 1.1.4, and 4.3 will be assessed (1.1.13), leading to a decision by mid FY81 of whether to proceed to a Subsystem Development and Test activity (1.1.8) for the first generation TES system. This activity will be completed in FY84. The schedule for second generation system lags behind the first generation program by approximately a 1-1/2 years.

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\*Numbers in parentheses identify specific projects in the TEST program. Detailed discussions of these projects for FY78 are given in Section IV of this report.

## TES FOR SOLAR UTILITIES TBS 1.1



### MILESTONES

- 1 – TECHNICAL & ECONOMIC FEASIBILITY OF TES FOR 3 SOLAR THERMAL SYSTEMS; IDENTIFICATION OF 1 OR MORE REACTIONS FOR FURTHER INVESTIGATION
- 2 – SAME AS 1, BUT FOR ADVANCED SOLAR THERMAL SYSTEMS
- 3 – LAB SCALE INVESTIGATIONS COMPLETED FOR SELECTED REACTIONS; INFORMATION REQUIRED FOR MORE REFINED SYSTEMS MODELING AVAILABLE
- 4 – DETAILED ANALYSES COMPLETE; DECISION TO PROCEED TO SYS. DEV. & TEST
- 5 – LAB SCALE INVESTIGATIONS FOR AHS COMPLETE
- 6 – SO<sub>2</sub>/SO<sub>3</sub> CATALYST DEVELOPMENT COMPLETE
- 7 – LAB SCALE INVESTIGATIONS FOR SECOND GENERATION TES SYSTEMS COMPLETE
- 8 – MORE DETAILED SYSTEMS MODELING; DECISION TO PROCEED TO SYS. DEV. & TEST
- 9 – POTENTIAL REACTIONS IDENTIFIED FOR SECOND GENERATION SYSTEMS
- 10 – FIRST GENERATION SYSTEM DEV. & TEST COMPLETE

FIGURE 2. Long-range Plan for TES for Solar Utilities



## TES for Non-Solar Electric Utilities (TBS 1.2)

The objectives of this subelement are to assess and develop energy storage and transport technologies for use in nonsolar electric utilities. The second phase of the systems study (1.2.1) initiated in FY78 to identify potential energy source/chemical reaction/ end user combinations will continue in FY79. Depending upon the outcome of that study, development of appropriate concepts may be initiated in FY80. At that time, long-range plans consistent with the schedules of the selected users will be developed.

## Open-loop Thermochemical Pipelines (TBS 2.1)

This subelement is concerned with the development of open-loop energy transport systems. As shown in Figure 3, preliminary technical and economic feasibility was established in FY78; initial work in FY79 (2.1.2) will be conducted as part of the Sandia in-house research program, and will consist of a reassessment of previous work (2.1.1), and if warranted, the preparation of an RFQ. Research and technology development of a coal gasification-based system (2.1.3) will begin in FY80 if the RFQ is issued, with system development and testing beginning in FY82. This relatively near-term technology could be demonstrated on a large scale by late FY83 in ample time to provide an alternative to other coal gasification schemes.

In mid FY79 to early FY80, a study (2.1.4) will be initiated to determine the possibility of interfacing open-loop thermochemical pipelines and advanced solar systems (2.1.5). System identification and development could begin in early FY81, with large-scale demonstration by late FY84.

## High Temperature Thermochemical Pipelines (TBS 2.2)

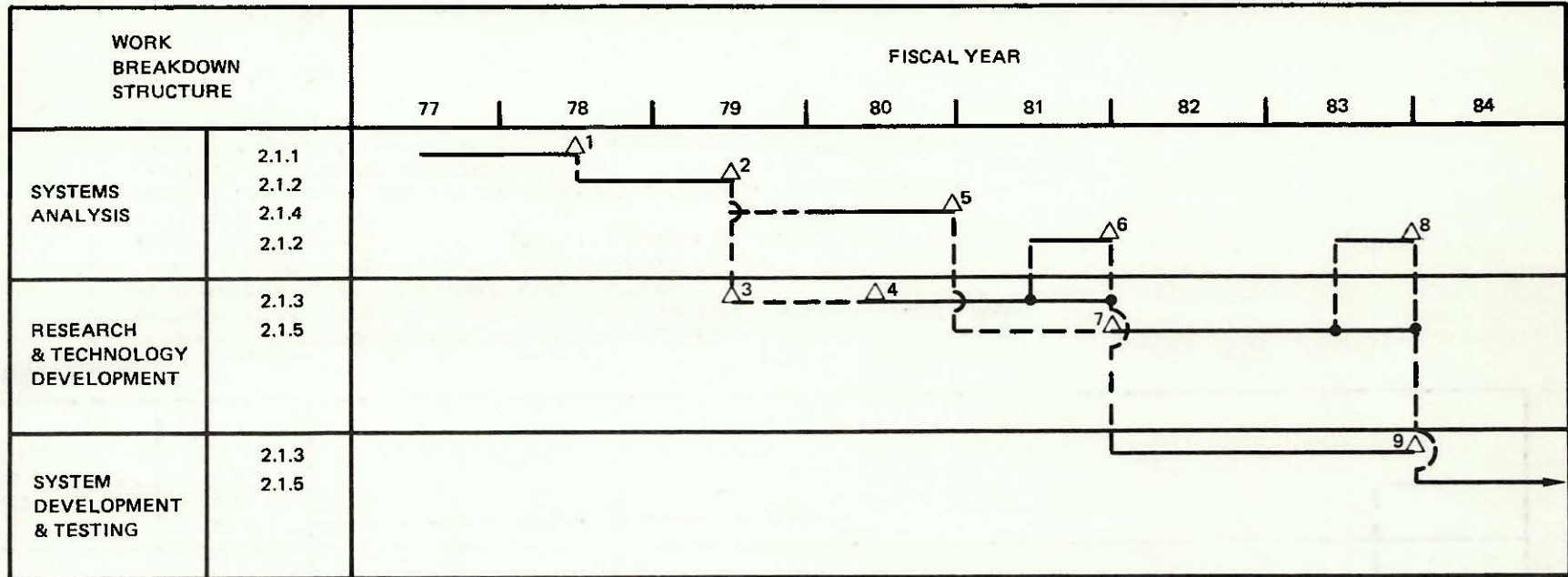
Technical and economic feasibility of this concept was established in FY77. FY79 activities in this subelement are addressing two areas (see Figure 4). The first is the development of a duplex steam reformer (2.2.2) for interfacing a thermochemical pipeline with a high-temperature, gas-cooled reactor. This activity, which is being supported jointly by the United States and Germany, will be completed in FY80.

The second activity (2.2.5), which will be addressed initially in the Sandia in-house research program, will assess the feasibility and desirability of interfacing a high-temperature thermochemical pipeline with a solar central receiver energy source. Assuming positive results from this study, an RFQ will be prepared in FY80 (2.2.6). Although development is feasible by FY84, the actual schedule will be established following the completion of 2.2.5. This program will be in parallel with the development of the solar interfaced open-loop thermochemical pipeline (2.1.4). Depending on the systems identified, the two programs could be combined into one.

## Low-Temperature Thermochemical Pipelines (TBS 2.3)

The objective of this subelement is to develop low-temperature technologies for energy transport systems which may be interfaced with nuclear or solar

### OPEN LOOP THERMOCHEMICAL PIPELINES TBS 2.1



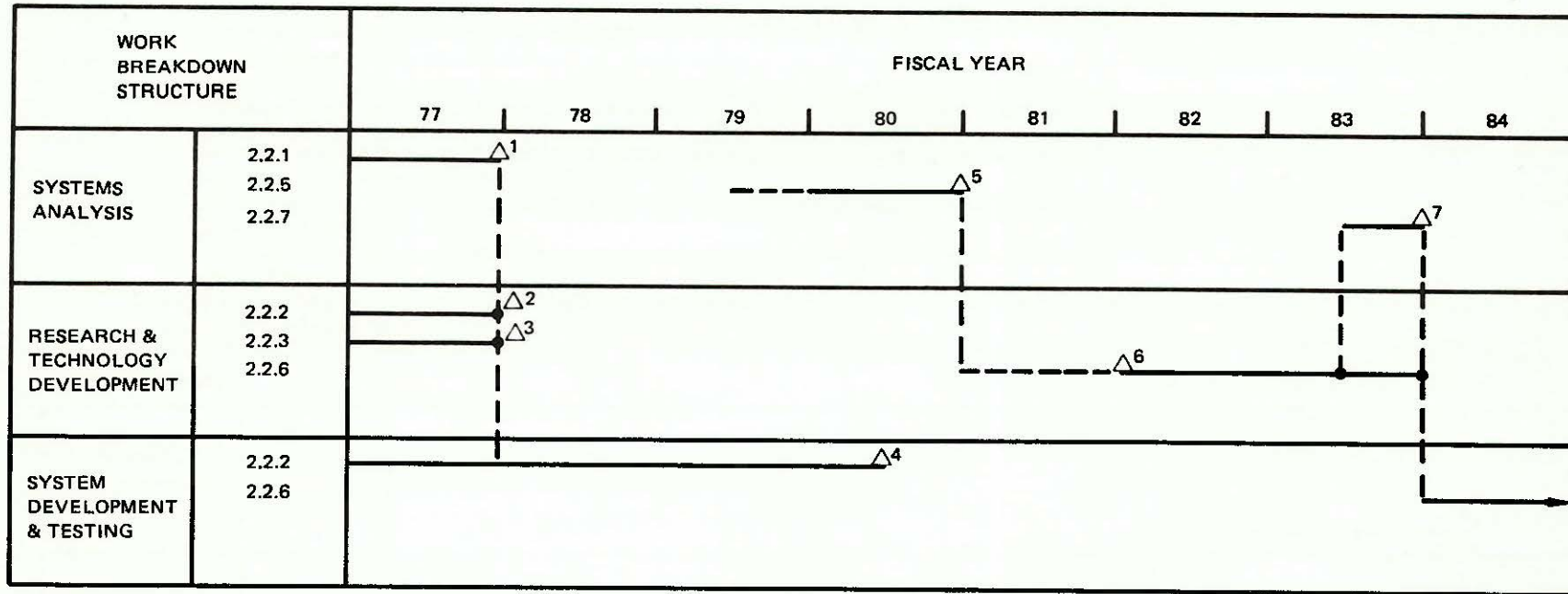
**MILESTONES**

- 1 – TECHNICAL AND ECONOMIC FEASIBILITY OF OPEN-LOOP THERMOCHEMICAL PIPELINE CONCEPT ESTABLISHED
- 2 – 2.1.1 REASSESSED, AND IF WARRANTED, RFQ PREPARED
- 3 – RFQ ISSUED
- 4 – CONTRACT AWARDED FOR RESEARCH AND TECHNICAL DEVELOPMENT OF METHANE-BASED SYSTEM
- 5 – INTERFACE OF OPEN-LOOP THERMOCHEMICAL PIPELINES AND SOLAR SYSTEMS EVALUATED, RFQ ISSUED, IF WARRANTED
- 6 – RE-EVALUATION OF METHANE-BASED SYSTEM AND DECISION TO PROCEED WITH SYSTEM DEVELOPMENT
- 7 – CONTRACT AWARDED FOR SOLAR INTERFACED SYSTEM TECHNOLOGY DEVELOPMENT
- 8 – RE-EVALUATION OF SOLAR INTERFACED SYSTEM AND DECISION TO PROCEED WITH SYSTEM DEVELOPMENT
- 9 – METHANE-BASED OPEN-LOOP THERMOCHEMICAL PIPELINE CONCEPT READY FOR COMMERCIALIZATION

FIGURE 3. Long-range Plan for Open-Loop Thermochemical Pipelines



## HIGH TEMPERATURE THERMOCHEMICAL PIPELINES TBS 2.2



## MILESTONES

- 1 – FEASIBILITY OF THERMOCHEMICAL PIPELINE ESTABLISHED
- 2 – DECISION TO PROCEED WITH SYSTEM DEVELOPMENT OF DUPLEX STEAM REFORMER (DSR)
- 3 – ALTERNATE CATALYST DESIGN COMPLETED AND EVALUATED
- 4 – TEST EVALUATION REPORT ISSUED FOR DSR DEVELOPMENT
- 5 – SOLAR INTERFACED HIGH TEMPERATURE THERMOCHEMICAL PIPELINE EVALUATED, RFQ ISSUED, IF WARRENTED
- 6 – CONTRACT AWARDED FOR SOLAR INTERFACED HIGH TEMPERATURE THERMOCHEMICAL PIPELINE TECHNOLOGY DEVELOPMENT
- 7 – RE-EVALUATION OF SOLAR INTERFACED SYSTEM AND DECISION TO PROCEED WITH SYSTEM DEVELOPMENT

FIGURE 4. Long-range Plan for High-Temperature Thermochemical Pipelines

energy sources; preliminary technical and economic feasibility was established in FY77. Activities in FY79 and 80 (see Figure 5) will establish the feasibility of using the benzene/cyclohexane reaction (2.3.1) for energy transport. In FY80, a detailed characterization of the potential market will be initiated (2.3.4), and preliminary investigations of alternate reactions will begin (2.3.5). A critical reassessment of the concept will be conducted in FY80 (2.3.3), and this, in conjunction with the results from (2.3.1), (2.3.4), and (2.3.5) will provide the information required to reach a decision regarding large scale system development and test (2.3.2). The target for large scale demonstration is FY83, subject to re-evaluation as the early studies are completed.

#### Transmission in Distributed Solar Systems (TBS 2.4)

The objective of this subelement is to develop energy transport systems for distributed solar systems. Activities in FY79 will be conducted in-house, and will consist of a preliminary analysis of the concept, the identification of required research, and, if warranted, the preparation of an RFQ for a more detailed systems analysis.

#### Chemical Heat Pump Storage (TBS 3.1)

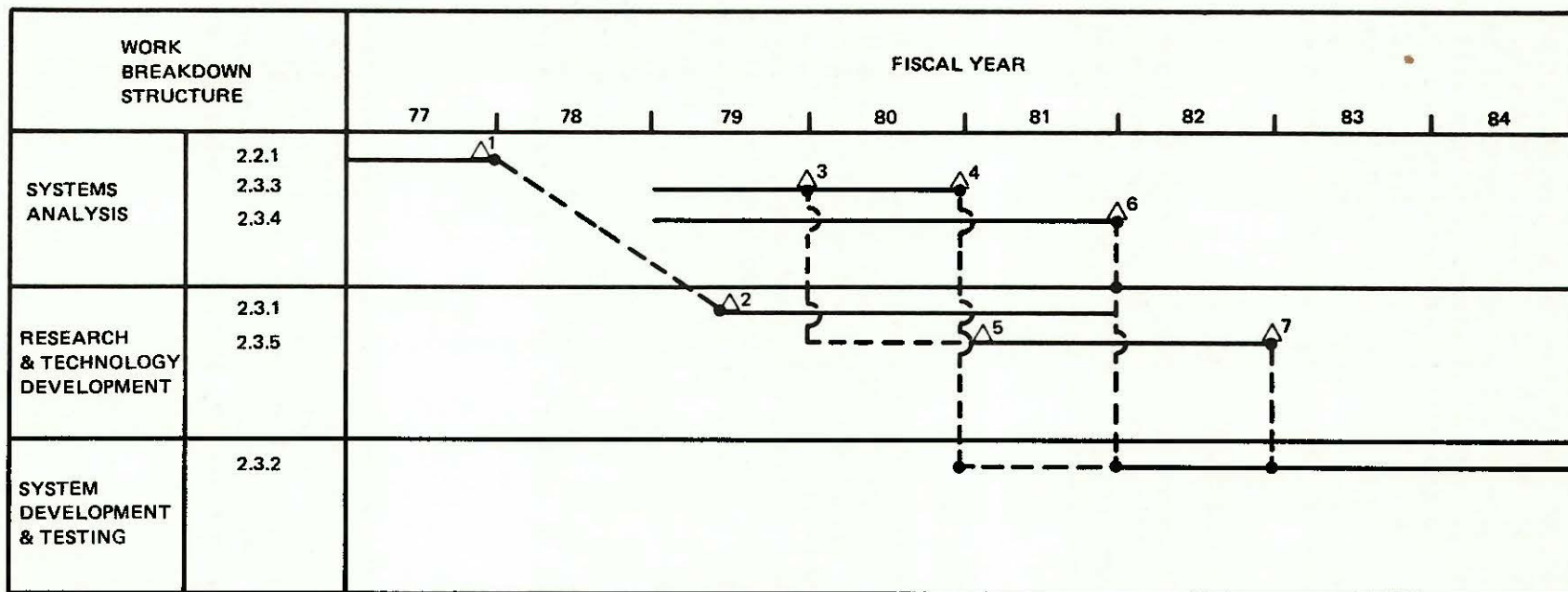
The objective of this subelement is to develop chemical reaction systems for use as chemical heat pump storage systems. Work in this area has been in progress since FY77. In FY79, experimental activities will concentrate on the sulfuric acid (3.1.1), methanolate (3.1.2), and ammoniate (3.1.4, 4.4) systems (see Figure 6). Systems analyses conducted in FY79 (3.1.5) will assess the potential of the sulfuric acid system and, coupled with the initial results of (3.1.6), will determine whether 3.1.6 is carried to the large scale development phase. Also part of 3.1.5 will be an evaluation of 3.1.2 and 3.1.4, which may lead to a demonstration project (3.1.8). The results of a workshop held in the first quarter of FY79 will be used to formulate an RFQ for advanced systems (3.1.7). This work will be conducted in FY80 and 81 and examined in detail in late FY80 (3.1.9). If warranted, closed-loop demonstrations will be conducted in FY82 and analyzed in FY83 (3.1.10).

#### Generic Research (TBS 4.0)

Long-range activities in the program subelement depend upon the evolution of the program. In FY79, the subcontracted activities consist of a study of the fundamental processes occurring in gas/solid TES systems (4.2),  $\text{SO}_2/\text{SO}_3$  catalyst development (4.3), and research on ammoniated salts (4.4). The Sandia in-house research consists of thermochemical/thermophysical characterization, coordination chemistry, corrosion research, and catalyst research, and systems analyses of solar thermal electric power plants.



