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Thermochemical Energy Storage and Transport Program Semiannual Report

(OCTOBER 1976 - MARCH 1977)

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THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT PROGRAM SEMIANNUAL REPORT

(October 1976 - March 1977)

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FOREWORD

This document summarizes the progress made by the Thermochemical Energy Storage and Transport (TEST) Program in the period October 1976 - March 1977.

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Introduction

TEST Program Scope

The Chemical and Thermal Storage Branch of the Energy Research and Development Administration (ERDA), Office of Conservation, Division of Energy Storage Systems has implemented a National Thermal Energy Storage (TES) Program. The objective of this National Program is to develop and disseminate thermal and thermochemical energy storage technology. The Program consists of three subprograms:

1. Low-Temperature Thermal Energy Storage Program - The objective is to develop sensible and latent heat technologies for low-temperature (≤250°C) applications.

2. High-Temperature Thermal Energy Storage Program - The objective is to develop sensible and latent heat technologies for high-temperature (≥250°C) applications.

3. Thermochemical Energy Storage and Transport (TEST) Program - The objective is to develop reversible chemical reaction technologies for thermal energy storage and transport applications.

The Chemical and Thermal Storage Branch has delegated the management responsibility for the Thermochemical Energy Storage and Transport Program to Sandia Laboratories, Livermore. (Oak Ridge National Laboratories and NASA Lewis Research Center are responsible for the Low-Temperature and High-Temperature Thermal Energy Storage Programs, respectively.)

TEST Program Objectives

Of the three approaches to the storage of thermal energy (sensible, latent, and thermochemical), thermochemical storage technology is the least advanced, and therefore the TEST Program will emphasize research and technology development. The basic objective of this Program is to establish an energy storage and transport technology base to support all viable applications, and to stimulate the development of an industrial and commercial capability for producing these systems. The specific tasks necessary to achieve this basic objective are:

- Identify and evaluate preferred users (current and future) of reversible chemical reactions for energy storage and transport.
- Identify specification requirements and evaluate available technology and technology needs for selected storage systems.
- Formulate and evaluate energy storage and transport concepts which meet the requirements established above
- Develop the most promising concepts and systems to a point of demonstration on a scale commensurate with commercial application. Only those concepts with potential for commercialization will be developed to completion.

The specific applications and concepts currently being addressed in the Program are:

- Thermal Energy Storage (TES) in electric power generating facilities
- TES for solar central receiver systems
- Open-ended methane based chemical heat pipe
- High-temperature chemical heat pipe
- Low-temperature chemical heat pipe
- Solar chemical heat pump storage

This list of specific applications is by no means inclusive, as other applications may surface as the Program progresses, or some of the applications shown may not prove feasible. The extent to which these specific applications and concepts apply to general application sectors (i.e., buildings, industry, and utilities) is illustrated in Figure 1.

Program goals have been established assuming at least one thermochemical storage or transport system will be developed for each application. The long-range program goals, milestones, and target dates selected for each application are given in Figure 2. This scheduling has been established on the assumption that all of the applications shown are and will remain of equal importance with regard to potential impact on energy conservation. However, as the thermochemical technologies are developed in this program, it is anticipated that several key applications will become the foci of this program.

Specific Applications Addressed in TEST Program \ General Application Areas Supported By TEST Program		Building		Industry		Utilities	
		Solar Heat/Cool	Other Heat	Source of Proc. Heat	Waste Heat Recovery	Solar	Non-Solar
Thermal Energy Storage	TES in electric power generation facilities						•
	TES for solar central receiver systems*					•	
Chemical Heat Pipe	Open-ended methane-based chemical heat pipe		•	•			
	High-temperature chemical heat pipe		•	•			
	Low-temperature chemical heat pipe		•	•			
Chemical Heat Pump Storage	Solar chemical heat pump storage	•					

* Includes TES for extended and seasonal storage.

Figure 1. A Comparison of General Application Areas (Program Objectives) and Specific Applications Currently Addressed in TEST Program