## LOW TEMPERATURE THERMOCHEMICAL PIPELINES TBS 2.3

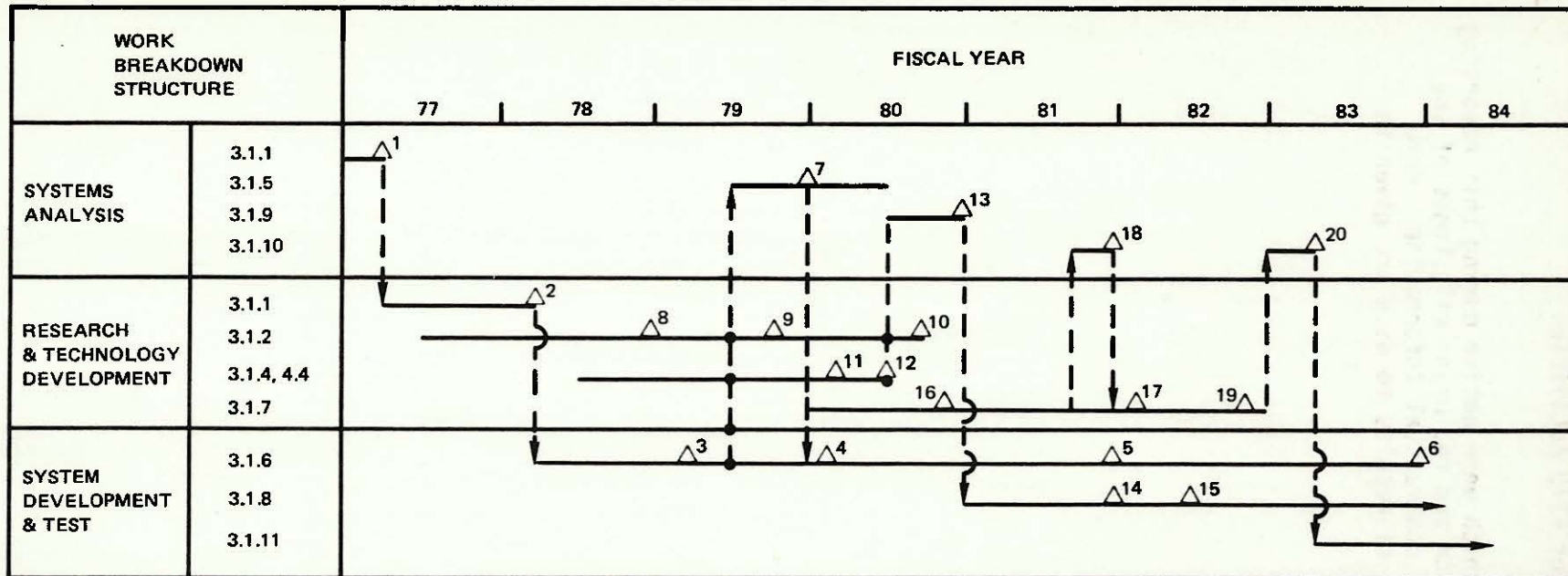


## MILESTONES

- 1 – TECHNICAL AND ECONOMIC FEASIBILITY OF THERMOCHEMICAL PIPELINE ESTABLISHED
- 2 – CONTRACT AWARDED FOR BENZENE/CYCLOHEXANE TECHNOLOGY DEVELOPMENT
- 3 – RFQ ISSUED FOR ALTERNATE REACTION(S) TECHNOLOGY DEVELOPMENT
- 4 – RFQ ISSUED FOR LOW TEMPERATURE THERMOCHEMICAL PIPELINE SYSTEM DEVELOPMENT
- 5 – CONTRACT AWARDED FOR ALTERNATE REACTION(S) TECHNOLOGY DEVELOPMENT
- 6 – MARKET ANALYSIS COMPLETE, DECISION TO PROCEED WITH SYSTEM DEVELOPMENT
- 7 – ALTERNATE REACTION(S) ASSESSED AND FINAL SYSTEM FOR DEVELOPMENT SELECTED

FIGURE 5. Long-range Plan for Low-Temperature Thermochemical Pipelines

### CHEMICAL HEAT PUMP STORAGE TBS 3.1



#### MILESTONES

- 1 – H<sub>2</sub>SO<sub>4</sub> CHEMICAL HEAT PUMP CONCEPT IDENTIFIED
- 2 – COMPONENT DEVELOPMENT COMPLETE; CLOSED-LOOP OPERATION DEMONSTRATED
- 3 – COMP. OPTIMIZATION & TRANSIENT TESTING COMPLETE
- 4 – PROTOTYPE DESIGN COMPLETE
- 5 – PROTOTYPE FABRICATION & TEST COMPLETE; SECOND GENERATION SYSTEM DESIGNED
- 6 – SECOND GEN. FAB. & TEST COMPLETE
- 7 – MARKET POTENTIAL FOR H<sub>2</sub>SO<sub>4</sub> ESTAB.; TECH. EVALUATION OF GAS/SOLID SYSTEMS COMPLETE
- 8 – CANDIDATE METHANOLATES IDENTIFIED
- 9 – METHANOLATE CHARACTERIZATION & HEAT TRANSFER EXPMTS. COMPLETE
- 10 – CLOSED-LOOP SYSTEM DEMONSTRATION
- 11 – AMMONIATE CHARACTERIZATION & HEAT TRANSFER EXPMTS. COMPLETE
- 12 – CLOSED-LOOP DEMONSTRATION
- 13 – COMPARATIVE EVALUATION OF GAS/SOLID HEAT PUMPS
- 14 – COMPONENT OPTIMIZATION COMPLETE
- 15 – DETAILED PROTOTYPE DESIGN COMPLETE
- 16 – ALTERNATIVE CHEMICAL SYSTEMS IDENTIFIED
- 17 – CHEMISTRY OF ALTERNATIVE SYSTEMS CHARACTERIZED
- 18 – SELECTION OF ADVANCED SYSTEMS FOR CLOSED-LOOP DEMONSTRATION
- 19 – CLOSED-LOOP DEMONSTRATION COMPLETE
- 20 – SELECTION OF ADVANCED SYSTEM FOR SYSTEM DEV. & TEST

FIGURE 6. Long-range Plan for Chemical Heat Pumps

## FY78 and First Quarter FY79 Activities

Table I summarizes the projects which were active during this reporting period, and presents a brief description and the major milestones of the projects. Table II provides additional contractual information. More detailed discussions and an assessment of results to date are given in Section IV.



TABLE I  
FY78 PROJECT DESCRIPTIONS AND GOALS

Technology Sector	Contractor	Reaction	Major Goals of Projects in Progress in FY78
<u>Thermal Energy Storage Projects</u> 1.1.1 and 1.1.2	Rocket Research Corp. Sandia Labs	Part of a reaction screening study	Select reactions or reaction sequences for solar thermal power plant appli- cations  Evaluate selected reactions on basis of thermodynamics and kinetics  Perform preliminary design and modeling of reversible chemical reaction storage systems  Establish technical and economic feasibility of extended duration storage for solar power plants
1.1.4	University of Houston	$\text{NH}_4\text{HSO}_4 + \text{Q} \rightarrow \text{NH}_3 + \text{H}_2\text{O} + \text{SO}_3$	Conduct literature survey and experimental study to identify reaction sequences for ammonium hydrogen sulfate decomposition  Perform kinetic and thermodynamic measurements  Design and test flow mode bench scale reactor  Evaluate technical and economic feasibility  Conduct solar input configuration studies

TABLE I (continued)

Technology Sector	Contractor	Reaction	Major Goals of Projects in Progress in FY78
1.1.5	Atomics International	$\text{Ca(OH}_2\text{)} + \text{Q} \rightarrow \text{CaO} + \text{H}_2\text{O}$	Determine basic hydration/dehydration properties of $\text{CaO/Ca(OH}_2\text{)}$  Evaluate technical and economic feasibility of fixed-bed, fluidized bed, and rotating drum reactor systems
1.1.6	Lawrence Berkeley Laboratory	$2\text{SO}_3 + \text{Q} \rightarrow 2\text{SO}_2 + \text{O}_2$ $\text{CH}_4 + \text{H}_2\text{O} + \text{Q} \rightarrow \text{CO} + 3\text{H}_2$	Synthesize and evaluate technically feasible flow sheets of storage systems based upon the sulfur trioxide and methane/water chemical systems
1.2.1	Gilbert Associates	Based upon a previously completed reaction screening study	Identify and characterize reversible chemical reaction systems and applications of interest to non-solar electric utilities  Prepare preliminary conceptual designs  Assess the technical and economic viability of promising reaction sequences and applications.
<u>Thermochemical Pipeline Projects</u> 2.1.1	IGT	$\text{CH}_4 + \text{H}_2\text{O} + \text{Q} \rightarrow \text{CO} + 3\text{H}_2$	Preliminary design of a nuclear (HTGR) and methane-based open-loop system  Evaluate energy sources as alternatives to those in the preliminary design (e.g., coal gasification and HTGR/LNG)  Assess the feasibility of using existing natural gas pipelines and storage systems for the synthesis gas

TABLE I (continued)

Technology Sector	Contractor	Reaction	Major Goals of Projects in Progress in FY78
2.1.1 (cont.)			<p>Assess existing methanation technologies and interchangeability of the SNG with natural gas</p> <p>Evaluate the various alternative energy end-uses for heat, SNG, and electricity</p> <p>Develop two conceptual designs and evaluate their economics and environmental impacts</p>
2.2.1	General Electric/ Corporate Research and Development	Primarily $\text{CH}_4 + \text{H}_2\text{O} + \text{Q} \rightarrow \text{CO} + 3\text{H}_2$ $\text{C}_6\text{H}_{12} + \text{Q} \rightarrow \text{C}_6\text{H}_6 + 3\text{H}_2$	<p>Evaluate potential energy sources for thermochemical pipeline systems</p> <p>Evaluate alternate chemical systems</p> <p>Establish technical and economic feasibility of methane/steam and benzene/hydrogen systems</p> <p>Assess market for thermochemical pipelines</p> <p>Identify critical R&amp;D needs</p>
2.2.2	General Electric/ Energy Systems Program Department	$\text{CH}_4 + \text{H}_2\text{O} + \text{Q} \rightarrow \text{CO} + 3\text{H}_2$	<p>Design and fabricate two duplex steam reformer (DSR) tubes</p> <p>Design and fabricate adapter to mate DSR tubes to EVA test facility</p> <p>Design and fabricate catalyst for DSR tubes</p>



TABLE I (continued)

32	Technology Sector	Contractor	Reaction	Major Goals of Projects in Progress in FY78
	2.2.2 (cont.)			Design and fabricate instrumentation for DSR tubes  Assemble test section  Develop test program for EVA facility  Evaluate metallurgical performance  Evaluate reformer performance  Develop analytical model for DSR performance  Prepare licensing evaluation report
	2.2.4	University of Houston	$\text{CH}_4 + \text{H}_2\text{O} + \text{Q} \rightarrow \text{CO} + 3\text{H}_2$	Optimize process stages and determine process parameters at the steam-reformer-liquid sodium interface of an advanced central receiver solar thermal power plant
	Chemical Heat Pump Projects			
	3.1.1	Rocket Research Corp.	$\text{H}_2\text{SO}_4$ Concentration/Dilution	Select concept for detailed sizing and scaling analysis  Design and construct a sub-scale closed-loop demonstration system  Conduct operational tests to verify system performance  Conduct economic analysis of major system variables affecting total total integrated system design and cost

TABLE I (continued)

Technology Sector	Contractor	Reaction	Major Goals of Projects in Progress in FY78
3.1.1 (cont.)			Perform transient and component optimization testing
			Assess commercialization potential
3.1.2	EIC Corporation	$\text{Salt} \cdot (\text{CH}_3\text{OH}) + \text{Q} \rightarrow \text{Salt} + \text{CH}_3\text{OH}$	Identify combinations of inorganic salt substrates and carrier gases ( $\text{CH}_3\text{OH}$ ) suitable for chemical heat pump systems
			Experimentally determine thermodynamic, kinetic, and heat transfer data
			Perform engineering design and economic analysis
			Design, procurement, and fabrication of prototype, closed-loop system
			Test of prototype, closed-loop system
3.1.3	CES	$\text{MgCl}_2 \cdot n\text{H}_2\text{O} + \text{Q} \rightarrow \text{MgCl}_2 \cdot m\text{H}_2\text{O} + (n - m)\text{H}_2\text{O}$	Perform preliminary design and analysis of chemical heat pump configuration
			Experimentally investigate rates of water desorption from various salt hydrates
3.1.4	Martin Marietta	Ammoniates	Establish feasibility of constructing chemical heat pump based upon paired ammoniates
			Perform and verify engineering analysis and design
			Design prototype system



TABLE I (continued)

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Technology Sector	Contractor	Reaction	Major Goals of Projects in Progress in FY78
<u>Generic Research Projects</u>			
4.2	University of California at Davis	Research generic to gas- solid reactions	Identify and select potential chemical reactions for thermochemical energy storage systems  Experimentally investigate reaction kinetics
4.3	Rocket Research Corporation	$2\text{SO}_3 + \text{Q} \rightarrow 2\text{SO}_2 + \text{O}_2$	Evaluate commercial catalysts and develop a standard activity test  If required, develop new catalyst  Conduct accelerated aging tests
4.4	Martin Marietta	Research generic to ammoniates	Determine reaction rates, heats of reaction, bulk density for selected ammoniates  Design, fabricate, and test a subscale reaction system  Upgrade system performance computer models

TABLE II - TEST PROGRAM PROJECTS SUMMARY

TEST Project Number	Project Title	Principal Investigator	Organization	Contract Number	Contract Period	Funding Level	Funding Source	Sandia's Technical Manager
1.1.1	Chemical Energy Storage for Thermal Conversion	R. D. Smith	Rocket Research Corp. York Center Redmond, WA 98052	SLL 18-2563 NSF AER 75-2476	Jul 1976- Jul 1979	SLL 149,816 NSF 120,000	Sandia Laboratories National Science Foundation	J. J. Iannucci
1.1.2	Chemical Energy Storage for Solar Thermal Conversion	J. J. Iannucci	Sandia Laboratories Livermore, CA 94550	AD-03-01	Oct 1977- Oct 1978	50,000	DOE, Advanced Solar Thermal Power Systems	T. T. Bramlette
1.1.4	Development of Operational Chemical Cycles for the Storage of Energy	W. E. Wentworth	University of Houston Dept. of Chemistry Houston, TX 77004	EG-77-6-01-3974	May 1978- May 1979	227,300	DOE, Advanced Solar Thermal Power Systems	R. E. Mitchell
1.1.5	Solar Energy Storage by Reversible Chemical Processes	T. H. Springer	Rockwell Internat'l Corp Energy Systems Group 8900 DeSoto Ave. Canoga Park, CA 91304	FA0-92-7671	Aug 1977- Jan 1978	96,800	Sandia Laboratories	M. C. Nichols
1.1.6	Chemical Storage of Thermal Energy	A. S. Foss S. Lynn	Lawrence Berkeley Laboratory Berkeley, CA 94720	W-7405-ENG-48	Oct 1977- Oct 1979	125,000	Sandia Laboratories	C. C. Hiller
1.2.1	An Assessment of the Use of Chemical Reaction Systems in Electric Utility Applications, Phase II		Gilbert Associates P.O. Box 1498 Reading, PA 19603	18-6284	Jan 1979- Jun 1979	83,397	Sandia Laboratories	J. D. Fish
2.1.1	Transmission of Energy by Open Loop Chemical Energy Pipelines	N. R. Baker	Institute of Gas Technology IIT Center 3424 South States St. Chicago, IL 60616	87-9181	May 1977- Jan 1978	96,400	Sandia Laboratories	R. E. Mitchell

TABLE II - (Continued)

TEST Project Number	Project Title	Principal Investigator	Organization	Contract Number	Contract Period	Funding Level	Funding Source	Sandia's Technical Manager
2.2.1	Closed Loop Chemical Systems	H. Vakil J. Flock	General Electric/CRD	EY-76-C-02-2676	Jun 1975- Aug 1978	336,447	( )	J. J. Bartel
2.2.2	Duplex Steam Reformer Development	G. R. Pflasterer D. C. Allen	General Electric Co. Advanced Reactor Systems Dept 310 DeGuigue Dr. Sunnyvale, CA 94086	EY-76-C-02-2841		1,126,000	DOE, Division of Energy Stor- age Systems and Nuclear Power Development	T. T. Bramlette
2.2.4	Cyclic Catalytic Storage Systems	J. Richardson	University of Houston Dept. of _____  Houston, Texas 77004	EG-77-C-01-3974	May 1977- May 1978	25,000	DOE, Advanced Solar Thermal Power Systems	R. E. Mitchell
3.1.1	Sulfuric Acid and Water Chemical Heat Pump/Thermal Energy Storage	E. C. Clark	Rocket Research Co. York Center Redmond, WA 98052	18-4958	Oct 1977- Feb 1979	250,000	Sandia Labora- tories	C. C. Hiller
3.1.2	Methanol-Based Heat Pumps for Storage of Solar Thermal Energy	P. O'D. Offenhartz	EIC Corp. 55 Chapel St. Newton, MA 02158	87-9118 18-8423	Apr 1977- Jul 1979	120,000 276,000	Sandia Labora- tories	R. W. Mar
3.1.3	The Chemical Heat Pump - A Simple Means to Conserve Energy	L. Greiner	Chemical Energy Specialists	87-9835A	Aug 1977- Dec 1977	40,000	Sandia Labora- tories	R. W. Carling
3.1.4	Thermal Storage for Solar Cooling Using Paired Ammoniated Salt Reactions	F. Jaeger W. Haas	Martin-Marietta Aerospace Denver Division P. O. Box 179 Denver, CO 80201	EM-78-C-02-4700	May 1978- Apr 1980	363,563	DOE, Conserva- tion and Solar Applications Solar Heating & Cooling Branch	R. M. Green



TABLE II - (Continued)

TEST Project Number	Project Title	Principal Investigator	Organization	Contract Number	Contract Period	Funding Level	Funding Source	Sandia's Technical Manager
4.2	The Kinetics of Dissociative Chemical Reactions in Thermochemical Energy Storage	Z. Munir	University of California at Davis Davis, CA	18-0438	Jul 1977- Jul 1979	125,000	Sandia Laboratories	R. W. Mar
4.3	Development of a Long-Life, High-Temperature Catalyst for the SO <sub>2</sub> /SO <sub>3</sub> Energy Storage System	E. W. Schmidt	Rocket Research Corp York Center Redmond, WA 98052	87-9119	Apr 1977- Nov 1979	320,274	Sandia Laboratories	B. E. Mills
4.4	Development of Ammoniated Salts Thermochemical Energy Storage Systems - Phases Ib and II	F. Jaeger W. Haas	Martin-Marietta Aerospace Denver Division P. O. Box 179 Denver CO 80201	EY-76-6-03-1229, 18-6825	Feb 1977- Sep 1977, Jul 1978- Jun 1979	211,548 112,000	DOE, Division of Energy Storage Systems, Sandia Laboratories	R. M. Green

## SUMMARY OF ACCOMPLISHMENTS

### Highlights

The following list highlights the major accomplishments for this reporting period.

#### Rocket Research Corporation and Sandia Laboratories, (1.1.1 and 1.1.2)

Twenty-four reactions have been identified for thermal energy storage applications, and conceptual designs have been generated to determine relative power and energy costs.

$\text{CaO}/\text{Ca}(\text{OH})_2$  and  $\text{SO}_2/\text{SO}_3$  have been selected for detailed design.

The overall simulation/economic evaluation computer model has been completed and used to evaluate solar thermal electric conversion systems at various geographical locations.

University of Houston, (1.1.4)--Two reaction mechanisms have been identified which are equivalent to the net thermal decomposition of  $\text{NH}_4\text{HSO}_4$  and which allow separation of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  from the sulfur oxide product at high temperature by formation of an intermediate compound. The energy regeneration reaction has been investigated, and temperatures in excess of  $400^\circ\text{C}$  have been achieved.

A bench-scale flow reactor has been designed and is now operational. The unit is being used to study the energy storage reactions identified as promising. A conceptual  $\text{NH}_4\text{HSO}_4$ /cogeneration cycle has been developed, costed, and performance is being calculated.

Atomics International, (1.1.5)--A substantial amount of information about the  $\text{CaO} - \text{Ca}(\text{OH})_2$  reaction has been developed to date: the rates of reaction are acceptable, the heat of reaction is as expected, and the material can be cycled at least 1000 times without inherent degradation. Although uncertainties remain at this time, inorganic oxide-hydroxide thermal storage appears to be attractive.

The final report for this project has been received, reviewed, and revised.

Lawrence Berkeley Laboratory, (1.1.6)--A technically feasible flowsheet has been developed that maximizes the efficiency of the combined steam-cycle power plant and energy storage system through energy interchange between the two. Equipment for the storage system flowsheet has been sized and costed. The sensitivity of the efficiency of the system to changing several of the key parameters has been determined.



The final report for this project has been received and reviewed.

Gilbert Associates, (1.2.1)--The EPRI sponsored Phase I of this program has been completed; Phase II, sponsored by Sandia, was initiated December 19, 1978.

Institute of Gas Technology, (2.1.1)--The major conclusions from this study are that the open-loop chemical energy pipeline is technically feasible, existing natural gas transmission systems could be used, transmission of coal synthesis gases over long distances is more attractive economically than shipment of coal by rail and ample markets exist for the process steam electricity and SNG produced from the system.

The final report for this project has been approved for publication.

General Electric/Corporate Research and Development, (2.2.1)--Of the fifteen reactions considered for high-temperature thermochemical pipelines, the steam reforming of methane was selected as most attractive. For low-temperature applications, the benzene/cyclohexane system was selected.

A flexible package of computer programs has been developed to perform thermochemical pipeline design analysis.

The potential market for thermochemical pipelines is large, although poorly characterized with regard to geographic location, energy consumption as a function of temperature and capacity, duty cycle, and type of fuel presently used.

The final report for this project has been published.

General Electric Company, (2.2.2)--In spite of delays in receiving tube raw material, one duplex steam reformer tube has been fabricated successfully and shipped to KFA for testing in the EVA test facility. Testing is scheduled for May, 1979.

Rocket Research Corporation, (3.1.1)--A 300,000 BTU  $H_2SO_4$  closed-loop chemical heat pump demonstration facility has been designed, fabricated, and tested. This facility has also been used for component optimization.

An economic analysis of the major system variables affecting the total integrated system design and cost, and an assessment of the ability to commercialize this system are in progress.

A draft of the Phase 2a final report is in preparation.

EIC Corporation, (3.1.2)--The reaction of anhydrous  $CaCl_2$  to form solid  $CaCl_2 \cdot 2CH_3OH$  has been selected. Thermodynamic, kinetic, and heat transfer data on this reaction have been obtained. No side reactions or corrosion of Al or Cu have been observed. Over 300 methanolation/demethanolation cycles have been carried out without apparent degradation of performance.



A low-cost heat exchanger has been designed, based on the use of pelletized  $\text{CaCl}_2$  loaded on externally finned tubes.

A small-scale prototype has been constructed and tests are now being carried out. Preliminary data indicate the unit performs as expected. Design of the large scale prototype is complete.

The final report for this first phase of the project has been approved.

CES, (3.1.3)--The final report for this project has been received and reviewed.

Martin Marietta, (3.1.4)--A set of candidate construction materials has been selected for material compatibility tests. The experimental apparatus has been fabricated, and the tests are in progress.

The experimental apparatus for the subscale system tests has been designed and fabrication is nearly complete.

University of California at Davis, (4.2)--A draft of the progress report for the first year of this program has been received and reviewed.

Rocket Research Corporation, (4.3)--Test of commercially available catalysts have been completed; development of new catalysts is in progress.

Martin Marietta, (4.4)--The phase 1b final report has been approved.

#### Achievement of TEST Program Goals

The following is a list of program milestones which were reached during this reporting period:

- Technical and economic feasibility of TES for three solar thermal systems determined
- Technical and economic feasibility of open-loop thermochemical pipelines determined
- Technical and economic feasibility of high- and low-temperature closed loop thermochemical pipelines determined
- Technical feasibility of detnaforming duplex steam reformer tubes established
- Technical and economic feasibility of  $\text{H}_2\text{SO}_4$  chemical heat pump system established
- $\text{H}_2\text{SO}_4$  chemical heat pump component development complete; closed loop demonstration complete.

## Achievement of Project Goals

The project goals which have been met during the current reporting period are so indicated in Table III.

TABLE III  
STATUS OF GOALS FOR FY78 PROJECTS

Project Number and Title	Goal Descriptions	Status
1.1.1, 1.1.2	Select reactions or reaction sequences for solar thermal power plant applications	Complete
Chemical Energy Storage for Thermal Conversion	Evaluate selected reactions on basis of thermodynamics and kinetics	Complete
	Perform preliminary design and modeling of reversible chemical reaction storage systems	Complete
	Establish technical and economic feasibility of extended duration storage for solar power plants	In Progress
1.1.4	Conduct literature survey and experimental study to identify reaction sequence for ammonium hydrogen sulfate decomposition	Complete
Development of Operational Chemical Cycles for the Storage of Energy	Perform kinetic and thermodynamic measurements	In Progress
	Design and test flow mode bench scale reactor	In Progress
	Evaluate technical and economic feasibility	In Progress
	Conduct solar input configuration studies	In Progress
1.1.5	Determine basic hydration/dehydration properties of $\text{CaO}/\text{Ca}(\text{OH})_2$	Complete
Solar Energy Storage by Reversible Chemical Processes	Evaluate technical and economic feasibility of fixed-bed, fluidized bed, and rotating drum reactor systems	Complete
1.1.6	Synthesize and evaluate technically feasible flow sheets of storage systems based upon the sulfur trioxide and methane/water chemical systems	Complete
Chemical Storage of Thermal Energy		
1.2.1	Identify and characterize reversible chemical reaction systems and applications of interest to non-solar electric utilities	Complete
An Assessment of the Use of Chemical Reaction Systems in Electric Utility Applications, Phase II	Prepare preliminary conceptual designs	Complete
	Assess the technical and economic viability of promising reaction sequences and applications	In Progress



TABLE III (Continued)

Project Number and Title	Goal Descriptions	Status
2.1.1	Preliminary design of a nuclear (HTGR) and methane-based open-loop system	Complete
Transmission of Energy by Open Loop Chemical Energy Pipelines	Evaluate energy sources as alternatives to those in the preliminary design (e.g., coal gasification and HTGR/LNG)	Complete
	Assess the feasibility of using existing natural gas pipelines and storage systems for the synthesis gas	Complete
	Assess existing methanation technologies and interchangeability of the SNG with natural gas	Complete
	Evaluate the various alternative energy end-uses for heat, SNG, and electricity	Complete
	Develop two conceptual designs and evaluate their economics and environmental impacts	Complete
2.2.1	Evaluate potential energy sources for thermochemical pipeline systems	Complete
Closed Loop Chemical Systems	Evaluate alternate chemical systems	Complete
	Establish technical and economic feasibility of methane/steam and benzene/hydrogen systems	Complete
	Assess market for thermochemical pipelines	Complete
	Identify critical R&D needs	Complete
2.2.2	Design and fabricate two duplex steam reformer (DSR) tubes	In Progress
Duplex Steam Reformer Development	Design and fabricate adapter to mate DSR tubes to EVA test facility	Complete
	Design and fabricate catalyst for DSR tubes	Complete
	Design and fabricate instrumentation for DSR tubes	Complete
	Assemble test section	In Progress
	Develop test program for EVA facility	Complete
	Evaluate metallurgical performance	In Progress
	Evaluate reformer performance	In Progress
	Develop analytical model for DSR performance	Complete
Prepare licensing evaluation report	Complete	

TABLE III (Continued)

Project Number and Title	Goal Descriptions	Status
2.2.4 Cyclic Catalytic Storage Systems	Optimize process stages and determine process parameters at the steam-reformer liquid sodium interface of an advanced central receiver solar thermal power plant	Complete
3.1.1 Sulfuric Acid and Water Chemical Heat Pump/Thermal Energy Storage	Select concept for detailed sizing and scaling analysis	Complete
	Design and construct a sub-scale closed-loop demonstration system	Complete
	Conduct operational tests to verify system performance	Complete
	Conduct economic analysis of major system variables affecting total integrated system design and cost	Complete
	Perform transient and component optimization testing	Complete
	Assess commercialization potential	Complete
3.1.2 Methanol-Based Heat Pumps for Storage of Solar Thermal Energy	Identify combinations of inorganic salt substrates and carrier gases (CH <sub>3</sub> OH) suitable for chemical heat pump systems	Complete
	Experimentally determine thermodynamic, kinetic, and heat transfer data	Complete
	Perform engineering design and economic analysis	Complete
	Design, procurement, and fabrication of prototype, closed-loop system	In Progress
	Test of prototype, closed-loop system	No Activity
3.1.3 The Chemical Heat Pump - A Simple Means to Conserve Energy	Perform preliminary design and analysis of chemical heat pump configuration	Complete
	Experimentally investigate rates of water desorption from various salt hydrates	Complete

TABLE III (Continued)

Project Number and Title	Goal Descriptions	Status
3.1.4	Establish feasibility of constructing chemical heat pump based upon paired ammoniates	Complete
Thermal Storage for Solar Cooling Using Paired Ammoniated Salt Reactions	Perform and verify engineering analysis and design	In Progress
	Design prototype system	In Progress
	Test prototype system	No Activity
4.2	Identify and select potential chemical reactions for thermochemical energy storage systems	Complete
The Kinetics of Dissociative Chemical Reactions in Thermochemical Energy Storage	Experimentally investigate reaction kinetics	In Progress
4.3	Evaluate commercial catalysts and develop a standard activity test	Complete
Development of a Long-Life, High-Temperature Catalyst for the SO <sub>2</sub> /SO <sub>3</sub> Energy Storage System	If required, develop new catalyst	In Progress
	Conduct accelerated aging tests	No Activity
4.4	Determine reaction rates, heats of reaction, bulk density for selected ammoniates	Complete
Development of Ammoniated Salts Thermochemical Energy Storage Systems - Phases Ib and II	Design, fabricate, and test a subscale reaction system	In Progress
	Upgrade system performance computer models	In Progress



## THERMAL ENERGY STORAGE AND TRANSPORT PROJECTS

In this section, detailed discussions are given of the individual projects which comprised the TEST program during this reporting period. Topics discussed are: (1) Project Objectives, (2) Project Tasks, (3) Technical Progress, (4) Technical Problems, and (5) Publications. The projects are organized by Technology Breakdown Structure.

Chemical Energy Storage For Solar Thermal  
Conversion/Extended Storage Studies -  
Rocket Research Corporation (1.1.1)  
Sandia Laboratories, Livermore (1.1.2)

### Objectives

The overall objective 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 thermodynamic and kinetic bases, and preliminary design and modeling of energy storage subsystems based on these reactions. A flexible computer model of a solar-thermal, power generation facility (including various RCR energy storage subsystems) is being used to study the technical and economic feasibility of extending the solar thermal electric conversion (STEC) concept to include baseload power generation and the value of hybridization.

### Tasks

During the two years which have passed since the original proposal was submitted to NSF, certain changes have taken place in the concept of how reversible chemical reactions (RCR) for energy storage should be utilized with solar thermal electric conversion (STEC) systems.

While early concepts were generally tied to a short-term energy storage system (nominally 6 hours), it became apparent that long-term storage should be investigated also. The scope of the original program has therefore been expanded to include a detailed analysis of extending the original concepts to include solar-thermal conversion for baseload (extended storage time) power plants. Tasks 1, 2, and 3 are the original tasks as proposed for the NSF contract, while Subtasks 1 through 6 represent the work being funded by DOE (ERDA) to extend the original concepts to include baseload applications. These Subtasks have been inserted between Task 1 and Task 2 both in practice and in this description.

Task 1. Conceptual Development: The objectives of this task are to: (1) select reactions or reaction sequences which may be useful in chemical energy storage systems; (2) tabulate physical, thermochemical, and kinetic properties for these reactions; (3) evaluate the applicable temperature ranges of these reactions; and (4) define a series of baseline cases. A preliminary evaluation of the potential reactions will be performed, and those showing the most promise will be separated into groups suitable for inclusion in the low-temperature (Task 2) and high-temperature (Task 3) studies.

Subtask 1. System Selection: Three solar thermal-electric power plant concepts will be selected to integrate with chemical energy storage for a detailed study at baseload capability. The selected concepts will be reduced to mathematical equations describing costs of the components and subassemblies as a function of size and performance.



Subtask 2. Baseload System Sizing: Four sites for the location of the baseload solar thermal-electric power plant models will be selected, and by using historical data for each selected site, an average electrical demand load model will be established. Then, by using a storage subsystem with designated round-trip efficiencies, each system will be sized for baseload capacity, and the capital costs of the storage subsystem will be established.

Subtask 3. Effect of RCR Energy Storage Subsystems Upon Solar Power Plants and Cost Sensitivity Studies: Guidelines for parasitic powers and heat loss effects will be established. Sandia\* will: (1) determine the impact on total electrical output for variable levels of parasitic powers and heat losses, and establish scaling relationships for the STEC system, based upon parasitic and storage operational characteristics; (2) identify the unique power plant/storage facilities interfaces and quantify the potential beneficial or detrimental effects; and (3) conduct cost and performance comparisons of the total STEC plant using the idealized storage relationships established in Subtask 1. The studies will be conducted for grid-connected or grid-independent baseloads and for winter and summer peaking for the locations identified in Subtask 2.

Subtask 4. RCR Energy Storage: An integrated, computerized math model will be developed for sizing, performance evaluation, and cost estimation of RCR energy storage sub-systems based on the reactions of interest identified in Task 1.

Subtask 5. Optimization of Solar Thermal-Electric Power Plants: Each of the three STEC systems selected in Subtask 1 will be optimized for baseload capability (plus intermediate and peaking, if applicable) with the SO<sub>2</sub>/SO<sub>3</sub> storage system. Capital costs and energy costs will be calculated. Parametric studies will be performed on each system to identify the cost sensitivities of various parasitic powers in the major components and subsystems.

Recommendations for pursuing baseload solar power plants will be provided by RRC and Sandia,\* and a detailed development plan to attain long-range goals will be established.

Subtask 6. Chemical Energy Storage Plant Specifications: Two sets of power plant requirements will be established for use in the preliminary design effort of the basic NSF/DOE program. The requirements will be nominally for a high- and low-temperature system.

The specifications will be generalized from the optimum plant sizes established in Subtask 5. The specifications that will be fixed include: power level(s), operating temperature(s), storage capacity, and site location.

Tasks 2 and 3. Low- and High-Temperature Systems Analysis: Five reactions or reaction sequences in the temperature range of 400 to 1300 K will be selected for a detailed engineering study and evaluation.

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\*This work performed as part of project 1.1.2.



## Technical Progress

Tasks 1, 2, and 3 - Reaction Selection and Evaluation: All of Task 1 and the thermodynamic and kinetic analyses of Tasks 2 and 3 are complete. The 24 reactions have been ranked as to relative power and energy related costs. The reaction specification has been refined to five reactions per temperature regime. Final reaction selection (two most promising) has yielded  $\text{CaO}/\text{Ca}(\text{OH})_2$  and  $\text{SO}_2/\text{SO}_3$ . Detailed flow sheets, efficiencies, and cost data are soon to be completed.

Subtasks 1, 2, 3, 4, 5, and 6 - Extended Storage Study.

Subtask 1. System Selection: The selection has been completed, as described in the previous semi-annual report. The results are:

- Central receiver collection, Rankine cycle power generation (783 K)
- Central receiver collection, open-Brayton cycle power generation (1310 K)
- Distributed collection, Rankine cycle power generation (588 K)

Subtask 2. Baseload System Sizing: The sizing has been partly completed, as reported previously. Four location sites have been selected for a STEC power plant: 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. Baseload sizings have been calculated for both high-temperature, Brayton cycle STEC and an intermediate temperature Rankine cycle STEC for both 100-MW<sub>e</sub> baseload service and as part of a solar/fossil hybrid (see Subtask 4 below).

Subtask 3. Effect of RCR Energy Storage Subsystems Upon Solar Power Plants and Cost Sensitivity Studies: Sandia has used its central STEC plant cost/performance expertise for system selection, baseload sizing, and general modeling concepts required by this study. Rocket Research has provided chemical process analysis and detailed load information required to analyze the worth of long-term storage in "stand alone" plants (see in-house research discussion). Subtask 3 information exchanges will continue until the completion of the other RRC subtasks.

Subtask 4. RCR Energy Storage: The overall simulation/economic evaluation computer model has been completed. This program uses 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 a specified load profile (baseload, baseload plus intermediate, or grid independent) and storage round-trip efficiency. The code is flexible enough to determine optimum sizing for components based on busbar energy costs for both Brayton and Rankine cycle systems and for both autonomous (pure solar) operation and hybrid operation when an alternate energy source cost is specified.



Subtask 5. Optimization of Solar Thermal-Electric Power Plants: All three systems A (Distributed Trough, Rankine), B (Central Receiver, Open-Brayton Cycle), and C (Central Receiver, Rankine) have been examined in depth. Assuming reasonable costs for solar plant components and alternate energy backup, analysis of these systems has yielded preliminary busbar energy costs and component size ranges. The value of yearly averaging storage has been examined in some detail.

In both the autonomous and hybrid cases, a tradeoff exists between mirrors and storage. The minimum cost solution appears to involve "oversizing" the mirror field somewhat to reduce required storage sizes appreciably. In the hybrid cases the optimum storage capacity is in general less than 15 hours (at full plant output) using idealized insolation. The previous idealized insolation data, although a good approximation to the total annual energy available, lacked the unpredictable nature of "real" insolation. Results of simulations of STEC plants using these detailed hourly insolation data show that for both autonomous and hybrid baseload operation, costs and storage requirements are larger with "real" insolation data. Further, the Brayton system appears to have a slight edge over the Rankine system for cases studied to date.

Subtask 6. Chemical Energy Storage Plant Specifications: Work is completed on the chemical engineering aspects of this contract.

The storage of energy by use of the reversible chemical reaction  $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca(OH)}_2$  was considered for inclusion into an intermediate temperature autonomous baseload STEC plant. As shown in previous sections of this work (and by J. Iannucci at Sandia) extremely large charge/discharge ratios are needed by such autonomous plants, which makes the economic design of the chemical reactor crucial to the plant's viability. Comparison of fixed bed, moving bed, and fluidized bed concepts led to the selection and design of a moving bed with one-eighth inch diameter pellets. The design entails a long vertical reactor column with co-current nitrogen as the heat transfer medium in direct contact with the chemical. Process flow diagrams and balance sheets for both the exothermic and endothermic modes have been developed and efficiencies have been estimated from them.

#### Technical Problems

No technical problems will be encountered in the completion of this work. Subtask 5 is specific to  $\text{SO}_2/\text{SO}_3$ , but RRC feels the spirit of the study intended for several chemical systems to be optimized. Sandia concurs and supports such a broadening of the statement of Subtask 5 to include other candidate reactions; hence, the  $\text{CaO}/\text{Ca(OH)}_2$  reaction has also been chosen for detailed design and analysis.