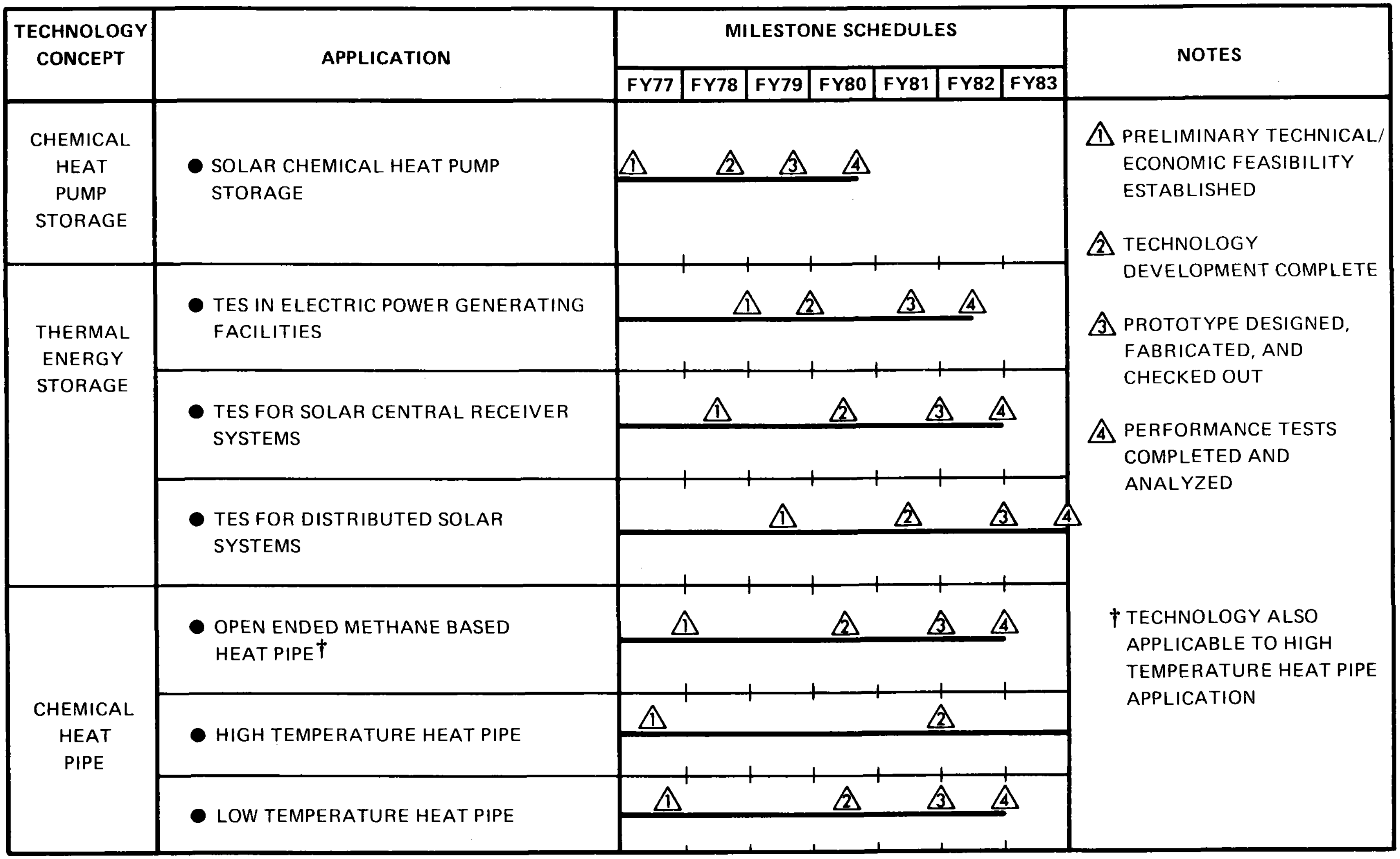

Figure 2. Long-Range Program Goals, Milestones, and Target Dates

Assessment of Technology

Presently, no reversible chemical reaction is well enough researched and understood to allow its immediate incorporation into a storage system. Consequently, a considerable amount of research and development is required to characterize any potentially useful reaction with respect to such parameters as reaction rates, side reactions, reversibility, cyclability, long-term performance, reproducibility, reliability, and impurity effects. For catalyzed reactions, additional questions concerning catalyst lifetime, degradation, and poisoning must be addressed.

The heat transfer technology pertinent to thermochemical storage systems is largely undeveloped. Exothermic and endothermic reactors must be designed to allow for the complete control of reactions, along with efficient heat removal or input. The heat transfer problems may be formidable, depending upon the reaction characteristics. Heat exchange during liquid phase reactions can be accomplished efficiently. On the other hand, gas/solid reactions cannot be handled as easily due to inherent low heat transfer rates, variable bed characteristics, and bed density changes that occur upon reaction cycling. Catalytic reactors coupled to a heat exchange function are also not well developed.

Material compatibility problems can be significant depending upon the temperatures of operation and the chemicals involved. Ambient storage mitigates the material problems to the extent that the corrosive conditions may be confined to a fairly small portion of the total system. Unfortunately, the highest temperatures (and therefore the most corrosive environment) are generally found in the most complex and expensive components of the system: the reactor and heat exchanger.

Almost all thermochemical reaction cycles for storage or transport applications contain steps which are potentially wasteful of energy; the net result is a much reduced effective energy density. As an example, consider the reaction

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

which has an attractively large heat of reaction of 380 cal/gm. However, if one considers that 142 cals/gm are lost due to the condensation of H_2O and the sensible heats associated with H_2O and CaO, the net energy density is only 238 cal/gm. The solution, of course, is to use the heat of condensation and sensible heats for secondary purposes; therein lies one of the technical challenges that must be met if the thermochemical system is to be used to its best advantage. Operational cycle optimization, and recovery and use of potentially rejected energies are necessities for the development of economically viable thermochemical energy storage and transport systems.

Current Project Goals

The TEST Program is comprised of numerous projects, either contracted by ERDA and NSF, or subcontracted by Sandia, to industrial, university, and government laboratories. During this reporting period, the following projects were initiated or in progress:

- Atomics International (AI) - $CaO/Ca(OH)_2$ Storage
- Martin Marietta (MM) - Ammoniated Chloride Salts
- Rocket Research Corp. (RRC) - Extended Storage for Solar
- Chemical Energy Specialists (CES) - Hydrated Salt Heat Pump Storage
- Rocket Research Corp. (RRC) - Sulfuric Acid Dilution
- General Electric Corporate Research and Development (GE/CRD) - Chemical Heat Pipe Feasibility
- General Electric Energy and Systems Technology Division (GE/ESTD) - Alternate Catalyst for Duplex Steam Reformer
- Lawrence Berkeley Laboratory (LBL) - High Temperature Storage
- Colorado State University/Martin Marietta (CSU/MM) - Experimental Heat Transfer Studies

Additional projects are in the process of procurement (see page 36). The correlation between these projects and the specific applications identified on page 13 is illustrated on Figure 3. The technical goals that have been established for each subcontracted project are given in Table I.