## Publications

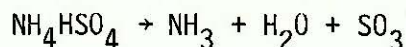
1. J. J. Iannucci, R. D. Smith, C. J. Swet, "Energy Storage Requirements for Autonomous and Hybrid Solar Thermal Electric Power Plants" Proceedings of the International Solar Energy Congress, New Dehli, India, January 1978.
2. Huxtable, D. D. and Schmidt, G., "Chemical Energy Storage for Solar Thermal Conversion," Interim Report No. 2, 77-R-558, Rocket Research Corp., Redmond, Washington, April 1977.
3. Huxtable, D. D. and Schmidt, G., "Chemical Energy Storage for Solar Thermal Conversion," Quarterly Report No. 1, 76-R-538, Rocket Research Corp., Redmond, Washington, October 1976.
4. J. J. Iannucci, "The Value of Seasonal Storage of Solar Energy," Proceedings of the Applications Workshop on Thermal Storage Integrated into Solar Power Plants, February 1978.
5. J. J. Iannucci and P. J. Eicker, "Central Solar/Fossil Hybrid Electrical Generation: Storage Impacts," Proceedings of the Annual Meeting of the American Section of the International Solar Energy Society, Denver, August 1978.
6. R. D. Smith, "Chemical Energy Storage for Solar Thermal Electric Conversion," Proceedings of Focus on Solar Technology: A Review of Advanced Solar Thermal Power Systems, Denver, November 1978.
7. J. J. Iannucci, "Goals of Chemical Energy Storage," Proceedings of Focus on Solar Technology: A Review of Advanced Solar Thermal Power Systems, Denver, November 1978.
8. R. D. Smith, "Chemical Energy Storage for Solar Thermal Conversion," Proceedings of Thermal Energy Storage Contractor's Review Meeting, Springfield, Virginia, December 1978.
9. J. J. Iannucci, "Systems Impact of Thermochemical Energy Storage for Solar Applications," Proceedings of Thermal Energy Storage Contractor's Review Meeting, Springfield, Virginia, December 1978.



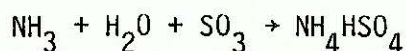
Development of Operational Chemical Cycles For  
The Storage Of Energy -  
University of Houston (1.1.4)

Objectives

The overall objective of this program is to find, develop, and demonstrate a chemical reaction cycle which can be used for solar storage and regeneration in electrical power generation systems which operate within the temperature range of 450 - 500°C. In particular, the thermal decomposition of ammonium hydrogen sulfate ( $\text{NH}_4\text{HSO}_4$ ) into ammonia ( $\text{NH}_3$ ), water ( $\text{H}_2\text{O}$ ), and sulfur trioxide ( $\text{SO}_3$ ) is being investigated for the energy storage step



and the reverse recombination reaction for the energy regeneration step



Tasks

The program includes the efforts of three research groups (identified as Phases 1A, 1B, and 1C) which work separately but coordinate their efforts and planning through bi-weekly meetings. The first phase is a laboratory investigation which addresses fundamental chemistry problems; the second phase is concerned with the chemical engineering aspects of the system; and the third phase is concerned with characterizing the solar energy input conditions.

Phase 1A. Chemical Reaction Fundamentals: Various reaction mechanisms will be screened (by means of literature surveys and experiments) in search of net reaction cycles which are equivalent to the energy storage and regeneration reactions and which allow satisfactory separation of  $\text{SO}_3$  from  $\text{NH}_3$  and  $\text{H}_2\text{O}$  at high temperature. After suitable reaction mechanisms (including separation procedures) 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. A high-pressure reactor will then be designed to study the individual mechanisms under operational conditions and to test their long-term reversibility.

Phase 1B. Process and Engineering Configuration: The most suitable chemical reaction cycle selected through the work of Phase 1A will be investigated in a flow mode. 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.

Phase 1C. Solar Energy Input Configuration: Solar input configuration studies will be conducted simultaneously with the work of Phases 1A and 1B. These will involve location and evaluation of parabolic solar concentration systems, establishment of specifications, procurement of a suitable concentrator, and preliminary heat transfer studies. Materials suitable for a solar-heated reactor will be identified. A conceptual design will be developed for a full-scale demonstration plant including storage. The basic cost estimates will also be developed for the chemical storage portion of a solar tower electrical system.

### Technical Progress

#### Phase 1A. Chemical Reaction Fundamentals:

- A series of experiments using mixtures of  $\text{NH}_4\text{HSO}_4$  plus each of the 1A metal sulfates was carried out. The experiments involved: (1) monitoring the pressures above the reacting mixtures at various temperatures (and hence, indicated the appearance of a gaseous product) and (2) thermogravimetric techniques (which measured the disappearance of the reactant  $\text{NH}_4\text{HSO}_4$ ).
- Mixtures containing  $\text{NH}_4\text{HSO}_4$  plus each of three metal sulfates ( $\text{K}_2\text{SO}_4$ ,  $\text{Rb}_2\text{SO}_4$ , and  $\text{Cs}_2\text{SO}_4$ ) were selected as the most promising in effecting the decomposition of the  $\text{NH}_4\text{HSO}_4$  with separation of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  from  $\text{SO}_3$  during energy storage.
- A laboratory reactor system and a chemical analysis procedure were developed for the study of  $\text{NH}_3$  and  $\text{SO}_3$  product yield from these reaction mixtures.
- Experiments were carried out to determine the effect of reactant mixture ratio. A series of tests designed to determine the effect of the mole ratio of mixtures of  $\text{NH}_4\text{HSO}_4$  and  $n\text{Rb}_2\text{SO}_4$  on  $\text{SO}_3$  and  $\text{NH}_3$  yield indicated: (1) the total percent recovery for both  $\text{NH}_3$  and  $\text{SO}_3$  increases as the mole ratio ( $\text{Rb}_2\text{SO}_4$  to  $\text{NH}_4\text{HSO}_4$  in the initial reaction mixture) is increased from 1.0 to 1.1; (2) the percent yield of volatile  $\text{NH}_3$  appears to reach a maximum at a mole ratio between 1.2 and 1.5; and (3) the percent yield of volatile  $\text{SO}_3$  is negligible at low mole ratios, but becomes significant at a mole ratio of 1.5.
- Mixtures containing  $\text{NH}_4\text{HSO}_4$  with each of eight metal oxides were screened for suitability as a means of providing energy storage. A mixture containing  $\text{NH}_4\text{HSO}_4$  plus  $\text{ZnO}$  was selected as the most promising.
- A series of tests designed to determine the effect of mole ratio (of  $\text{ZnO}$  to  $\text{NH}_4\text{HSO}_4$ ) and temperature on the yield of  $\text{NH}_3$  and  $\text{SO}_3$  indicated: (1) the yield of  $\text{NH}_3$  increases from ~ 5 percent at  $250^\circ\text{C}$  to greater than 90



percent at 450°C; (2) the yield of SO<sub>3</sub> is negligible at all temperatures in the range 250 - 450°C; and (3) the yield of NH<sub>3</sub> at each temperature in the range 300 - 450°C is greater for the mixture in which ZnO/NH<sub>4</sub>HSO<sub>4</sub> = 2.0.

- Studies designed to identify metals suitable for construction of a high pressure reactor required for separation of NH<sub>3</sub> and H<sub>2</sub>O from SO<sub>3</sub> by a condensation technique revealed that all metals examined were found to promote unidentified, but definitely undesirable, side reactions when exposed to NH<sub>4</sub>HSO<sub>4</sub>-metal sulfate mixtures at 400°C. Vicor glass, however, does not promote the side reactions to any observable extent. The results suggest that any metal reactor system designed for use in NH<sub>4</sub>HSO<sub>4</sub> decomposition may have to be glass-lined.
- An experimental apparatus was designed and constructed for laboratory study of the energy regeneration, recombination reaction.
- Equilibrium vapor pressure measurements were used to determine the appropriate thermodynamic properties.

#### Phase 1B. Process and Engineering Configuration:

- A bench-scale design has been completed for the flow system in which the AHS decomposition reactions are to occur. The flow system is to be used to determine reaction characteristics and kinetics in a flow mode, operating space velocities and operating heat flux values. Shakedown runs have been completed.
- Heat transfer characteristics of the fluids in the AHS-cycle when heated by solar radiation have been investigated in order to discern any problems which may be encountered. Preliminary results indicate heat flux and film coefficient values in the radiant section typical of those values experienced in commercial steam generation processes.
- Transport property data for the species considered were obtained from the literature and tabulated.
- A mathematical model and computer design program for tubular flow reactors were developed.
- Heat transfer considerations and preliminary economics and performance for a full-scale conceptual chemical storage system were explored.
- The effectiveness of Cassegrainian solar concentrators was investigated.

#### Phase 1C. Solar Energy Input Configuration:

- The probable optical performance of a parabolic dish was studied in detail by deriving simple analytical formulas relating the attainable concentration ratios to the inaccuracies of the reflecting surface and dimensions of the concentrator. Approximate expressions for the thermal efficiency of cavity receivers and external receivers were derived which related efficiency to the absorptivity of the surfaces, the emissivity



and geometry. The flux distribution on focal and off-focal planes, and on the inside walls of cavity receivers of different configurations was studied in order to fix the optimum shape of the cavity furnace.

- A preliminary review was made of the applicability of refractory metal alloys in solar reactors. They offer a twofold advantage over nickel-chromium alloys in that they are both stronger and have higher thermal conductivities.
- Potential suppliers of parabolic dish systems usable as solar concentrations were identified and contacted. System specifications, performance and cost data were obtained from each potential supplier.
- The thermophysical properties of various steels, alloys, and refractories suitable for high temperature use in solar furnaces were reviewed.
- The engineering feasibility of liquid sodium loops, sodium heat pipes, air, helium, and superheated steam was investigated.
- Heliostat requirements for 900°C external receivers were analyzed using published data on collector field characteristics for generating high flux densities ( $\sim 1.7 \text{ mW/m}^2$ ).

#### Technical Problems

There are currently no problems of a magnitude such that overall program costs or objectives will be affected. Due to the second year budget as approved by DOE (\$227,300) being less than that requested (\$289,210) some scheduling revisions were necessary. The most significant change is that some work on the recombination reaction has been shifted to a later date.

#### Publications

1. W. E. Wentworth, C. F. Batten, G. E. Corbett, and E. C. M. Chen, "An Ionic Model for the Systematic Selection of Chemical Decomposition Reactions for Energy Storage," in the Proceedings of the 1977 Annual Meeting (published by the American Section of the International Solar Energy Society, 300 State Road 401, Cape Canaveral, Florida, 32920, 1977) p. 18-1.
2. W. E. Wentworth, A. F. Hildebrandt, C. F. Batten, G. E. Corbett, and E. C. M. Chen, "Thermal Chemical Conversion Cycles for Storage of Solar Energy," submitted for publication in Review Internationale des Hautes Temperatures et des Refractaires.
3. W. E. Wentworth, C. F. Batten, and E. C. M. Chen, "Thermochemical Conversion and Storage of Solar Energy," submitted for publication in the Proceedings of the International Symposium on Energy Sources and Development (Barcelona, Spain).

4. C. E. Mauk, H. W. Prengle, Jr., and E. Sun, "Off-Axis Concentration in a Cassegrainian Solar Collector," to be published.
5. J. C. Ray, Jr., "Chemical Storage of Solar Energy: A Survey of Inorganic Sulfates and Oxides which Separate Sulfur Trioxide from the Decomposition Gases of Ammonium Bisulfate," Masters Degree Thesis (May 1978) Department of Sciences and Technologies, University of Houston-Clear Lake City, Clear Lake City, Texas.



Solar Energy Reversible Chemical Processes  
Atomics International (1.1.5)

Objective

The objectives of this study were to study the basic hydration/dehydration properties of the  $\text{CaO}/\text{Ca}(\text{OH})_2$  system and to generate conceptual designs and evaluations of various methods of inputting and extracting energy.

Tasks

The program is divided into six tasks.

Task 1. Characterization of storage material: The objective of this task is to characterize the starting materials used, both to discover anticipated problem areas and to help explain the results obtained in succeeding tasks.

Task 2. Cycling Experiments: The purpose of this task is to better understand the cycling behavior of  $\text{CaO}/\text{Ca}(\text{OH})_2$  as related to its behavior in a fixed bed environment.

Task 3. Calorimetry and kinetics: The purpose of this task is to measure the heat evolved/absorbed during the hydration/dehydration process and to measure the time required for the reaction to take place.

Task 4. Fluidized Bed System Analysis: Tasks 4 & 5 compare two possible  $\text{CaO}/\text{Ca}(\text{OH})_2$  concepts with each other by means of system designs and analysis using common energy storage requirements, charge rates etc.

Task 5. Rotating Drum System Analysis: See task 4 which pertains to both the Rotating Drum and Fluidized Bed studies.

Task 6. Alternate system evaluation, assessment, and ranking: This task compares the systems studied in Tasks 4 & 5 with the fixed bed system previously studied. An initial assessment and ranking of the three  $\text{CaO}/\text{Ca}(\text{OH})_2$  storage concepts is made.

Technical Progress

Task 1. Characterization of the analytical-grade  $\text{Ca}(\text{OH})_2$  starting material included wet chemical analysis, surface area determination, particle size analysis, ESCS, SEM and gas chromatography for evolved gases.



Task 2. Cycling experiments were conducted at dehydration temperatures of 550°C for 44 minutes; hydration began to occur when the reaction cooled to 375°C and took ~14 minutes using 110°C steam. As many as 1100 cycles were run on one of the three experimental sizes.

Task 3. A pressure differential scanning calorimeter (PDSC) was used to confirm the equilibrium constants for the reaction in the range 450 to 550°C, to confirm that the heat of reaction came within 90-95% of the published value, and to determine a value of 36 kcal/mole for the activation energy for the reaction  $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$ .

Task 4 and 5. Fluidized bed and rotating drum system analyses were conducted to allow comparison the performance of these two systems with the fixed bed system in Task 6.

Task 6. Compares and gives a ranking to the three "systems" mentioned above.

The major conclusions reached are

- The reaction  $\text{Ca(OH)}_2 \rightleftharpoons \text{CaO} + \text{H}_2\text{O}$  is completely reversible.
- The rate of reaction is not so slow as to eliminate it from contention as a possible chemical energy storage material.
- The heats of reaction are as indicated in previous investigations.
- The material can be cycled 1000 times without "inherent" degradation.
- The rotating drum concept ranked lower than the fixed or fluidized bed designs.

### Technical Problems

Technical problems related to this investigation and to a  $\text{Ca(OH)}_2/\text{CaO}$  system include:

- Significant corrosion took place during the cycling tests, the cause of which was not determined.
- The efficiency of the beds during cycling changed as a function of time down to values as low as 30%. While the beds could be regenerated by outgassing and heating, the actual cause of the degradation was never fully explained.
- No scheduled work was completed at elevated steam pressures due to the failure of the PDSC on pressurized steam.

## Publications

1. D. K. Chung, "Application of Seasonal Solar Heat Storage for Crop Drying, Process Steam Generation, Electrical Power Generation, and Water Pumping," AI Internal Document No. N162TI130006, October 25, 1978.
2. R. D. Rennick, R. L. Gay, and G. Ervin, "Conceptual Fluidized Bed Design for Calcium Oxide Solar Energy Storage," AI Internal Document No. N162TI130009, September 27, 1977 (to be released).
3. D. K. Chung, "An Economic Assessment of the Application of a  $\text{CaO}/\text{Ca}(\text{OH})_2$  Thermal Energy Storage System Applied to a Commercial Solar Power Station," AI Internal Document No. N162TI120008, September 19, 1977 (to be released).
4. G. P. Hajela, "Solar Heating and Cooling of Buildings Using  $\text{MgO}/\text{Mg}(\text{OH})_2$  Thermal Storage," AI Internal Document No. N162TI130007, September 28, 1977 (to be released).
5. J. K. Rosemary, "Comparison Study and Evaluation of  $\text{CaO}/\text{Ca}(\text{OH})_2$  Heat Storage System Concepts Applied to a Commercial Solar Power Station." Draft of final report submitted to Sandia Livermore Laboratory on February 14, 1978, under Contract FA0-92-7671.
6. G. Ervin, "Solar Heat Storage Using Chemical Reactions," *Journal of Solid-State Chemistry*, 22, 1, 51 (1977).
7. Atomics International, "Solar Energy Storage By Reversible Chemical Processes, Final Report," Contract FA0-92-7671, (1979).



Chemical Storage Of Thermal Energy -  
Lawrence Berkeley Laboratory (1.1.6)

Objectives

The two primary objectives of the present program are to investigate performance and costs for the  $\text{SO}_2/\text{SO}_3$  and  $\text{CH}_4/\text{H}_2\text{O}$  high temperature reversible chemical energy storage systems, and to thoroughly document, for the above two systems, the benefits of various alternative storage system designs and methods of storage/power plant integration.

Tasks

Task 1. The first undertaking shall be to identify alternative system designs, operating modes and methods of integration with the electrical generating plant for the  $\text{SO}_2/\text{SO}_3$  storage system. Examination of cost and performance trade-offs shall proceed concurrently during this effort. Alternatives to be considered shall include but not be limited to the following:

- Integration studies with several types of electric power plants such as high temperature (greater than  $800^\circ\text{C}$ ) and medium temperature (greater than  $500^\circ\text{C}$  but less than  $800^\circ\text{C}$ ) open and closed Brayton cycles, and steam Rankine cycles with and without reheat.
- Effects of various operating pressures and temperatures during charge and discharge modes.
- $\text{SO}_3$ ,  $\text{SO}_2$ ,  $\text{O}_2$  storage pressures and related cost effectiveness.
- Direct separation in receiver vs. indirect through an intermediate working fluid.
- Heat transfer and pressure drop cost performance trade-offs for heat exchangers, piping and other components.
- Examine the necessity of separating liquid  $\text{SO}_2$  and liquid  $\text{SO}_3$ .
- Examine the cost effectiveness and effect on relative storage/plant sizings of utilization of low and medium grade heat from the storage and generating plant systems.
  - Examine the worth of extraction of medium grade heat from the turbo-machinery of the generating plant for use in the storage system.



- Examine the worth of extraction of low grade heat from the generating plant for use in the storage system.
- Examine the worth of utilization of low and medium grade heat from the  $\text{SO}_2/\text{SO}_3$  system in the generating plant.

Task 2. The second task will be to study the performance and cost effectiveness of the  $\text{CH}_4/\text{H}_2\text{O}$  storage system for those configurations identified in Task 1 which appear most advantageous.

Task 3. The third task shall consist of making comparisons of several of the most cost effective  $\text{SO}_2/\text{SO}_3$  and  $\text{CH}_4/\text{H}_2\text{O}$  system designs. This exercise will establish methods of comparison of competing systems and will produce recommendations for future emphasis.

Task 4. Earlier work which was initially directed toward comparing chemical storage systems with sensible storage systems has produced a new high-temperature heat storage concept. In this concept thermal energy is stored in magnesia bricks, using steam directly as the heat transport medium. Steam appears to hold promise compared to helium which has been previously proposed by other investigators, with respect to system costs, pumping power requirements, and operating modes. With the concurrence of NASA-Lewis, which has DOE responsibility for the high-temperature sensible and latent energy storage programs, a short duration, low level of effort study will be performed on the latter concept to evaluate cost-effectiveness for a power plant application. At the suggestion of NASA-Lewis, this program will include an assessment of using a prestressed cast iron containment vessel.

Task 5. In addition to the primary objectives described above, periodic review and analysis of selected research reports, and correlations of the present work with the work of other selected investigations shall be performed as may be requested by Sandia.