Application \ Subcontracted Project	AI - $CaO/Ca(OH)_2$ storage	MM - Ammoniated salts	RRC - Extended solar storage	CES - Hydrated salt heat pump	RRC - H_2SO_4 dilution	GE/CRD - Chemical heat pipe	LBL - High-temperature storage	GE/ESTD - Alternate catalyst for DSR	CSU/MM - Experimental heat transfer
TES in electric power generating facilities		•							•
TES for solar central receiver systems	•		•				•		
Open-ended methane based chemical heat pipe								•	
High-temperature chemical heat pipe						•	•		
Low-temperature chemical heat pipe						•			
Solar chemical heat pump storage				•	•				

Figure 3. Correlation Between Subcontracted Projects and Applications Under Development in the TEST Program. (While data generated may be applicable to several applications, only the primary intended application of the project is indicated here.)

TABLE I

FY77 PROJECT GOALS

Technology Sector	Contractor	Reaction	Goals (to complete the following tasks)
Thermal Energy Storage	Atomics International	$CaO + H_2O = Ca(OH)_2 + Q$	◎ Identify viable applications • Perform preliminary analysis of moving solids and fluidized bed exchangers • Conduct preliminary heat transfer experiments • Conduct preliminary chemistry and materials experiments
	Martin-Marietta	Ammoniates, for example, $MgCl_2 \cdot 2NH_3 + Q = MgCl_2 + 2NH_3$ $CaCl_2 \cdot 8NH_3 + Q = CaCl_2 \cdot 4NH_3 + 4NH_3$	• Develop analytical model for heat transfer in packed beds • Conduct heat transfer experiments • Conduct chemistry experiments (coupled reaction experiments, cycling effects, moisture effects) • Conduct economic analyses
	Rocket Research Corporation	Part of a reaction screening study	• Determine technical and economic feasibility of extended storage for solar thermal power plants
Chemical Heat Pump Storage	Chemical Energy Specialists	$MgCl_2 \cdot nH_2O + Q = MgCl_2 \cdot mH_2O + (n-m)H_2O$	• Experimentally investigate the process of vaporization and absorption • Investigate compatibility, scaling, and cycling problems • Develop preliminary system design
	Rocket Research Corporation	H_2SO_4 concentration/dilution	◎ Select a system for detailed sizing and scaling analysis • Design and construct H_2SO_4 heat pump • Test and evaluate integrated system • Define Phase III program (full-scale system H_2SO_4 program)
Chemical Heat Pipes	General Electric (Corporate Research and Development)	$CH_4 + H_2O = 3H_2 + CO$	◎ Determine technical and economic feasibility of high and low temperature closed loop chemical heat pipes • Identify critical R&D problems
	Lawrence Berkeley Laboratory	$2SO_3 + Q = 2SO_2 + O_2$	◎ Optimize process for SO_3/SO_2 storage system • Perform screening experiments to identify corrosion resistant materials
	General Electric (Energy Systems Programs Dept.)	Technology relevant to $CH_4 + H_2O = 3H_2 + CO$	◎ Design alternate catalyst configuration • Fabricate alternate catalyst

◎ Completed

Summary of Accomplishments

Highlights

The following is a list of highlights accomplished during this reporting period. Each project is discussed in more detail under "Program Activities."

General Electric Corporate Research & Development

- A review of methanation technology has been completed and documented

Lawrence Berkeley Laboratory

- Detailed flowsheet analysis of the $2SO_3 = 2SO_2 + O_2$ for storage has been completed and documented

Atomics International

- Potentially viable applications for $CaO/Ca(OH)_2$ have been identified

Rocket Research Corporation

- A novel use of sulfuric acid dilution has been identified: solar chemical heat pump storage
- Final documentation of the experimental laboratory feasibility study for sulfuric acid storage schemes has been completed, and submitted to ERDA

Boeing

- Boeing Engineering Company energy storage project final review was completed

Martin-Marietta

- Phase I final report emphasizing the rates of ammoniate dissociation and recombination has been completed and submitted to ERDA

Sandia Laboratories

- The TEST Program Plan was completed and submitted to ERDA for review

- The FY77 Annual Operating Plan was completed and submitted to ERDA for review
- Experimental apparatus for vapor pressure measurements was designed and fabricated
- Subcontract was placed with MM/CSU

Achievement of TEST Program Goals

The TEST Program goals (see Figure 2) which were accomplished during this reporting period are:

- Preliminary technical feasibility of the solar chemical heat pump storage concept has been established
- Preliminary technical/economic feasibility of high-temperature chemical heat pipe has been established

Achievement of Project Goals

The FY77 Project goals which have been accomplished are so indicated in Table I, page 18.

Program Activities

The discussion of program activities has been structured to be consistent with the TEST Program Work Breakdown Structure (WBS) shown in Figure 4.

Program Management (WBS 1.0)

Program Planning (WBS 1.1)--Preliminary drafts of the TEST Program Plan and the FY77 Annual Operating Plan were submitted to ERDA Headquarters on December 15, 1976, for review. Comments and suggestions from reviewers have been included in revised drafts. Final versions of the Program Plan (Sandia report SAND77-8014) and the FY77 Annual Operation Plan (SAND77-8226) are currently undergoing final review.

Review and Evaluation (WBS 1.2)--The Atomics International project (AT(04-3)-701) for the development of hydroxide/oxide storage schemes was reviewed. Based upon the apparent absence of a viable application, it was recommended that the project be redirected to address this concern. Also, it was decided that this effort should concentrate on one chemical system, $Ca(OH)_2/CaO$.

The Martin Marietta project (E(04-3)-1229) on ammoniated halide salts was reviewed, and the continuation of the project into Phase II was not recommended. Rather, the Martin Marietta and Sandia personnel jointly worked to define an additional project phase, referred to as Phase Ib, to define some of the remaining chemistry and heat transfer uncertainties.

The Rocket Research Corporation reaction screening project (NSF Grant AER 75-22176) was modified and extended, at the suggestion of the RRC investigators, to evaluate the use of chemical energy storage to extend intermediate load solar power plants to baseload capability.

The following projects were reviewed critically, and no major changes in direction or scope were recommended:

- Chemical Energy Specialists - hydrated salt heat pump storage
- Rocket Research Corporation - H_2SO_4 dilution
- Lawrence Berkeley Laboratory - high temperature CHP and storage analysis
- General Electric - chemical heat pipe feasibility
- Boeing Engineering Company - TES for solar Brayton

The final technical review session for the Boeing study (Advanced Thermal Energy Storage Concept Definition Study to Solar Brayton Power Plants, ERDA Project E(04-3)-1300) was held at Livermore, California, on January 28, 1977.

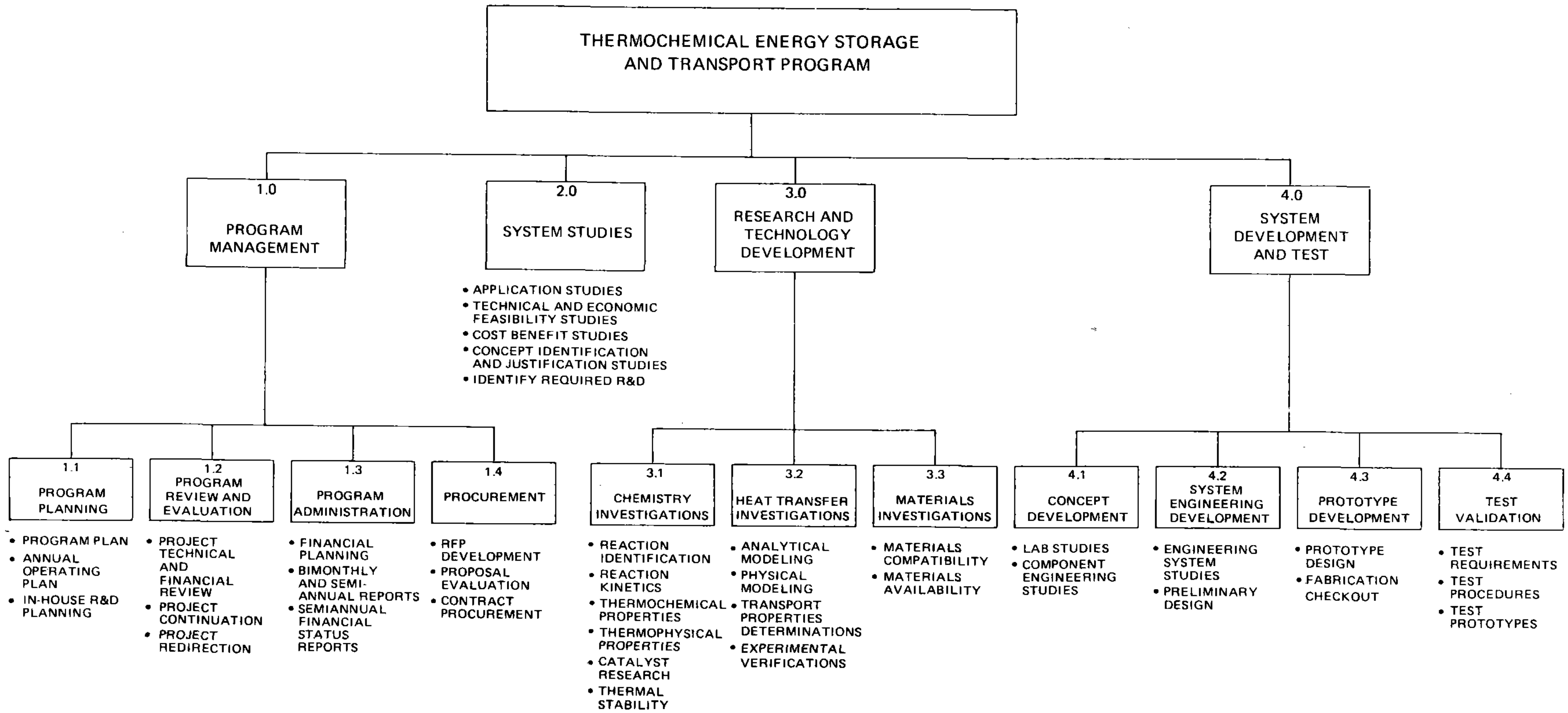

Figure 4. Thermochemical Energy Storage and Transport Program Work Breakdown Structure

The final report has been reviewed and returned to BEC for revision and final publication.