### Technical Progress

Evaluation of alternative system configurations as described in Task 1 has proceeded very slowly, and only limited results have been obtained. Tasks 2 and 3 have not been started. Task 4 is also proceeding slowly, and the assessment of prestressed cast iron containment vessels has not as yet been initiated. A partial draft final report on the  $\text{SO}_2/\text{SO}_3/\text{O}_2$  work was received in October 1978, reviewed, and returned for major revision.

### Technical Problems

Scheduled milestones have not been met.

## Publications

1. Mathew, R. J., "Chemical Energy Storage Using the Methane-Steam Reaction," M.S. Thesis, June 1978 (for work done in FY76).
2. Hill, S. A., "Adaptation of the Sulfur Oxide System for Chemical Storage of Solar Energy," M.S. Thesis, September 1978 (for work done in FY77).



An Assessment Of The Use Of Chemical Reaction Systems  
In Electric Utility Applications,  
Phase II - Gilbert Associates, Inc (1.2.1)

Objectives

Total investment, operating and maintenance costs, and life cycle cost will be determined for three of the systems for which conceptual designs and equipment cost estimates were performed in Phase 1.\* A cost and benefits/limitations comparison will be made between those systems and alternative thermal storage/transportation systems not based on chemical reactions. The market potential for chemical reaction systems (CRS) will also be estimated.

Tasks

Task 1. Revision of the benzene/cyclohexane CRS Conceptual Design: The conceptual design of the benzene/cyclohexane chemical reaction system performed in Phase 1 will be revised to utilize a new thermal source. The revision will include:

- A new thermal source which is capable of charging the CRS at a temperature higher than 670°F will be selected from the final candidate sources given in the Phase 1 report.
- Redesign of endothermic reactors and other equipment associated with charging operation.
- Redesign of transmission lines and associated equipment.
- Redesign of exothermic reactor(s) and equipment associated with discharging operation.

Selection of a new end use, if appropriate.

In addition, the direct capital cost for all major equipment involved in the revised design will be developed in a manner consistent with the procedure used in the Phase 1 report.

Task 2. Life Cycle Costs and Benefits: The equipment direct capital costs developed in the Phase 1 report and Task 1 of Phase 2 will be expanded to include indirect costs such as engineering, construction management, contingency, interest on funds employed during construction, engineering fee and escalation as appropriate. In addition to the direct and indirect project costs, an allowance for startup costs and working capital will be provided to complete the total investment cost.

\*Funded by Electric Power Research Institute



An annual operating and maintenance cost will be computed from the following expense items: fuel, labor, utilities, overhead, and expendable materials.

Using the aforementioned total investment and O & M costs, Chapter V of the EPRI Technical Assessment Guide (8/77) will be followed to arrive at a total Levelized revenue requirement expressed in dollars for each of the 3 CRS systems being examined. The fixed charge rate percentages including tax preferences found on Page V-2 of the Guide will be used to determine the capital component of the levelized revenue requirements while a 6% inflation rate will be consistently applied to the levelized expense component.

An annual energy production, levelized over the life of the unit, will also be calculated for each of the 3 CRS systems. Depending upon the end use of the system, it is anticipated that the results will be expressed as either millions of BTU's (MMBTU) or millions of BTU's per mile (MMBTU/mile).

A life cycle cost per unit of energy will then be calculated for each of the 3 CRS systems.

Depending upon the end use of the system, the life cycle cost will be expressed as either \$/MMBTU or \$/MMBTU/mile. The life cycle costs will also be separated into and reported as power-related costs (\$/kW(e)) and energy-related costs (\$/kW(e)h).

In addition, potential benefits to be realized by commercialization of the selected CRS systems will be qualitatively discussed - quantified wherever feasible - in terms of fuel consumption, reliability, financing requirements, environmental impacts, and unique technical characteristics.

The life cycle cost calculations will be developed and documented in such a manner to serve as a generic methodology easily applied to different source/user applications.

Task 3. Alternative Technology: Contemporary, competitive alternative thermal storage and/or transportation systems will be technically evaluated, capital and O & M costs estimated, and a life cycle cost per unit of energy calculated. Benefit considerations as described in Task 2 will also be accomplished.

To minimize estimating costs, it is anticipated that only the most viable alternative system will be selected for each of the 3 CRS.

Task 4. Comparison: A comparative matrix will be developed comparing life cycle costs and benefits/limitations for the CRS systems and alternatives.

Task 5. Market Potential: The market potential for "practical scale" thermal storage and/or transportation systems in the 1980 and 2000 time frame for electric utilities will be estimated. Another estimate will then be made of the extent that CRS systems with lower life cycle costs than appropriate alternative technologies can penetrate this market. The impact that this penetration will have upon conservation will be discussed and quantified as appropriate.

Task 6. Cost Sensitivity Analysis: Determine the cost sensitivity to variations in key parameters such as load factor and system size for those CRS systems, if any, with lower life cycle costs than appropriate alternative technologies as defined in Task 5.

Task 7. Final Report: A final report will be prepared summarizing the work performed in Phase 2. This will include recommending those areas, if any, where further research or development would enhance the applicability of CRS.

#### Technical Progress

Kickoff of Phase 2 and final review of Phase 1 took place on December 19, 1978.

#### Technical Problems

None

#### Publications

1. Stewart, J. D., et al., "An Assessment of the Use of Chemical Reaction Systems in Electric Utility Applications," Phase I Final Report EPRI contract RP 1086-1, Gilbert Associates, December, 1978.



Transmission Of Energy By Open-Loop  
Chemical Energy Pipelines -  
Institute of Gas Technology (2.1.1)

Objective

The program objective is to assess the techno-economic possibility of two specific near-term and mid-term cases of energy transport via open-loop, methane-based, reversible chemical reactions. The near-term case consists of a coal gasification plant producing carbon monoxide and hydrogen, a 1000-mile pipeline transmitting the product gas to a methanator producing heat (as steam) and SNG, which is then available for use in the existing natural gas (LNG) distribution system. In the mid-term version, a high-temperature gas-cooled nuclear reactor (HTGR) is supplied with hydrocarbons by a liquified natural gas (LNG) receiving terminal. The entire complex is situated on a floating platform off the U. S. coastline. An undersea pipeline connects the complex to the shore and to the remaining system components, which are the same as those of the near-term case.

Tasks

The program is divided into six tasks: Task 1 is the preliminary design; Tasks 2-5 are the detailed subsystem designs; Task 6 is the techno-economic evaluation.

Task 1. Preliminary design: The objective of this task is to develop a preliminary design for an open-loop system. This work consists of: the synthesis and techno-economic evaluation of an open-loop, reversible chemical reaction energy transport and storage system; the preliminary identification of institutional and safety problems associated with the system; and the selection of two specific cases (a near-term and a mid-term) for more detailed analysis during the remainder of the program.

Task 2. Alternative Energy Sources: This task is aimed at identifying energy sources, other than nuclear, capable of driving the methane reforming reactions.

Task 3. Synthesis Gas Storage and Pipelines: The cost of transmitting and storing CO/H<sub>2</sub> mixtures in the existing natural gas pipeline system will be assessed. An evaluation of the alternatives of modifying or replacing the natural gas compressors and of adding additional pipelines will be carried out.

Task 4. Methanation Technology and Synthetic Natural Gas (SNG) Interchangeability: In this task, various methanation process schemes will be reviewed and that scheme which has the most advantage with regard to thermal duties and SNG quality will be optimized and evaluated economically.



Task 5. Alternative Energy Uses: Utilization scenarios for SNG and heat (the end-products of the thermochemical pipeline) will be developed. Bounds will be identified for determining under what conditions the product heat should be used for electrical generation. Other uses of the heat, such as process steam, district heating, etc., will be evaluated for feasibility and economics.

Task 6. Techno-economic Evaluation and Conceptual Design: The economics and environmental impact of the thermochemical pipeline systems synthesized in the above tasks will be assessed. Areas which may require further development before an operating system could be built will be identified.

### Technical Progress

Task 1. Three open-loop systems have been evaluated. The first, which forms a "base" case, consists of: (1) an HTGR supplying heat for the steam reforming of methane, and (2) a 161-km (100-mile) pipeline transmitting the reformed gas to a methanator producing heat (as steam) and SNG that is available for use in the existing natural gas distribution system. In what is known as the near-term case, the HTGR/reformer is replaced by a coal gasification plant producing carbon monoxide and hydrogen, while the rest of the system (pipeline, methanator, end-use) remains conceptually the same as in the base case. In the mid-term version of the open-loop chemical energy pipeline, the HTGR/reformer is supplied with hydrocarbons by a liquified natural gas (LNG) receiving terminal, with the whole complex situated on a floating platform 4.8 km (three miles) or less off the United States coastline. An undersea pipeline connects the complex to the shore and to the remaining system components.

Task 2. Since the base case design was assembled using components from the work of others, the selection of the heat source was based upon design and cost information availability. As a result, the base case heat source selected was a design published by General Atomic, and consists of an HTGR, reformer module, and steam generator. The heat source for the near-term case is a coal gasification plant, and after a review of potential candidate designs, the Ash Agglomerator Gasifier (AAG) process was selected because of its product composition and efficiency.

Task 3. Existing natural gas transmission systems were assessed with regard to potential conversion to reformed or coal-synthesis gas operation. In particular, problems associated with materials compatibility, compressor adaptability, and compressor driver conversion were analyzed. In general, no problems of a serious nature were identified, but a detailed analysis of each existing natural gas pipeline system is required before specific conclusions may be reached.

Storage of the reformed or synthesis gas was evaluated for three different methods: linepack, high-pressure pipe-bottle, and underground storage. Linepack storage in the transmission systems was evaluated under both static and dynamic flow conditions with regard to cost and contained volume. All three methods of storage were found to be feasible and could provide increased system versatility.



Task 4. The principal methanation processes were reviewed, and selection of the process used in the current study, the cold gas recycle scheme, was based upon its stage of development, temperature control, operating flexibility, and cost.

Task 5. Markets were identified for the thermal, gaseous, and electric products. District heating, as a load for the low-temperature products, was considered marginal at best, and alternative loads were examined from a location and time of energy use viewpoint.

Task 6. The installed plant costs for the base case system (one HTGR-reformer, pipeline, and methanation complex) totaled approximately \$1.03 billion and annual operating and maintenance costs, including fuels, were estimated at \$596 million/year. As was the case for the near- and mid-term designs, the base case economics were analyzed using the Discounted Cash Flow-Net Present Value method. This produced an annual revenue requirement of \$835.5 million, which must be raised by the sale of the two system products: process steam and SNG.

For the near-term case, the system was designed such that the coal gasification plant feeds two separate methanation complexes. Only one end-use site was specified: that in Escanaba, Michigan, some 1790 km (1110 mi) from the coal plant in Montana.

The mid-term design was set to have one VHTR-reformer-LNG terminal supplying six separate methanation complexes. The one end-use site specified is Perth Amboy, New Jersey, and the floating complex 145 km (90 miles) southeast and just off the coastline north of Atlantic City.

The major conclusions reached in this study may be summarized as follows:

- The open-loop chemical energy pipeline is technically feasible. No major problems were found in mating the various components of the systems designed.
- Existing natural gas transmission systems potentially could be converted for use as part of a chemical energy pipeline. Identification of a specific pipeline for conversion will require a detailed study, based upon current capacity, compressor and/or driver type, and materials used in its construction.
- Transmission of coal synthesis gases over long distances is more economically attractive than the shipment of coal by rail, for the tonnages involved in the near-term coal-gasification-based thermochemical pipeline.
- No significant problems are envisioned in converting or building storage capacity for the gases produced by or formed in the thermochemical pipeline.
- Design of the methanation plant and heat exchanger train is inherently a function of the thermal products desired. Supplementation of these products by SNG combustion is not suggested by the economics involved.



- Ample markets exist for the process steam, electricity, and SNG products from the system. Several potential markets have been identified for the lower temperature thermal energy. In general, however, loads for this energy are difficult to quantify, and in particular, difficult to justify economically when used for residual district heating.
- No major problems should exist for domestic gas equipment when the product SNG's are substituted for typical natural gases.
- The base case design did not produce product prices that were competitive, either now or in the near future.
- Product prices calculated for the near-term case may be competitive currently and would almost certainly be attractive in the immediate future.
- The mid-term design, while not producing product prices competitive now, could be economically viable in the 1980 to 1990 time frame.
- No serious or unique institutional or safety problems have been identified to prevent the implementation of an open-loop chemical energy pipeline.
- It is felt that these systems are environmentally benign. In particular, locating the methanation plant at the load site should contribute minimum air pollution and would replace existing boilers with a heat source with little waste heat.
- The thermochemical pipeline is very versatile with respect to site locations for both the heat sources and methanation plants. Remote siting of heat sources, far from the end-use sites, is a major advantage of this system.
- The open-loop chemical energy pipeline may not be an energy concept whose sole purpose is to provide experience and component development necessary for the transition to a closed-loop mode. In view of the results of the near-term (coal-based) design economic analysis, the open-loop concept has merit in itself, independent of the implementation of a closed-loop system.
- Future work in this area should be directed at decreasing system costs, optimizing methanation plant operation and quality of products, and experimentally providing a data base from which further work could be identified.

### Technical Problems

During the course of this project, no problems occurred which affected overall program costs, schedule, or objectives.



## Publications

1. Baker, N. R., "Transmission of Energy by Open-Loop Chemical Energy Pipelines," Final Report, SLL Contract 87-9181, Institute of Gas Technology, to be published.

Closed Loop Chemical Systems For Energy Storage  
and Transmission - General Electric/Corporate  
Research & Development (2.2.1)

Objectives

The objectives of this program are to assess the technical and economic feasibility of high and low temperature energy transport systems based upon the use of reversible chemical reactions, and to identify required research and development.

Tasks

Task 1. Process Design Development: A preliminary process design is to be developed for each of the closed-loop chemical systems for energy storage and transport. The major goal is the development of computer codes to study the effect of various design choices on heat exchanger sizes, volume of gases to be pumped (or stored), storage density, compressor/expander duties, and overall first law efficiency. In addition to total heating and cooling duty, temperature levels at which heat is supplied (or withdrawn) are obtained.

Task 2. Assessment of Chemical Reactions: Various alternatives to the Adam/Eva or  $\text{CH}_4/\text{CO}_2$  (HYCO) reactions shall be examined. Variations of the  $\text{CO}/\text{H}_2$  ratios between one (HYCO) and three (Adam/Eva) shall also be examined. A search shall be conducted for suitable reactions that can be coupled to intermediate temperature primary sources.

Task 3. Technical Evaluation and Conceptual Design Studies:

- Thermal Sources - other than nuclear (specifically solar and coal).
- Chemical Reactors - This subtask will examine both reforming and methanation reactors. Reactor design requirements shall be determined for application to thermochemical pipeline systems. Various chemical reactor types (adiabatic, isothermal, and recycle) shall be compared on an energy efficiency basis.
- Heat Exchanges - The heat exchange requirements for the methanation and reforming processes shall be parametrically examined. Recommendations as to heat exchanger type, sizes, and process flows will be developed. A similar analysis will be performed for condensers.
- Catalysts - High activity catalysts shall be evaluated for reforming/methanation reactions, and those identified which are most suitable for thermochemical pipeline applications. Existing data applicable to reaction kinetics will be examined. Guidelines shall be developed for future catalyst research directed toward resolving problems unique to this application.



- Pipeline Transmission/Storage - The technical problems associated with the transport of  $\text{CO}/\text{H}_2$  and  $\text{CH}_4/\text{CO}_2$  mixtures shall be assessed and the pumping requirements as a function of various design parameters shall be examined.

Task 4. Determine Customer Needs: The critical problem and needs of utility and potential industrial users of thermal energy supplied by chemical heat pipes shall be assessed. System operating modes with the highest user impact shall be identified.

Task 5. Preparation of an Economic Analysis: Using the data from Tasks 1-4, a preliminary economic analysis of selected system operating modes shall be developed.

Task 6. Conceptual Design for a Thermochemical Pipeline (as modified): Preparation of a conceptual design based upon the benzene hydrogenation/cyclohexane dehydrogenation reversible reactions. A preliminary technical and economic analysis shall be performed for this system coupled with near term U. S. primary energy sources, namely light water nuclear reactors, liquid metal fast breeder reactors and low temperature solar sources.

Task 7. Thermochemical Pipeline/Solar Interface (as modified): Critically evaluate the technical problems associated with combining various focused solar concepts with the thermochemical pipeline.

Task 8. Documentation (as modified): Upon completion of Task 7, a final technical report shall be prepared.

### Technical Progress

Task 1. Process Design - Complete: A flexible package of computer programs has been developed to perform design analyses of methane-based thermochemical pipelines.

A new design concept, the mixed feed evaporator (MFE), has been invented that allows a major improvement in the match of heating and cooling duties. The feed boiler and gas heater functions are combined into a single unit, which results in a decrease in entropy of mixing.

A significant fraction (up to 10%) of the delivered energy can be extracted from a single shaft compressor/expander at the methanator (user) end of the thermochemical pipeline.

Task 2. Chemical Reactions - Complete: Methane System -  $\text{CO}_2$  addition favors conversion at the methanator (user) end of the system while requiring increased reformer heating duty loads and pipeline flow rates. The addition of  $\text{CO}_2$  is justified only when high quality (temperature) heat is required at the user end offsetting the drop in energy efficiency. Increasing the  $\text{H}_2\text{O}$  recycle has essentially the same advantages and disadvantages as  $\text{CO}_2$  addition, though the major effect of  $\text{H}_2\text{O}$  recycle is upon catalyst lifetime.



Alternate Reactions - Of the 15 different high-temperature reactions evaluated, the methane reforming couple is most attractive for high-temperature systems. For lower-temperature sources, benzene hydrogenation/cyclohexane dehydrogenation is the best.

Task 3. Complete:

- Thermal Sources - The minimum reformation temperature, consistent with the process parameters, is 950 K; this restriction limits consideration of available sources to the pebble bed nuclear reactor and direct coal fired.
- Chemical Reactors - Significant improvements are possible for methanators via the use of state-of-the-art techniques, i.e., adiabatic reactor stages with intercoolers. The KFA steam reformer design can be improved and must be modified for domestic USA use. (See Project Number 2.2.2, The Duplex Steam Reformer.)
- Heat Exchangers - A trade-off between heat exchanger area, cost, and temperature drop has been performed. The issues are primarily investment capital cost versus availability loss, not technical barriers.
- Catalysts - Reforming Rachtig ring catalysts are state-of-the-art. Lifetime performance can be improved by the use of H<sub>2</sub>O recycle. Flame sprayed catalysts or catalysts with improved support geometrics which allow speedy removal or in-situ regeneration are a general improvement desirable for, but not limited to, the thermochemical reformer.
- Pipeline Transmission/Storage - The technical problems associated with the transmission and storage of CO/H<sub>2</sub> and CH<sub>4</sub>/CO<sub>2</sub> mixtures are not insurmountable. Line packing with a  $\pm 2 \times 10^6$  newtons/meter<sup>2</sup> variation about  $4 \times 10^6$  N/m<sup>2</sup> nominal pipeline pressure will yield approximately 5 hours of storage in a 160 km, 1.6 m diameter pipeline, assuming a nominal energy transmission of 100 MJ/s.