Numerous meetings were held at Sandia over the past six months for varied reasons, e.g., proposal presentation, project review, and information interchange. A list of such activities is given in Table II.

Sandia personnel visited various installations for subcontractors and program reviews. A list of these activities is given in Table III.

Presentations made by Sandia personnel during this reporting period are given in Table IV.

Procurement (WBS 1.4)--Generally, the procurement process proceeds sequentially as follows:

1. Work statement requested by SLL
2. Work statement received by SLL
3. Work statement reviewed by SLL
4. Work statement revised by contractor
5. Work statement accepted by SLL
6. Work statement approved by ERDA/STOR
7. Procurement initiated
8. Procurement complete; contract awarded
9. Work in progress

The current procurement status of all subcontracts anticipated for FY77 funding is illustrated in Figure 5.

TABLE II

SUMMARY OF MEETINGS HELD AT SANDIA LABORATORIES

Date	Company	Visiting Personnel	Purpose/Subject
10/5,6/76	ERDA/HQ	C. J. Swet	Discuss TEST Program
10/15/76	Rocketdyne	Dr. R. I. Wagner	Diels-Alder energy storage proposal
10/26/76	Rocket Research Corp.	D. Huxtable E. Schmidt	NSF screening study redirection; extended storage concept

TABLE II. (Continued)

Date	Company	Visiting Personnel	Purpose/Subject
10/27/76	Purdue Univ.	Prof. Viscanta	Heat transfer phenomena in TES systems
11/11/76	IGT	F. Kester J. Gahimer	IGT proposals on heat pipes and reaction screening; IGT capabilities and expertise
12/1/76	NASA-LeRC	R. Duscha	General program reviews; acquaint the NASA program participants with the SLL central receiver program
12/10/76	Atomics Int'l	T. Spring J. Guon D. Chung G. Erwin	Presentation of applications study results for $Ca(OH)_2/CaO$ reaction
1/11/77	Rocket Research Corp.	D. Huxtable C. Clark	Discuss H_2SO_4 chemical heat pump
1/12/77	Lawrence Berkeley Laboratory	C. F. Tsang M. Liepmann	Underground storage in possible support of RRC H_2SO_4 project
1/28/77	Rocket Research Corp.	D. Huxtable C. Clark	Interim review of RRC programs - H_2SO_4 emphasized
1/28/77	Boeing Engr. Company	J. Gintz W. Engle W. Eberle	BEC final project review
1/31 - 2/2/77	ERDA/HQ	C. J. Swet P. Graf	Discuss TEST program plan and annual operating plan
3/4/77	Chemical Energy Specialists	L. Greiner	CES project review
3/4/77	VEDA, Inc.	R. Kretchek T. Moore	"Unified Heliostat Array" presentation
3/11/77	EXXON	P. Joy A. Muenker	Chemical heat pump information exchange
3/15/77	Argonne Nat'l Laboratory	D. Gruen	Chemical heat pump information exchange
3/18/77	Univ. Calif., Davis	Prof. Munir	Thermal decomposition kinetics studies

TABLE III

SUMMARY OF VISITATIONS BY TEST PROGRAM PERSONNEL

Date	Company Visited	Purpose	Sandia Attendee(s)
10/12, 13/76	RRC	Program review	Bramlette Mar Mills
10/22/76	GE	Interim Program review	Bartel Bramlette
11/15/76	EPRI	Review of RRC program	Bramlette
12/6/76	SLL	10-MW pilot plant review	Bartel Mar Mills Nichols
12/8/76	LBL	National Research Council review of various SLL energy storage programs	Mar
12/11/76	CES	Program review	Carling
12/16/76	ERDA/HQ	TEST Program review	Bramlette Mar
2.7.77	Atomics Int'l	Project review and evaluation	Bartel Bramlette Mar Nichols
2/22/77	Univ. of Houston	Review of work statement and facilities tour	Bramlette Mitchell
2/24/77	ERDA/HQ	Area Mgrs. meeting	Mar
3/1/77	ERDA/SAN	Discuss AI contract	Mar
3/27, 28/77	ERDA/HQ	Review PRDA proposals	Bramlette

TABLE IV

SUMMARY OF PRESENTATIONS BY TEST PROGRAM PERSONNEL

Date	Authors	Purpose
1/18/77	Bartel	"Chemical Heat Pipe - Concept and Opportunities," presented to Sandia, Albuquerque staff
2/5/77	Mar	Review of Sandia Energy Programs for Senator Harkin and Staff
2/24/77	All	Review of TEST Program presented to the Sandia Solar Energy Projects Review Committee
3/12/77	Bramlette	Review TEST Program for Northern California Solar Energy Association