Task 4. Customer Needs - Complete: The best potential application for a thermochemical pipeline distributing process heat is the one- and two-shift industrial user for whom on-site coal based steam generation is too costly when stack clean up equipment is included in the cost. For cases where  $T < 800$  K, and the individual user size is below 200 MJ/s, the potential market is roughly 80 GW<sub>th</sub>.

Clearly identified is the lack of process heat market data with regard to: user geographic location; energy consumption as a function of temperature, capacity requirements; user duty cycles; and types of fuel presently used.

Task 5. Economic Analysis of Selected System Operating Modes - Complete: The cost of delivered process steam is competitive with options such as SNG fired boilers, electrode boilers, and perhaps small coal fired boilers with stack clean-up equipment. Applications that are most favorable economically include supplying process steam to small and part-time users; distributed



generation of peak electricity; and co-generation of electricity and heat for small users. The thermochemical pipeline is marginally competitive with other techniques for on-site thermal energy storage. Depending upon the assumptions made, the thermochemical pipeline can be considered as an alternate to on-site generation of process steam for large, continuous users.

Comparing energy transmission alternatives, the major strengths of thermochemical pipeline lie in the middle distances (80-320 km).

For solar thermochemical pipeline applications, the thermochemical pipeline is at a disadvantage due to the large capital cost of a reformer with a capacity factor of 1/3. Peak operation of the methanator is feasible, as its capital cost is not a major factor at the user end.

Task 6. Preparation of a Conceptual Design for a Thermochemical Pipeline Based Upon the Benzene Hydrogenation/Cyclohexane Dehydrogenation Reversible Reactions - Complete: Analysis of the low-temperature thermochemical pipeline indicates economics and performance characteristics superior to those of the methane-based thermochemical pipeline. Uncertainties which must be resolved experimentally include the degree of dehydrogenation catalyst selectivity, process optimization, and the maximum attainable hydrogenation temperature. The transportation system design must accommodate the relatively high freezing temperatures of benzene (5.50 C) and cyclohexane (6.5 C), the fire hazard of these and hydrogen, and the toxicity of benzene.

Task 7. Thermochemical Pipeline/Solar Interface - Complete: The operating characteristics of a concentrating solar thermal source are largely unknown. Diurnal thermal cycling is the minimum period of source temperature variation. The endothermic reactor must be "buffered" from this and other thermal shocks for catalyst longevity.

The nature of the source imposes severe economic capitalization penalties upon the endothermic equipment when compared to continuous operating sources such as the LMFBR and coal-fired dehydrogenators.

Task 8. A revised draft version of the final report has been received and accepted.

### Technical Problems

The major technical problems associated with this study have been the paucity of specific data. Examples are the detailed geographical characterization of the process heat user market, the duty cycles, and the steam temperature requirements. The characteristics of high-temperature solar thermal sources are not clearly specified at present, which limits the technical effort that can be expended upon Task 7.

### Publications

1. Vakil, H., and Flock, J., "Chemical Heat Pipe," Final Report, ERDA Contract EY-76-C-02-2676, General Electric Company, Schenectady, NY, February, 1978.



Duplex Steam Reformer (DSR) Development  
Program - General Electric Company (2.2.2)

Objectives

The objectives are to design, fabricate, test, and evaluate a full-scale duplex steam reformer (DSR) tube. Reforming steam produced by nuclear heat has potential industrial applications; the DSR provides double-walled isolation between a potentially radioactive high-temperature nuclear heat source and the industrial process gas. The DSR tube will be fabricated by the Foster Wheeler Development Corporation (FWDC) of Livingston, New Jersey, and tested in the EVA test facility of the Kernforschungsanlage (KFA) in Julich, West Germany.

Tasks

Work on the DSR program has been divided into five phases. Phase 1, Study and Planning, was completed in May 1976. Phase 2A, Duplex Tube Fabrication Feasibility Demonstration Program, was added to the original program in order to demonstrate the feasibility of the proposed kinetic construction process for fabricating the DSR. Phase 2A was completed on August 15, 1977. The remaining phases of the program are: Phase 2, Test Section Procurement; Phase 3, Steam Reformer Test and Performance Evaluation; and Phase 4, Post Test and Metallurgical Evaluation.

The following tasks have been identified to cover the work in Phases 2, 3, and 4:

Task 1. Program Management: Contract management services, including liaison with KFA, will be provided to ensure that the schedule for the duplex tube delivery to KFA is compatible with the scheduled availability of the EVA test facility.

Task 2. Duplex Tube Procurement: Two duplex steam reformer tubes will be fabricated by Foster Wheeler Development Corporation (FWDC) under subcontract to G. E.; one of these tubes will be shipped to KFA for testing in the EVA facility. This task shall be completed by issuance of a manufacturing report describing the materials used, the processes developed and used, the quality control measures, and a description of the final product.

Task 3. Test Section Assembly and Installation: KFA, under agreement with G. E., shall be responsible for test section assembly and installation, which includes: (1) design and fabrication of the adapters to mate the DSR tube with the EVA facility; (2) design and fabrication of the catalyst to be placed in the DSR tube during the test program; (3) design and fabrication of the instrumentation to be used to measure the DSR performance characteristics; and (4) assembly of the test section in preparation for the test program.



Task 4. Test Program: KFA has responsibility for preparing the test program specification and obtaining G.E. concurrence with this program. This program shall include testing at three helium inlet temperatures and three steam-methane ratios. Also, the hydrogen permeation rates shall be measured. Pretest predictions will be made which shall include tube temperatures and hydrogen permeation rates.

Task 5. Performance Evaluation: This task covers the evaluation of the metallurgical performance and reformer performance of the DSR tube, and includes: (1) the preparation of a metallurgical evaluation plan for the duplex tube including pretest and post-test evaluations; (2) the pretest evaluation of the metallurgical characteristics of the DSR tube, which will include tensile specimen tests and surface finish examination.

Task 6. Engineering: This task includes the following engineering activities to support the manufacture, test, and evaluation of the DSR tubes: (1) review and selection of an analytical model for predicting the DSR performance during testing in the EVA facility and performance of sensitivity studies to support the test program; (2) performance of the necessary metallurgical engineering to support the manufacture of the DSR tubes. This includes establishing the type of oxide film to be on the tubes, establishing annealing temperatures, and evaluating the effects of cold work and fatigue on the tube performance.

Task 7. Licensing Evaluation: The contractor shall prepare and submit to the U. S. Nuclear Regulatory Commission (NRC) a Preliminary Licensing Submittal (PLS) describing the use of a duplex steam reformer in conjunction with the gas-cooled nuclear reactor in the U. S.: The contractor shall also prepare responses to questions raised by the NRC in their review of the PLS.

### Technical Progress

Task 2. Duplex Tube Procurement: Several delays have been experienced in the fabrication of the duplex tubes. These resulted from tube raw material delivery delays and technical problems concerned with the detnaforming process. At the close of this reporting period (December 31, 1978), no slack time existed for tube fabrication. However, fabrication was successfully completed, and the tube was shipped to KFA on March 14, 1979.

Task 3. Test Sections Assembly and Installation: G.E. is continuing to coordinate with KFA the as-built configuration of the duplex tube for proper installation into the EVA test facility. The design and fabrication of the catalyst and instrumentation for the duplex tube has been completed by KFA. The adapters to mate the duplex tube with the EVA facility have been designed and are being fabricated.

Task 4. Test Program: Several iterations on the detailed plan for the EVA tests have taken place. G.E. comments have been incorporated into a final document prepared by KFA. The computer code for running the test cases of the KFA test procedure is operational, and is being utilized to generate the test predictions report.

Task 5. Performance Evaluation: The Metallurgical Evaluation plan has been prepared.

Task 6. Engineering: The computer code developed by LASL for predicting Duplex Steam Reformer performance has been modified and is now operational. Reports on the effects of residual cold working and annealing temperatures have been prepared. Studies to evaluate oxide films as hydrogen permeation barriers are in progress. The DSR structural analysis is nearly complete.

Task 7. Licensing Evaluation. The Licensing Technical Report was completed in October, 1978 and released to DOE for NRC review.

### Technical Problems

The contract for this program specified that two duplex steam reformer tubes would be fabricated: one for the EVA test, and one to serve as a backup. These tubes are being fabricated in series. The second tube has been rejected due to end cap misalignment and tube out-of-roundness. If desired, this problem can be corrected. However, due to the tight schedule and high fabrication costs, all work on the second tube has been stopped at present.

### Publications

1. Kimball, O. F. and Schroeder, J., Duplex Tube Combined Steam Reformer/ Intermediate Heat Exchanger Development Program - Phase IIA, Duplex Tube Fabrication Feasibility, Demonstration Program, AES 2841-(1), General Electric, Schenectady, N.Y., May 1977.
2. Bond, J., et al., Design of a Helium Heated Duplex Tube Steam Methane Reformer, ESTD 76-06, General Electric, Schenectady, N.Y., May 1976.



## Cyclic Catalytic Storage Systems University of Houston (2.2.4)

### Objectives

The objective of this study is to model the steam reforming-methanation process (EVA-ADAM) as applied to solar energy (SOLTHERM) and to use the model in an analysis of system process variables and alternatives. Preliminary economic evaluation is carried out in order to compare the SOLTHERM process with other methods of supplying steam and process heat to potential users. Critical areas for future research and development are identified.

### Tasks

Task 1. Computer Code Development: Computer programs will be developed which model each of the steps in the overall EVA-ADAM process. These include:

- steam reforming at the catalytic reforming reactor
- product gas cooling, water and carbon dioxide removal, and methane recycle
- gas transmission from the reactor site to the demand center
- storage
- catalytic methanation and heat removal at the demand site
- carbon dioxide and water removal
- gas transmission back to the reforming reactor

At each of the process stages, equilibrium composition is calculated as a function of pressure, and temperature, dependent upon the quantity of heat supplied.

Task 2. Comparison of Modes of Operation: The computer program developed will be used to compare the following possible modes of operation:

- open-loop and steady-state closed-loop operation
- isothermal and cyclic operation expected from current designs for a liquid sodium receiver, direct heat exchange at the solar tower collector, and the utilization of heat storage systems

Task 3. Process Configuration Optimization: The SOLTHERM simulation is used to study the effect of process variables for continuous operation. The

critical parameters are: (a) reformer temperature; (b) steam/carbon ratio; (c) pipeline length; (d) methanator temperature and pressure.

### Technical Progress

Each of the tasks described above has been completed and the analysis of the results dictate the following conclusions:

- High methane conversions and hence, better unit efficiency can be maintained by continuous operation at constant system pressure, and high reformer temperatures.
- Methanation temperatures depend upon need. For power generation, steam at  $\sim 510^{\circ}\text{C}$  is required, but for process heat  $350^{\circ}\text{C}$  is sufficient. At this temperature, the feed gas returning to the reformer is 98 percent methane. Lower temperatures give high methane yields, but with larger reactors. For high temperature operation, high pressures are necessary (and smaller units are possible).
- Optimum conditions involve different pressures at both ends of the SOLTHERM process.
- Pipeline distance has little effect on process efficiency, but considerable effect on process economics.
- Results of a preliminary economic analysis indicated that:
  - Reformer costs are six to seven times more than methanator costs.
  - Storage cost is very sensitive to pressure.
  - Increasing pipeline distance from 100 to 200 miles increases pipeline cost by 27 percent. Pipeline diameters are less sensitive.
  - The system may be optimized by operating storage, pipeline, and methanation at high pressure, and reformer at low pressure, assuming compression costs (for pressure drop compensation) are substantially recovered.

The economics indicate that SOLTHERM would be competitive with fossil fuels in the 1990's provided technical problems are solved (catalyst development and solar energy input reformer heat flux match) and economic process optimization is possible.



Sulfuric Acid/Water Integrated Chemical Energy  
Storage System, Phase 2 - Rocket Research Corp (3.1.1)

Objectives

The objectives of this program are to demonstrate the feasibility of using sulfuric acid and water as chemical energy storage media, to build and test a subscale (300,000 BTU) demonstration system, and to build and test a full-scale pilot plant.

Tasks

Task 1. System Selection, Detailed Sizing and Scaling Analysis: The sulfuric acid/water chemical energy storage system is intended to be applied to the heating and cooling of buildings. A detailed sizing and scaling analysis was conducted, with the Phase 1 system approach resulting in storage densities of 120 to 200 BTU/lbm of dilute acid. During this phase, the concept of using sulfuric acid as a chemical heat pump was identified. Because this concept results in storage densities in excess of 500 BTU/lbm, it has been pursued as the main approach for Tasks 2 through 4 below. Also as a part of this task, an economic study plan and a test plan for Task 4 were generated.

Task 2. Detailed Design, Equipment Selection and System Layout: The system was designed, with detailed drawings and flow diagrams produced. Preliminary laboratory scale separation tests were initiated early in the program to optimize the separation design. Material compatibility tests have been conducted to determine the dynamic effects of the hot concentrated sulfuric acid. In addition, a preliminary safety and hazard analysis of the system has been conducted. At the conclusion of Task 2, a design review will be conducted jointly with DOE and RRC personnel.

Task 3. Fabrication, Assembly, and Checkout: The procurement, fabrication and assembly of the system components and hardware have been performed during Task 3.

Task 4. Chemical Energy Storage Operation/Evaluation and Phase 3 Definition: The integrated system was tested and the performance evaluated and compared against predictions. The efficiencies of both components and the total system efficiencies were measured, and corrosive and wear characteristics of the system have been monitored. The program was concluded with the establishment of the requirements for a full-scale operational system and the recommendations for Phase 3.

Technical Progress

The program proceeded largely on schedule. The recombination tests identified an absorption column as being potentially the most cost effective

batch recombination approach, and as such was chosen for the baseline design. A continuous separation column approach was also identified as technically viable and was pursued as a backup to the baseline batch concept.

The computerized performance analysis identified the operating limits of the baseline system design, and enabled analysis of performance results obtained from the demonstration test system.

The demonstration test system was designed, procured, and assembled, and preliminary checkout operation was completed. Concurrent with the latter were the establishment of the testing program, operating procedure, and safety requirements. Safety requirements and other barriers to implementation of commercial systems are being analyzed as an ongoing effort.

### Technical Problems

Two problems were experienced after initial parts procurement was completed. The most significant problem was inability of the first acid pump to pump the very dense, highly viscous concentrated acid, despite manufacturer's claims. The pump was replaced with a larger commercial acid pump operating in a derated mode and performance has been totally acceptable. Vacuum leaks through threaded teflon fittings for instrumentation were also a significant problem, caused by yielding of the teflon. The situation was rectified by applying a sealant where possible and using a larger vacuum pump to remove the higher than expected amount of noncondensable gas. Testing delays of three to four additional weeks were incurred because of the above problems but testing has since been successfully completed. The slip in testing had little or no impact on project cost.

### Publications

See Phase 2a discussion.



Sulfuric Acid-Water Chemical Heat Pump/Thermal  
Energy Storage Program, Phase 2a - Rocket Research Corp (3.1.1)

Objective

The objective of this program is to further study the sulfuric acid heat pump system concept developed under the previous phase contract.

Tasks

Task 1. Conduct an economic analysis to study the major system variables affecting the total integrated system design and cost. The analysis will include the selection of two geographical areas within the conterminous United States. Building sizes of 2000 and 20,000 square feet will be studied along with diurnal, monthly, and seasonal storage duty cycles.

Task 2. Component and transient optimization testing for cost effectiveness will be conducted using the engineering demonstration system from the previous phase program.

Task 3. The ability for commercialization of the sulfuric acid system will be studied to consider such things as institutional barriers, building codes, and public acceptance.

Technical Progress

The program is proceeding largely on schedule. Optimization tests have shown that the absorption column can be considerably smaller than first designed and still function successfully. The preliminary cost-effectiveness study has shown attractive cost-performance thus far, and studies are continuing. The survey of institutional barriers and commercialization was subcontracted to an A&E firm and results are expected shortly.

Technical Problems

The report from the A&E firm on commercialization barriers is slightly behind schedule. Also, only one location has been studied for the cost-performance analysis thus far. Further study of a second location awaits standardized weather data from the DOE Solar Heating and Cooling Division subcontractor responsible for modeling standardization. Neither of the above problems are viewed as significant, and they will not adversely affect project cost.

## Publications

1. E. C. Clark, C. C. Hiller, "Sulfuric Acid-Water Chemical Heat Pump/Energy Storage System Demonstration," presented at the ASME Winter Annual Meeting, December 10-15, 1978.
2. E. C. Clark, "Sulfuric Acid-Water Chemical Heat Pump/Energy Storage System Development," presented at the DOE/Sandia sponsored Chemical Heat Pump Workshop in Dublin, California, November 7&8, 1978.
3. E. C. Clark, "Sulfuric Acid-Water Chemical Heat Pump/Energy Storage System Demonstration," presented at the Poster Sessions of the workshop on Solar Energy Storage Options, San Antonio, TX, March 19 and 20, 1979.
4. C. C. Hiller, and E. C. Clark, "Development of the Sulfuric Acid-Water Chemical Heat Pump/Chemical Energy Storage System for Solar Heating and Cooling," to be presented at the 1979 ISES Meeting, May 28 - June 1, 1979, Atlanta, GA.
5. E. C. Clark, and C. C. Hiller, "Development and Testing of the Sulfuric Acid-Water Chemical Heat Pump/Chemical Energy Storage System," to be presented at the 14th Annual IECEC Conference, August, 1979, Boston, MA.



One Substrate Solvate Energy Carrier Systems  
For Storage Of Solar Energy -  
EIC (3.1.2)

Objectives

The objective of this project is to construct a prototype chemical heat pump for solar heat pumping and thermal energy storage, based on the reaction of  $\text{CaCl}_2$  and  $\text{CH}_3\text{OH}$  vapor.

Tasks

Task 1. Fundamental Engineering Chemistry: Alternate salts will be investigated, a more detailed kinetic data base including the effects of particle size, commercial salt, etc., will be obtained, and corrosion studies performed.

Task 2. Design and Procurement of the (small scale) Plate Configuration Unit: A small scale (1000 BTU) plate configuration heat exchanger/reactor test unit will be designed and procured. Alternate designs may be studied which means several test units may be procured.

Task 3. Operation of the Plate Configuration Unit: The test units designed and procured in Task 2 will be operated for at least 20 test cycles. If the results of Task 2, or test results from this task indicate that additional cycles of exchanger-storage units should be evaluated, equipment changes and additional test work will be carried out.

Task 4. Design and Procurement of Services for the Prototype System: Items which are largely independent of the detailed design of the prototype, such as the methanol accumulator, the refrigeration unit, valves, piping, pumps, instruments and controls, and recorders will be procured. Initial work will focus on the development of designs and specifications for long lead items (such as the refrigeration unit, instruments, and custom fabricated equipment). Final specification for process piping and the control system, however, will not be set until preliminary data from Task 3 are available to confirm initial estimates of the dynamics of the system, e.g., the ratio of maximum and minimum to average transfer rates.

Task 5. Design Procurement and Construction of the Salt Storage/Heat Exchange System: Work on this task will begin when sufficient preliminary data are available from Task 3 to confirm initial design concepts for the storage-heat exchange unit. Final designs will not be fixed and procurement initiated, however, until completion of work on Task 3. If the data from Task 3 indicate that alternative designs should be tested, a redesign effort will be initiated in order to provide an alternative design for evaluation within four months of initiation of prototype testing.