Project		O	N	D	J	F	M	A	M	J	J	A	S
Thermal Energy Storage Projects	$Ca(OH)_2/CaO$ Reaction (AI)				1								
	Ammoniated Chloride Salts (MM)			6			7, 8						
	Extended Storage for Solar (RRC)	8											
	Ammonium Hydrogen Sulfate Decomposition (UH)					5, 6							
	Experimental Heat Transfer Studies (CSU)					7, 8							
	Thermal Decomposition Kinetics (UCD)						5, 6						
	SO_2/SO_3 Catalyst Development (RRC)				6								
Chemical Heat Pipe Projects	Chemical Heat Pipe Feasibility (GE)	8											
	Open Heat Pipe Feasibility (IGT)				4	6							
	High-Temperature CHP & Storage Analysis (LBL)	8											
	Benzene/Cyclohexane Heat Pipe (GE)												
	CH_4/H_2O CHP Solar Interface Study (UH)				4, 5, 6								
Chemical Heat Pump Storage Projects	Hydrated Salt Heat Pump Storage (CES)	8			9		2, 3, 4						
	H_2SO_4 Dilution (RRC)	8											
	MeOH Based Heat Pump Storage (EIC)				5, 6								
	Aquifer Studies (LBL)							2					

Legend:
1 - Work statement requested
2 - Work statement received
3 - Work statement reviewed
4 - Work statement revised
5 - Work statement accepted
6 - Procurement initiated
7 - Procurement completed; contract awarded
8 - Work in progress
9 - Current contract ends

Figure 5. Subcontract Status

System Studies (WBS 2.0)

The following projects were initiated or were ongoing during this reporting period:

- Chemical heat pipe feasibility (GE/CRD)
- Extended storage for solar (RRC)
- High-temperature CHP and storage analysis (LBL)

Project Title: Closed-Loop Chemical Systems for Energy Storage and Transmission

Contractor: General Electric Company

Contract No.: E(11-1)-1676

Activities and Results: Prior to this reporting period, GE had concluded that: 1) the technology is available to build a methane-based chemical heat pipe, 2) a high-temperature energy source is required, 3) there currently is no suitable energy source under development in the U.S., 4) solar sources do not seem feasible due to thermal cycling, energy flux mismatch, and poor economics, 5) the benzene/cylcohexane reaction appears to be an attractive chemical heat pipe reaction compatible with energy sources currently or potentially available in the U.S., and 6) chemical heat pipes can significantly impact the energy conservation program by storing and transporting thermal energy for process heat.

Activities during this reporting period included documentation of the methane-based heat pipe work, review of methanation technology, and analysis of the benzene/cyclohexane reaction, low-temperature chemical heat pipe. A review of methanation technology has been documented by the R. M. Parsons Company for GE. Equilibrium conversion calculations are being performed for the benzene/cyclohexane reaction to determine the interdependence of temperature, pressure, energy, and undesirable side products, and to analyze the economics of transport for this chemical system. It is premature to report conclusive results for these tasks.

Project Title: Chemical Energy Storage for Solar Thermal-Electric Conversion Systems

Contractor: Rocket Research Corporation

Contract No.: AER 75-22176

Activities and Results: This program was originally funded by NSF. The objectives of that program were to survey potential reactions for use with solar thermal conversion systems, and to synthesize storage systems for both low (400-600°F) and high (900-1000°F) temperature applications. The program was originally structured to be performed in three phases, the first phase being the reaction screening task, and the second and third phases being the detailed study of the high- and low-temperature systems.

At the program review held on October 12 and 13, 1976, it was decided to modify the program to take advantage of the developments which have occurred in the solar thermal-electric conversion programs. Accordingly, RRC was directed to delay the second and third phases of this program to allow system studies of selected solar thermal conversion concepts, and to extend the temperature range of the reaction screening task to include 400 to 1500°F.

The reaction screening task has been completed, and the system studies have been initiated.

Project Title: The Chemical Storage of Thermal Energy

Contractor: Lawrence Berkeley Laboratory

Contract No.: W-7405-ENG-48

Activities and Results: The major goal of the LBL work is to synthesize and evaluate feasible flowsheets for those heat storage processes that use SO_3/SO_2 and methanation/reformation reactions. The prime objectives are to identify and eliminate major sources of thermal inefficiency and to obtain estimated equipment sizes and costs.

A process flowsheet was developed, analyzed, and refined for the use of the SO_2/SO_3 reaction with a nuclear energy source (M. L. Bhakta, M.S. Thesis, U.C. Berkeley, 1976). The SO_3/SO_2 reaction as applied to central receiver solar power plants is currently under investigation; this effort is concentrating on the development of storage process configurations and their integration with the steam cycle in a manner that maximimizes the overall system efficiency. The methanation/reformation reaction is also being studied for comparison but the results are too preliminary to report here.

Research and Technology Development (WBS 3.0)

The following projects were initiated or were in progress during this reporting period:

- $Ca(OH)_2/CaO$ Reaction (AI)
- Ammoniated Chloride Salts (MM)

- Experimental Heat Transfer Studies (CSU/MM)*
- SLL In-House Technology Studies
- Alternate Catalyst Development for a Steam Reformer (GE/ESTD)
- Duplex Reformer Tube Fabrication (GE/ESTD)

Project Title: Solar Energy Storage System for Heating and Cooling of Buildings

Contractor: Atomics International

Contract No.: AT(04-3)-701, Task 33

Activities and Results: During this reporting period, an effort was made to define those applications for the $CaO/Ca(OH)_2$ concept that appear to be economically viable and to estimate the costs and/or conservation potential of such applications. Following the successful identification of viable applications, a pertinent experimental program was to be planned.