Task 6. Assembly of the Prototype System: This task will include the assembly of purchased components and piping, installation of instrument control loops, completion of mechanical integrity testing, development of material handling procedures, and calibrating instruments and controls.

Task 7. Prototype Testing.

### Technical Progress

Task 1. Attempts to find salts superior to  $\text{CaCl}_2$  have not succeeded;  $\text{CaCl}_2$  remains the baseline system. Experiments have been carried out to better understand the effects of parameters such as particle size, reaction cycling and end point compositions on the reaction rate. Long-term cycling experiments have shown mixed results. In some cases, salts have been cycled over 100 times with no apparent degradation in reaction rate; in other cases, the salt ceases to react after just several cycles. In the latter case, the salt beds tended to become compacted and crusted. While it is encouraging that the rates of methanolation remained rapid over several hundred cycles in some instances, it is disturbing that the reactivity of some samples degraded so rapidly. It remains to discover why some samples were well behaved, and others not. The use of pelletized  $\text{CaCl}_2$  is desirable since pressure drops through the salt bed are minimized. Experiments with  $\text{CaCl}_2$  have met with mixed results. Pure  $\text{CaCl}_2$  pellets tended to agglomerate on reaction cycling. Agglomeration was eliminated by the use of a small amount of binder (e.g., magnesium stearate); however, the pellets tended to become friable and fall apart on cycling. The optimum  $\text{CaCl}_2$  form and composition remains to be found.

Materials corrosion screening experiments have been performed, and both aluminum and copper based alloys appear to be compatible with the  $\text{CaCl}_2\text{-CH}_3\text{OH}$  system.

Task 2. A plate configuration test unit has been designed and constructed. The heat exchanger design consists of finned tubes held in a pelletized salt bed. Water has been adopted as the primary working fluid.

Task 3. Testing of the plate configuration unit has been initiated. To date, the results have been obscured by experimental difficulties such as leaky welds, etc.

Task 4. Various long lead items which are not design specific have been identified and sized (e.g., refrigeration units) and vendor quotes are being solicited.

### Technical Problems

Major concerns regarding the chemical behavior of the  $\text{CaCl}_2$  during cycling exist. It is not clear why the reaction rates of some salt samples decreased significantly on cycling. Also, suitable  $\text{CaCl}_2$  pellets have not yet been found.



### Publication and Presentations

P. O'D. Offenhartz, "Preliminary Heat Exchanger Design for the  $\text{CaCl}_2\text{-CH}_3\text{OH}$  Chemical Heat Pump," presented at the Sandia Chemical Heat Pump Workshop, November 7, 1978, Dublin, CA.

P. O'D. Offenhartz, "One Substrate-Solvate Energy Carrier Systems for Storage of Solar Energy," presented at the 3rd Annual TES Contractors Information Exchange Meeting, December 6, 1978, Springfield, VA.

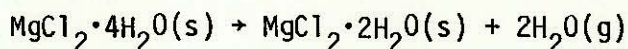
P. O'D. Offenhartz and J. M. Marston, "Preliminary Task Report - Engineering Chemistry Studies on the Reaction of  $\text{CH}_3\text{OH}$  and  $\text{CaCl}_2$ ," EIC Corporation Report, November 30, 1978.

P. O'D. Offenhartz, M. J. Turner, F. C. Brown, R. B. Warren, J. P. Demsler, and S. B. Brummer, "Methanol-Based Heat Pumps for Storage of Solar Thermal Energy. Phase I, Final Report for period April 25, 1977 - June 30, 1978," July, 1978.

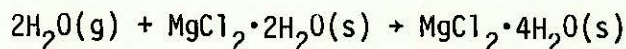
The Chemical Heat Pump: A Simple Means To Conserve Energy  
- Chemical Energy Specialists (3.1.3)

Objectives

The objective of this program was to develop a chemical heat pump for heating and cooling residences. The thermal decomposition of magnesium chloride tetrahydrate was investigated for the energy storage step



and the reverse reaction to recover the energy stored



Tasks

The tasks were essentially divided into two areas: (1) analytical and design and (2) experimental.

Task 1. Analytical and design: This area included establishing a means to collect the required solar energy under the conditions necessary for operation. It was felt a temperature of 300°F was necessary to dehydrate the salt. Such a high temperature necessitated development of a flat-plate solar collector capable of reaching 300°F. Hydrolysis of  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$  (production of HCl) at such temperatures further complicated construction of the heat pump.

Task 2. Experimental: This area included cycling of the salt to learn the effect of bed thickness, temperature, surface concentration, water contents, and internal pressure. Because of the hydrolysis problem, other salts were screened as potential heat pump candidates.

Technical Progress

Task 1. Because of hydrolysis of  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$  the heat pump has had to be constructed almost entirely of glass. A black cover is needed for the salt to get the temperatures needed. Again because of hydrolysis the black cover has to be glass cloth with a selective coating - something currently unavailable anywhere. Much of the development work on roof top flat plate collectors has been done previously.

Task 2. The experimental work is difficult to evaluate. No two experiments are ever quite alike and reported results are of questionable value. Again hydrolysis of  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$  has caused many problems. Other salt screening seems to suggest LiCl as a potential candidate. However, others have reported that it too hydrolyzes not to mention the exorbitant cost.



## Technical Problems

Most of the technical problems have revolved around the hydrolysis of  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ . Even if construction materials could be found and a selective black coating put on glass cloth, it is doubtful that the reverse reaction to recover the energy stored can be achieved.

Thermal Storage For Solar Cooling  
Using Paired Ammoniated Salt Reactions-  
Martin-Marietta (3.1.4)

Objectives

The objectives of this program are: to establish the feasibility of using paired ammoniated salt reactions configured to provide energy storage/heat pump capabilities in residential home cooling applications; to conduct the engineering analysis and design of a residential size solar cooling system; and to verify the technical feasibility of the concept by constructing and testing a prototype residential solar cooling system.

Tasks

Task 1. Feasibility: Obtain available data on the fundamental processes occurring in the system to provide a foundation for its engineering design, and document.

Task 2. Engineering Analysis and Design: Refine the design of the salt reactors. Select the candidate construction materials and perform compatibility tests of these materials and the various salts. Perform subscale system tests to verify the adequacy of the reactor design and establish performance characteristics. Design a residential sized system and evaluate the economic feasibility of its mass production.

Task 3. Prototype System Construction and Testing: Construct a prototype model of the reversible thermochemical storage system having at least a one-ton refrigeration capacity. Carry out a test program to demonstrate the system's operation and to obtain operation and performance data.

Technical Progress

A set of candidate construction materials has been selected for use in the material compatibility tests. This set of materials represents the most common classes of materials used in the design of this type of system, and should provide a representative data base upon which the engineering design can be made. A test plan for the materials compatibility tests was formulated and approved, and experiment fabrication was carried out. The tests consist of exposing the candidate construction materials to the various ammoniated salts and then determining whether any material degradation has occurred due to corrosion. Two exposure periods will be used--60 days and 1 year. The tests have been started and the 60 day exposure specimens will be removed in January 1979.

The cyclic testing of the reaction





has been completed. The results, which were based on particle size, surface area and bulk density measurements before and after various numbers of cycles, have indicated that there is no significant change in these properties due to the cycling.

The experimental apparatus for the subscale system tests has been designed and fabrication is nearly complete. Two reactor designs were considered so that liquid  $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$  could be tested along with the various solid salts. Furthermore, the system is being configured so that the reactors can be run in either a coupled mode or a separate mode. When operated separately, the individual performance characteristics of each reactor can be better evaluated. A test plan for the subscale system tests was formulated and approved, and testing should begin in January 1979.

The economic analysis of a residential size system has been started. Trade-off studies of the various system design options are being made and refined as the design of the system continues. The studies have clearly shown the economic advantage of a liquid salt system due to the high heat transfer capability of such a system. The economic analysis will be modified as new system performance data is obtained from the subscale system experiment.

#### Technical Problems

No major technical problems have been encountered, as yet, in this program. A minor problem was encountered, however, in the cyclic testing of  $\text{MnCl}_2 \cdot 6\text{NH}_3$ . It was noticed that a very large volume change occurred with initial ammoniation and resulted in salt compaction. Recognizing the potential impact of this effect, a test was run to verify the result. It was found, fortunately, that if compaction could be prevented on initial ammoniation, the volume change on subsequent cycling was more acceptable. This phenomenon will be watched carefully during the subscale system tests.

As the importance of using liquid salts in this system has become evident, it was recognized that an omission was made in the material compatibility tests in that no tests involving liquid  $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$  have been included.

The Kinetics Of Dissociative Chemical Reactions  
In Thermochemical Energy Storage-  
University of California at Davis (4.2)

Objectives

The basic objective is to provide a thorough understanding of the kinetics of dissociation and association of selected reactions for use in thermochemical storage schemes.

Tasks

Task 1. Identification of attractive chemical reactions for thermochemical energy storage systems and evaluation of existing data.

Task 2. Selection of systems for investigation.

Task 3. Identification and selection of experimental methods.

Task 4. Experimental kinetics.

Technical Progress

Task 1. A comprehensive literature search for relevant kinetic information for carbonate, hydroxide and sulfate systems has been carried out, and the experimental conditions (e.g., method of analysis, temperature, pressure, particle size, heating rate, etc.) along with results (i.e., activation energy) of all previous studies have been tabulated.

Task 2. This program is directed at the study of carbonate systems. Major emphasis will be on  $\text{CaCO}_3$ ;  $\text{ZnCO}_3$ ,  $\text{CdCO}_3$ , and  $\text{CoCO}_3$  will also be studied.

Task 3. Thermogravimetric analysis techniques will be used in the experimental portion of this study. The apparatus has been designed, constructed, and checked out. To complement the TGA studies, molecular effusion experiments will be performed using a torsion technique; these experiments will generate thermochemical data useful for understanding this generic class of compounds and selecting chemical systems for storage applications.

Technical Problems

Numerous minor experimental problems have been encountered during the course of this study, but no insurmountable technical problems are anticipated.



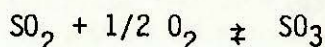
## Publications

E. Fuss, J. Rice, and Z. Munir, "Thermochemical Energy Storage, Progress Report," U. C. Davis report (draft), October, 1978.

Development Of A Long-Life High-Temperature  
Catalyst For the SO<sub>2</sub>/SO<sub>3</sub> Energy Storage System -  
Rocket Research Corp (4.3)

Objectives

The objective of this program is to develop a new, more durable catalyst for the reversible SO<sub>2</sub>/SO<sub>3</sub> reaction:



This reaction has been identified as one of the more promising reversible chemical reactions for the storage of thermal energy. The ultimate goal is a low cost catalyst capable of operation at the design temperature of 1089 K (1500°F).

Tasks

The program is subdivided into four technical tasks:

Task 1. Develop a standard activity test and use it to evaluate commercial catalysts. Analyze these catalysts to determine the degradation mechanism at high temperature.

Task 2. Develop at least 50 new catalysts of different active metals and supports. Test them for activity and select five for more detailed study. Supported, fluidized and molten catalysts will be studied.

Task 3. The economics of catalyst preparation and availability of raw materials will be surveyed. The trade-off between a more durable expensive catalyst and a less durable, inexpensive catalyst will be quantified. Other possible commercial uses for the new catalyst will also be identified.

Task 4. The catalyst selected in Task 2 and justified for economic viability in Task 3 will be subjected to a six-month accelerated life test. Samples will be withdrawn periodically during the test to monitor the rate of catalyst degradation. Toward the end of the six-month test, interim data will be assembled and DOE/SLL recommendations will be requested on whether the test should be terminated at six months as planned or if additional life should be demonstrated by extending the test beyond six months.

Tasks 5. Reporting.

Technical Progress

Task 1. The commercial catalysts have been tested. The degradation methods have been determined to be transport of active metal out of the catalyst area and loss of surface area. This task is complete.



Task 2. Molten catalysts and fluidized beds have been eliminated from consideration for now. They may present problems of active material transport and low or lowering surface area. Of 22 considered support materials, five were tested for degradation of surface area with time at 1155 K. The best two supports have been used to make developmental catalysts with 14 different active metals. Several test catalysts were made by co-precipitation. Some catalysts and support materials were tested with SO<sub>2</sub> chemisorption. This did not add any useful information, and has been abandoned for now. A microcatalytic reactor has been developed for quick screening tests. The test reactor has been replaced with a dual furnace system to double the speed of testing and to allow two long term tests simultaneously if necessary. An ultraviolet-visible spectrometer has been set up to continuously monitor the extent of reaction. This replaces the gas chromatograph, which had to be run in a batch mode, and the oxygen detector, which corroded.

Tasks 3 and 4 have not yet been started.

Task 5. 19 monthly reports have been made.

#### Technical Problems

The last technical problem seems to have been solved with the introduction of the UV-visible spectrophotometer.

Development of Ammoniated Salts  
Thermochemical Energy Storage Systems, Phase IB-  
Martin Marietta (4.4)

Objectives

The objectives of this program are: to demonstrate the feasibility of using paired ammoniated salts for thermochemical energy storage systems; to develop a computer model for predicting the performance of the system; to obtain additional information on the physical properties of the salts; to determine the effect of various impurities on the salt performance; to study various reactor designs; and to define any follow-on effort.

Tasks

Task 1. Modeling: Formulate a computerized mathematical model for predicting the performance of thermal storage systems using ammoniated salts.

Task 2. Coupled Reactions: Design, build, and test a laboratory scale thermal storage system.

Task 3. Additional Salts Information: Obtain theoretical densities on each of the three  $\text{CaCl}_2$  ammoniates. Determine the effects of association/dissociation cycling on each of the ammoniates in the free (10 cycles) and constrained volume condition. Determine particle size distribution at 0, 1, 5, 10, 20, 50, and 100 cycles in the constrained volume test. Determine the surface area of the six ammoniates after 0, 50, and 100 cycles.

Task 4. Moisture Effects Evaluation: Determine the effect of 1 to 6% moisture in the salt on the reaction kinetics of one ammoniate of each salt.

Task 5. Economics: Determine the economics of the fixed bed reactor using the data generated in Tasks 1 through 4.

Task 6. Alternate Bed Configuration - Fluidization: Analyze the effect of fluidization on performance of reversible thermal storage systems. Design and fabricate a small scale reactor to determine gas velocity required to fluidize a salt bed. Calculate power requirements for fluidization.

Task 7. Alternate Bed Configuration - Moving Salt and High Flow Fixed Bed: Prepare schematic flow diagrams, analyze performance and investigate potential areas of application of these concepts.

Task 8. Planning Phase 2: Review the Phase 2 plan presented in the Phase 1 report.

Task 9. Heat of Reaction Confirmation.



Task 10. Effect of Non-Aqueous Impurities: Determine probable impurities in commercial grades of  $\text{CaCl}_2$  and  $\text{MgCl}_2$ ; prepare samples; determine the effect on the reaction kinetics of three ammoniates of  $\text{CaCl}_2$  and  $\text{MgCl}_2$ .

### Technical Progress

A completely rewritten draft of the Phase IB final report was submitted for approval. It represented a significant improvement over the first draft. Approval was granted and the report was published in May 1978.

### Technical Problems

The analytical model which was developed for predicting the performance of the reactors is not a very flexible tool for use in making design calculations. Unfortunately, it is quite tedious to input, thus making design iterations on different reactor configurations unusually difficult. This problem will be addressed at the beginning of the Phase 2 contract.

The data obtained from the subscale systems tests turned out to be not very useful due to poor experiment design and a lack of detailed planning. This problem has been discussed at length with the appropriate personnel at Martin-Marietta and will be remedied in Phase 2. In addition, a much closer observation of the progress of the contractor will be made.

It appears that the "weak-link" in the system design will be heat transfer in the reactors. This problem area has been identified as a high priority item and will be thoroughly addressed in Phase 2.

### Publications

1. F. A. Jaeger, "Development of Ammoniated Salts Thermochemical Energy Storage Systems - Phase IB, Final Report, Martin-Marietta, Denver, CO, May, 1978.

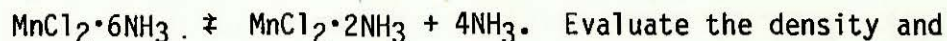
Development Of Ammoniated Salts  
Thermochemical Energy Storage Systems - Phase II  
Martin Marietta (4.4)

Objectives

The objectives of this project are: to demonstrate the feasibility of using paired ammoniated salts for thermochemical energy storage; to demonstrate the feasibility of using paired ammoniated salts as a chemical heat pump; to evaluate the reaction rates of various candidate salts at sub-atmospheric pressures; to experimentally evaluate system performance in a laboratory scale system; and to develop an analytical capability to predict system performance for purposes of detailed system design.

Tasks

Task 1. Chemical Tests: Evaluate the dissociation/recombination rates for  $MgCl_2 \cdot 6NH_3$ ,  $NH_4 \cdot 3NH_3$ ,  $MnCl_2 \cdot 6NH_3$ , and  $CaCl_2 \cdot 8NH_3$  at subatmospheric pressures. Determine the heats of reaction for the following reactions



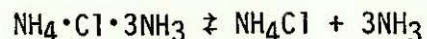
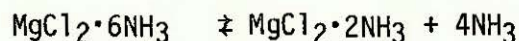
viscosity of  $NH_4Cl \cdot 3NH_3$ .

Task 2. Subscale System Tests: Demonstrate the feasibility of operating with various pairs of salts at various conditions. Obtain performance data for use in developing an analytical model of the system. Evaluate the effect of forced ammonia recirculation on solid-bed reactor performance. Obtain design and operating data to be used on a fullscale home heat pump design. Evaluate the performance of a liquid reactor for use with  $NH_4Cl \cdot 3NH_3$ .

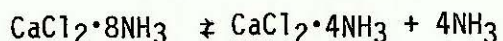
Task 3. Analytical Modeling: Upgrade the reactor model developed in Phase IB using data from Task 1. Construct a computer model of a heat pump system and evaluate the performance of a prototype home cooling system.

Technical Progress

The chemical tests performed under Task 1 are nearly completed. The reaction rate determinations for the following reactions have been completed:







There were no serious problems encountered, and the reaction rates at the operating conditions of interest appear to be adequate to support the necessary system performance. In addition, it was shown that the presence of up to 6 percent water would not adversely affect the reaction rate of  $\text{MnCl}_2 \cdot 6\text{NH}_3$ .

All of the other Task 1 chemical data have been obtained with the exception of the viscosity of  $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$ . Because this substance behaves somewhat abnormally, the Ostwald Viscometer cannot be used to measure its viscosity. Sandia Laboratories, Livermore, has an instrument which will work with  $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$ , and has offered to obtain the required data. The data should be available by March, 1979.

The solid-bed salt reactor has been completely redesigned from the Phase IB configuration to allow the use of forced ammonia recirculation to enhance heat transfer in the subscale system experiments. In addition, a liquid salt reactor using a turbine stirring device was designed for use with  $\text{NH}_3\text{Cl} \cdot 3\text{NH}_3$ . These reactors are nearly fabricated and will be assembled into the subscale system very soon. The system itself has been extensively modified from its Phase IB configuration and is much improved. The instrumentation set up has been modified also and should be far superior to that used in Phase IB. A comprehensive test plan was drawn up for the subscale experiments and was approved. Testing should begin early in CY1979.