Conceptual designs, performance analyses, and cost assessments were made for four applications: 1) solar total energy application for a potash manufacturing plant, 2) storage for solar thermal electric plants, 3) seasonal storage for heating and cooling of buildings, and 4) topping cycle for solar central receiver systems. Atomics International feels they have adequately shown the $CaO/Ca(OH)_2$ system to be competitive with other storage approaches using a fixed-bed design, and that substantial cost reductions may be realized upon successful development of a flowing solids heat exchange process. It is our opinion that most of the applications proposed are not viable, due primarily to the requirement for a very expensive front-end system, and that the cost comparisons presented by Atomics International did not adequately reflect the synergistic costs. However, we feel there is potential for the use of the $Ca(OH)_2/CaO$ reaction in second and third generation central receivers, with an emphasis on long-term storage approaches.

Atomic International is currently planning an experimental program to further characterize the $CaO/Ca(OH)_2$ reaction. The technical feasibility of the moving solids and fluidized bed concepts will be assessed in greater detail.

*This project has just been initiated; progress will not be discussed below.

Project Title: Development of Ammoniated Salts Thermochemical Energy Storage Systems

Contractor: Martin Marietta Corporation

Contract No.: E(04-3)-1229

Activities and Results: Phase I of this contract was completed prior to the beginning of this reporting period. The following objectives were met: 1) eight ammoniated salts were selected for further study, 2) the thermal stability of NH_3 was determined at 350°C, 3) the dissociation and recombination rates and heats of reaction of selected salts were determined, 4) design concepts were developed for a bench-scale system, and 5) a test plan was developed. Martin Marietta and Sandia personnel decided that additional tasks should be performed prior to initiating a large-scale design. Consequently, a Phase Ib was defined. Contract negotiations have been completed for the Phase Ib activity (current contract is administered by ERDA/SAN), and work has just commenced.

The Phase I final report was completed (Martin Marietta Corporation Report No. MCR-76-562) and transmitted to ERDA Headquarters on November 10, 1976.

Project Title: Evaluation of an Alternate Catalyst for a Helium Heated Steam Reformer

Contractor: General Electric Company

Contract No.: E(11-1)-2929

Activities and Results: The goal of this program is to evaluate an improved reformer catalyst. Longer catalyst lifetime, easier replacement, and in situ regeneration of catalytic sites are the advantages sought in this program. Foster Wheeler is subcontracted to G.E. in this effort and has supplied the latter with a detailed design for a catalyst and support which will be compatible with a steam reformer.

Plans call for fabrication of the alternate catalyst and testing in a reformer.

Project Title: Duplex Reformer Tube Fabrication Feasibility Demonstration

Contractor: General Electric Company

Contract No.: E(11-1)-2841 Mod #1

Activities and Results: Although funded and monitored by the ERDA Division of Nuclear Research and Applications, Sandia is following the progress of this contract due to the importance of the DSR to the nuclear-based chemical heat pipe, and the generic importance of advanced reformers to chemical heat pipes.

Two stainless steel duplex tubes ten feet long have been fabricated. Destructive testing and metallurgical examination of these items are under way.

Project Title: SLL In-House Technology Studies

Contractor: Sandia Laboratories, Livermore

Contract No.: HC0103

Activities and Results: The purpose of the in-house technology studies is to assure the maintenance of the high level of technical expertise required to provide effective program management. The in-house research program will provide a link for technical interaction between the various subcontractors, as well as provide some of the analysis capabilities needed to perform the project management. An attempt will be made to generate new and novel uses of chemical reactions, and research generic to chemical reaction schemes will be conducted.

Sandia personnel have concentrated on the managerial and administrative aspects of the TEST program to date, and therefore the in-house technology studies have proceeded slowly. Nevertheless, a reasonable amount of progress has been made.

Shot Tower - The shot tower is a novel counter-current, direct-contact, heat exchange concept which uses a latent heat of fusion (HOF) material and a mutually immiscible heat transfer fluid (HTF). The process uses two storage tanks (one each for "cool" and "hot" HOF material, respectively) in conjunction with one or two direct contact external heat exchange towers (which can be small relative to the size of the storage tanks). This simple external heat exchanger enables the system to be considerably less complex and potentially less expensive than any other latent heat of fusion thermal energy storage (TES) system described to date.

A computer program to predict the heat transfer process has been developed. Preliminary calculations indicate very compact heat exchangers are possible; parametric studies are under way.

Small scale laboratory experiments using a parafin/water system have provided qualitative data on droplet formation and size as a function of orifice size and injection rate.

SO_2/Alloy Compatibility - A literature survey of high-temperature corrosion of alloys in SO_2 environments is being conducted to determine the severity of the corrosion problems and to identify candidate materials for subsequent in-house corrosion tests.

A preliminary scanning of the literature indicates that commercial alloys with acceptable corrosion resistance probably exist. Very little work on coated alloys has been reported; however, these alloys could be good candidate materials for non-erosive environments, such as a TES system.