An attempt was made at simplifying the MITAS computer model developed in Phase IB. Easier input and shorter running times were the objectives. After a short while it became clear that this model cannot be easily modified, and is too inflexible to be very useful. Thus a simpler ("zero-dimensional") model was conceived and formulated. The initial results obtained from this model are encouraging, and the verification of its adequacy is awaiting the arrival of subscale system experiment data.

### Technical Problems

At this stage of the program, there have been no significant technical problems. The few minor difficulties which have arisen have all been adequately dealt with and solved with an insignificant impact on the schedule and budget.

### Publications

In-House Research Program  
Sandia Laboratories, Livermore

Objectives

The Sandia in-house research is intended to augment and complement the contracted portions of the TEST program. Research topics are selected to maintain technical expertise, study problems generic to several projects, and to perform confirming investigations where the results are controversial.

Tasks

Task 1. Extended Duration Storage of Solar Energy (J. J. Iannucci):  
The purpose of this study is to assess the economic and performance impact of chemical energy storage on solar thermal electric conversion plants, especially for extended duration storage.

Task 2. Thermochemistry of Hydrated Salts (R. W. Mar, R. W. Carling):  
This study is concerned with the development of correlations which will aid in: the identification of hydrated salt candidates, the identification of erroneous data in the literature, and the estimation of the behavior of analogous compounds such as ammoniates and methanolates.

Task 3. Vapor Pressure Measurements (R. W. Mar, R. W. Carling):  
The purpose of this task is to establish the capability for measuring the vapor pressure of hydrates, ammoniates, and methanolates as a function of temperature.

Task 4. Dehydrogenation/Hydrogenation Catalyst Studies (Dave Haaland):  
This experimental program to study the dehydrogenation/hydrogenation catalytic reaction mechanisms for the cyclohexane/benzene system supports the Low Temperature Thermochemical Pipeline portion of the program, and involves the direct observation of the catalytic reactions on the surface of the catalyst by infrared spectroscopic techniques.

Technical Progress

Task 1. Extended Duration Storage of Solar Energy: The work done in this study has been multi-faceted. The previous work on extended storage and hybridization has continued and expanded to attempt to answer the more general questions: How much storage is optimal for a given system?, and how does hybridization affect storage requirements? This has led to examination of how storage could or should be utilized depending on the goals of a utility and the insolation available. When a storage system (based on the  $\text{SO}_3/\text{SO}_2/\text{O}_2$  reaction) is included in such a hybrid plant the optimum storage capacity is relatively small (7 to 12 hours) while providing a large percentage of the annual energy



requirements (85 to 95%). Other reactions (with power and energy related costs differing from the  $\text{SO}_3/\text{SO}_2/\text{O}_2$  reaction) have also been examined, as well as expanded sensitivity studies with respect to component costs. Work has been completed examining the value of storage (not specifically chemical) at diverse geographical locations, and further the sensitivity of the value to insolation varying over a period of many years. It has been determined that for an economically optimized solar plant with backup, the marginal cost per kwhr benefit of each energy handling component (mirrors, receivers, chemical reactors, heat exchangers, storage, etc.) is approximately equal to the backup fuel cost. This has been confirmed computationally and analytically. Further analytical models have been developed to examine the impact of storage for idealized load and insolation data; this has aided in illuminating the transition from daily to longer period storage.

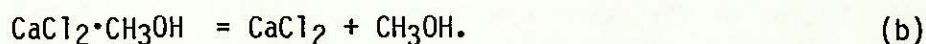
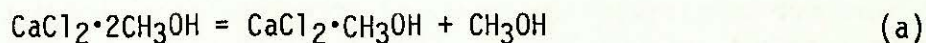
More recent work during this reporting period has centered upon adding cost sensitivity studies to previous performance calculations. A range of storage costs characteristic of present and future chemical systems and current sensible cost goals was considered to see where (geographically) and when (in terms of alternate energy costs) which storage systems look best. These estimates for chemical storage costs cover an order of magnitude in capital investment. For each of these cost estimates, for each of four locations (Albuquerque, Miami, Madison, and New York), and for each of three alternate energy cost scenarios, both hybrid and autonomous solar plants were designed optimally. As a first cut, baseload demand was examined. When hybrid operation is allowed (meaning that the solar plant provides whatever fraction of the total demand is economically justified, and sizes itself accordingly) at poorer solar localities, no storage capability is economically justified unless the alternate energy costs are very high. When storage was economically justified, less expensive storage was more important at the poorer solar localities. At a locality such as Albuquerque less storage is required so that its cost is not as crucial. The same effect is more dramatic when autonomous (pure) solar plant designs are generated. In this case the busbar energy costs are even more dominated by the storage subsystem at poorer solar localities. So much more storage is required for baseload autonomous operation that very inexpensive storage is imperative. At better localities, such as Albuquerque, costs are much lower overall, and inexpensive storage is beneficial, but not as necessary. Results using other loads, characteristic of 50, 70, and 90% load factors show similar results. True seasonal storage has not been proven economically justified by the work done to date although extended duration storage (greater than 20 hours) is needed for high (greater than 60%) capacity factor plants in low insolation areas.

The detailed analysis above was synthesized to provide cost and performance goals that chemical storage must point towards. These goals are both indigenous and exogenous in nature. The indigenous hurdles correspond to success of the chemical aspects of a chosen reaction: reversibility, receiver compatibility, and simplicity of inclusion. These form the basis for the Rocket Research companion effort. The exogenous goals come from examining the competition: sensible and latent storage to compare overall solar system costs and efficiencies. By leveraging front end (heliostat and receiver) costs by the chemical storage efficiencies, cost and efficiency goals were obtained. Chemical storage appears unattractive for diurnal storage due to its low roundtrip efficiency.



Task 2. Thermochemistry of Hydrated Salts (R. W. Mar, R. W. Carling): The thermodynamic behavior of hydrates formed by salts (whose cations have an inert gas electron configuration) with 2, 4, and 6 water molecules has been studied in an attempt to identify useful correlations. A simple electrostatic model involving an ion-dipole interaction between the cation and polarized ligand (water in this case) suffices to explain the qualitative observations that the enthalpy of hydration increase with cation ionic potential, decrease in ligand coordination number, and acid strength of the anion acid. These effects were empirically treated, and expressions were derived for the enthalpy of formation and absolute entropy of the crystal hydrate. Enthalpies and entropies for numerous hydrates have been estimated.

Task 3. Vapor Pressure Measurements on CaCl Methanolates (R. W. Mar, R. W. Carling): Vapor pressures were measured over the temperature range 307 - 383 K for the following reactions:



The data were fitted by the method of least squares, to give

$$\ln P(\text{atm}) = 14.88 - 6115.3/T(\text{K}) \quad (\text{c})$$

$$\ln P(\text{atm}) = 15.94 - 6531.0/T(\text{K}) \quad (\text{d})$$

for reactions (a) and (b) respectively. The enthalpies of demethanolation of  $\text{CaCl}_2 \cdot 2\text{CH}_3\text{OH}$  and  $\text{CaCl}_2 \cdot \text{CH}_3\text{OH}$  as determined by the second law method are 12.1 kcal/mole  $\text{CH}_3\text{OH}$  and 12.9 kcal/mole  $\text{CH}_3\text{OH}$  respectively. The entropies of demethanolation are found to be 29.6 cal/deg.-mole  $\text{CH}_3\text{OH}$  and 31.7 cal/deg.-mole  $\text{CH}_3\text{OH}$ .

Task 4. Dehydrogenation/Hydrogenation Catalyst Studies (Dave Haaland): The program has consisted of two phases. The first consisted of spectroscopic IR catalyst studies using an available Perkin - Elmer 421 grating spectrometer. The second phase utilized a recently acquired Nicolet 7199 Fourier transform infrared (FTIR) spectrometer. The FTIR technique is several orders of magnitude more sensitive than the grating spectrometer used.

A portion of the work to date has involved the construction of apparatus and development of techniques required for completing the IR surface experiments. For the grating spectrometer studies, these included: 1) construction of a portable high-vacuum system capable of  $10^{-6}$  torr operation, 2) design and fabrication of infrared sample cells which allow in situ catalyst pretreatment, observation of the sample or the vapor phase, and external heating of the sample, and 3) assembly of a vapor introduction system. Also, the apparatus and techniques were developed for the difficult task of



pressing optical quality discs of supported catalysts. Catalyst samples of  $\text{H}_2\text{PtCl}_6$ ,  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ , or  $\text{NiNO}_3$  impregnated silicas and aluminas were reduced and pretreated under a variety of conditions before being examined with the Perkin - Elmer spectrometer. It was found that preparation of good catalyst samples with the proper optical qualities was a very tedious task which was not always reproducible. A variety of Pt and Ni catalyst loadings (0.5 - 10% with sample thickness from 10 to 60  $\text{mg}/\text{cm}^2$ ) and several sample pretreatments were investigated with only partial success using the grating spectrometer. The infrared spectra of chemisorbed cyclohexane and hydrogen as well as physisorbed benzene (but not chemisorbed benzene) were observed on some of the catalysts. Indirect evidence for chemisorbed benzene was available, however, since the addition of hydrogen to a catalyst sample treated with benzene resulted in the formation of adsorbed cyclohexane which was observed by IR spectroscopy. Thus, sufficient sensitivity for observing chemisorbed benzene did not exist with the grating spectrometer. Since high temperature/high pressure experiments and studies with alloy catalysts require the observation of chemisorbed benzene, greater spectra sensitivity was required.

Greater sensitivity was achieved after the procurement of the FTIR system. The procurement process involved demonstration experiments at both manufacturers' locations, detailed evaluation of the systems available, and a careful documentation of stringent specifications. After the installation of the FTIR spectrometer, the system was thoroughly tested to assure that all specifications were met. In addition, compatibility with the system required redesign and assembly of much of the catalyst experimental equipment. Thus, a new vacuum system incorporating a turbomolecular pump was built, and a greaseless infrared sample cell was designed which was capable of independently examining the metal catalyst surface and the surface of the support. Also a new multiple gas and vapor introduction system was assembled.

Catalyst samples of 10% Pt on alumina were investigated with the new FTIR system, and its greater sensitivity resulted in the observation of well-defined infrared absorptions of benzene adsorbed on the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts. The direct digital subtraction of the gas phase and bare catalyst spectra from the spectrum of the catalyst in the presence of benzene has allowed the effects of adsorbed benzene on the  $\text{Pt}/\text{Al}_2\text{O}_3$  sample to be observed directly. Absorption peaks have been identified which correspond to adsorbed benzene, impurity carbonates, and modifications of the  $\text{Al}_2\text{O}_3$  support caused by the presence of adsorbed benzene. Comparison of the spectrum of chemisorbed benzene on the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst with that of the support alone allowed identification of infrared absorptions which are due to chemisorbed benzene on platinum. A number of these bonds were identified, several of which have not been observed in the literature previously. The results confirm that the chemisorbed benzene molecule forms a  $\pi$ -bond with the platinum, and the plane of the molecule is parallel to the metal surface. Further experiments with deuterated molecules and partially hydrogenated  $\text{C}_6$ -ring molecules should allow complete assignment of the observed IR bonds. The critical high temperature experiments will then follow.



## Technical Problems

None

## Publications

J. J. Iannucci, R. D. Smith, C. J. Swet, "Energy Storage Requirement for Autonomous and Hybrid Solar Thermal Electric Power Plants," Proceedings of the International Solar Energy Congress, New Dehli, India, January 1978.

J. J. Iannucci, "The Value of Seasonal Storage of Solar Energy," Proceedings of the Applications Workshop on Thermal Storage Integrated into Solar Power Plants, February 1978.

J. J. Iannucci and P. J. Eicker, "Central Solar/Fossil Hybrid Electrical Generation: Storage Impacts," Proceedings of the Annual Meeting of the American Section of the International Solar Energy Society, Denver, August 1978.

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## V. SUMMARY AND RECOMMENDATIONS

The purpose of this section is to briefly summarize the progress made in the TEST program during the past fifteen months, and to recommend future avenues of investigation.

In the thermal energy storage area, activities have consisted of: systems analyses of both solar and non-solar electric utility systems, parallel laboratory investigations of three promising chemical reactions, and reaction screening to identify additional candidate reactions for energy storage.

Results obtained to date in the analysis of solar electric systems suggest that the use of reversible reactions for energy storage is not an attractive option. There are several reasons for this conclusion. First, the near-term need for autonomous (i.e., 100% solar) operation of solar electric power plants has not been established. Thus, chemical storage is forced to compete with both short-term ( $\leq 20$  hours) sensible heat storage and hybrid systems (i.e., systems with a fossil fuel backup). In each case, the chemical system is not competitive. When compared with sensible heat storage, the chemical systems suffer because of problems associated with storage efficiency: because storage inefficiencies are leveraged back through expensive upstream components (heliostats and receivers), solar electric systems with chemical storage are at a distinct economic disadvantage. When compared with hybrid systems, it is found that with as little 10% of the annual energy supplied by fossil fuel, the storage requirements for the hybrid plant can be reduced from about 850 hours to about 20 hours, i.e., to the region where sensible heat systems look more attractive. The analysis for non-solar electric utility applications is still in progress; however, to date no particularly attractive applications have been identified. These results suggest that future efforts should concentrate on areas where chemical reactions offer unique capabilities, for example, as high temperature chemical heat pumps or as energy transport systems.

Three chemical reactor systems have been investigated experimentally:  $\text{Ca(OH)}_2 + Q \rightleftharpoons \text{CaO} + \text{H}_2\text{O}$ ;  $\text{SO}_3 + Q \rightleftharpoons \text{SO}_2 + 1/2 \text{O}_2$ ; and  $\text{NH}_4 \text{HSO}_4 + Q \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3 + \text{SO}_3$ . The objectives of the calcium hydroxide work were to study the basic hydration/dehydration properties of the reaction, and to generate conceptual designs and evaluations of various methods of inputting and extracting energy. After characterizing the composition of the as-received  $\text{Ca(OH)}_2$ , it was thermally cycled many times. It was found that cycling continually decreased the amount of water that could be reacted with the system (34% of the initial amount after 140 cycles). The reason for this decrease is not fully understood, although it has been postulated to be due to the presence of noncondensable gases (primarily  $\text{H}_2$ ) on the surface of the reacting materials. An as yet unidentified corrosion mechanism is suspected to be responsible for the  $\text{H}_2$  generation. Conceptual designs of the three methods for transferring energy into and out of the system showed the economics of the fixed and fluidized bed systems to be about equal and both to be superior to the rotating drum.



While there is a possibility that the calcium hydroxide reaction may be attractive from an economic standpoint, considerable basic research is needed before a thermal energy storage system of significant size can be built, tested, and evaluated. Because of the potential for heat pumping with this reaction, continued investigation of the system is recommended.

Research on the sulfur trioxide system has been concerned with the development of durable, high temperature catalysts. Commercially available catalysts have been tested, and their degradation mechanisms identified. New catalysts have been developed and are undergoing evaluations. In view of the results of systems studies discussed above, it is likely that this reaction system will be used for transport rather than for storage. Before initiating additional work on this reaction, it is recommended that the transport application be analyzed in more detail.

The objectives of the ammonium hydrogen sulfate project are to develop a reaction mechanism which will allow reaction product separation, select materials of containment, and develop efficient operational cycles. Two potential reaction mechanisms have been identified and are currently being investigated. Initial investigations of materials compatibility revealed unidentified, but undesirable, side reactions. Several conceptual designs of solar thermal electric systems employing the ammonium hydrogen sulfate energy storage subsystem have been synthesized, and their technical and economic characteristics are being analyzed currently. If the results of these analyses are not positive, it is recommended that research on this reaction be phased out.

In addition to the experimental investigations describe above, a reaction screening task has identified other potential reactions capable of operating at one of three nominal temperatures (588, 783, or 1310°K). The physical, thermochemical, and kinetic properties of each of these reactions have been tabulated, and conceptual designs of storage subsystems for specified solar thermal electric power plants have been developed. Before any laboratory investigations are initiated for these reactions, detailed studies of potential applications should be conducted.

Detailed systems studies have been conducted for both closed-(high and low-temperature) and open-loop thermochemical pipeline systems. The major conclusions drawn from the closed-loop study suggest that this is a viable area for additional research. The potential market is quite large, although not well characterized by size, geographical location, or end-use temperature requirements. For the high temperature case, the steam reforming of methane to produce carbon monoxide and hydrogen is recommended as the preferred reaction; for the low temperature case, the choice is the benzene/cyclohexane reaction. The preferred high-temperature primary energy source is the very high-temperature gas-cooled reactor (VHTR); coal and solar-based systems are anticipated to encounter serious source/reformer interface problems. Potential low-temperature primary energy sources include light water reactors, gas-cooled breeder reactors, coal, and solar. Major barriers to implementation are VHTR development for the high-temperature case, and technical feasibility of cyclic operation of the benzene/cyclohexane reaction for the low-temperature case. Economics for both systems are attractive. It is recommended that the



technical feasibility of the lower-temperature system be established, since there are several potential thermal energy sources for this system being developed in the United States. Further, additional information is required regarding the characteristics of the potential market to be served by these systems.

Results from the open-loop study are also encouraging. Three concepts were investigated; a base-case consisting of a high-temperature gas-cooled reactor (HTGR) for the steam reforming of methane, a 160-km pipeline, and a methanator to produce process heat and substitute natural gas (SNG); a near-term case consisting of a coal gasification plant to produce  $H_2$  and  $CO$ , with the rest of the system (pipeline, methanator) remaining essentially unchanged; and a mid-term case consisting of a floating HTGR/reformer complex supplied with hydrocarbons from a liquified natural gas (LNG) terminal, and an undersea pipeline which connects the complex with the shore and the rest of the system. All three systems were found to be technically feasible. Although the base-case was not competitive economically with alternate energy delivery systems, the near-term case was, and the mid-term case may be in the future. Significant markets were found to exist for the heat and synthetic natural gas delivered by these systems. Moreover, existing pipelines could be converted to form part of a distribution system; no significant problems were anticipated in converting or building storage capacity for the gases produced in or formed by the system. Because the most attractive case considered is basically a competitor to various coal gasification schemes, it is recommended that no additional activities be initiated until expression of interest are obtained from those individuals within DOE who are responsible for these programs.

The other major activity in the area of thermochemical pipelines is the design, fabrication and test of a duplex steam reformer tube. Based upon the uncertain future of very high temperature, gas-cooled reactor development in the U.S., it is recommended that no additional work be initiated in this area unless it continues as part of a cooperative international program.

Four different chemical heat pumps projects were investigated during this reporting period. These systems were based upon the use of sulfuric acid concentration/dilution, ammoniates, methanolates, and hydrates. Results obtained to date for the first three systems are encouraging. Large-scale, closed-loop demonstration of the  $H_2SO_4$  system has been accomplished, and methanolates for heating and cooling and ammoniates for cooling have been identified and investigated in laboratory-scale experiments. Results obtained for the hydrates systems are inconclusive. The chemical heat pump application is felt to be an important area for future research. The following activities are recommended. For the  $H_2SO_4$  system, development is significantly advanced, so that investigations into system operations are appropriate. For the methanolates and ammoniates, additional work is required to demonstrate closed-loop operation. For hydrates, additional work to identify suitable hydrates should be initiated. Comparisons of these systems with each other, and with competing technologies are required in order to reduce the number of different systems being considered.



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