Vapor Pressure Measurements - An apparatus to measure vapor pressures and gaseous decomposition products has been constructed. The system is all stainless steel with the sample container submerged in a bath of Dow Corning 550 fluid. The bath is stirred and temperature controlled. The upper limit of the bath fluid and the temperature controller is 250°C. A water-cooled copper coil establishes the lower temperature limit of 20°C. Vapor pressure measurements are made using a commercial diaphragm gauge fitted with a 1000-Torr bakeable head. The system is also fitted with a gas sampling baffle, which allows the gaseous decomposition products to be analyzed by mass spectrometry.

The first system to be studied will be the hydrates of magnesium chloride. The vapor pressures of the following equilibria will be determined:

1. $MgCl_2 \cdot 6H_2O(S) = MgCL_2\ 4H_2O(S) + 2H_2O(g)$

2. $MgCl_2 \cdot 4H_2O(S) = MgCl_2 \cdot 2H_2O(S) + 2H_2O(g)$

3. $MgCl_2 \cdot 2H_2O(S) = MgCl_2 \cdot H_2O(S) + H_2O(g)$

4. $MgCl_2 \cdot H_2O(S) = MgCl_2(S) + H_2O(g)$

From the vapor pressure measurements, the following information will be obtained: rate at which equilibrium is obtained, energy of vaporization, and the reversibility of the reaction. At lower hydrate values, it is speculated that HCl may be a decomposition product; mass spectrometry will be used to detect the HCl.

Salt/Alloy Compatibility Studies - Numerous energy storage schemes involving the use of sulfur-oxygen compounds have been proposed, e.g., $Na_2S_2O_7$, Na_2SO_4, NH_4HSO_4. These materials are known to be corrosive; however, the compatibility of these salts with common and less common construction materials is undefined. A compatibility screening apparatus has been designed and constructed, and a test matrix which includes low carbon steels, 300 and 400 series stainless steels, and superalloy materials has been developed. These representative structural metals will be evaluated in the liquid phase of the above mentioned salts. Quick elimination of the unsuitable materials and a rough estimate of containment material cost are sought. Those materials which survive these screening tests will be evaluated on a longer term basis to establish accurate corrosion rates.

System Development and Test (WBS 4.0)

The following projects were initiated or ongoing during this reporting period:

- Hydrated Salt Heap Pump Storage (CES)
- H_2SO_4 Dilution (RRC)

Project Title: The Chemical Heat Pump: A Simple Means to Conserve Energy

Contractor: Chemical Energy Specialists

Contract No.: E(04-3)-1332

Activities and Results: Chemical Energy Specialists (CES) is designing and developing a chemical heat pump system for heating and cooling private residences with solar energy. In this system, the solar energy is collected by dehydration of $MgCl_2 \cdot 4H_2O$; the energy is stored as $MgCl_2 \cdot 2H_2O$ and water.

A preliminary design has been completed and performance modeling is in progress. The purpose of these studies is to optimize the number of solar panels, distance between panels, distance of first panel to absorber, pump requirements for blowing air across absorber, and angle of panels to the sun.

To date, the absorber material has been placed in a thin-walled aluminum container and dehydrated by means of radiant energy. These studies have been hampered by vacuum problems. However, some data have been obtained on the rate, temperature, and cycling effects associated with hydration and dehydration. A draft of this final report was submitted for review on February 18, 1977.

Project Title: Sulfuric Acid and Water Chemical Energy Storage for Solar-Thermal Conversion

Contractor: Rocket Research Corporation

Contract No.: E(04-3)-1185

Activities and Results: The technical feasibility of a sulfuric acid/water storage system was demonstrated via laboratory experiments prior to this reporting period and final documentation has been published (Rocket Research Corporation Report RRC-76-R-530).

The activities in this reporting period were initially directed at the design, fabrication, and testing of a prototype storage system for seasonal solar heating and cooling of buildings. Several separator designs were tested, various materials were subjected to corrosion tests, process flowsheets were analyzed, and components were sized.

A new concept was identified: the use of the reaction as a chemical heat pump. In view of the significant advantages that appear to be possible (greater energy density, reduced system costs, and reduced system complexity), this application is currently being evaluated.

Future Activities

Program Planning (WBS 1.1)

Drafts of the FY78 Annual Operating Plan will be prepared and submitted to the TES Program Manager in August, 1977.

Project Review and Evaluation (WBS 1.2)

The following documents are scheduled for review:

Report Description	Due Date	Contractor
High-Temperature Chemical Heat Pipe	5/77	GE
Low-Temperature Chemical Heat Pipe	9/77	GE
Open-Loop Chemical Heat Pipe Feasibility Study Interim & Final Reports	6/77 9/77	IGT
LBL Interim & Final Reports	4/77 7/77	LBL

Report Description	Due Date	Contractor
Phase Ib Final Report	8/77	MM
Phase I Final Report	4/77	CES

The following programs are scheduled for formal review:

Program	Date	Contractor
Thermochemical Energy Storage by Reversible Ammoniated Salts	4/77	MM
H_2SO_4 Chemical Energy Storage	5/77	RRC
One Substrate Solvate Energy Carrier System for Storage of Solar Thermal Energy	8/77	EIC

Program Administration (WBS 1.3)

The five-year TEST program chart will be updated and submitted to the ERDA TES Program Manager in August, 1977.

Procurement (WBS 1.4)

The following contracts will be awarded:

Program	Anticipated Award Date	Contractor
MeOH-based Heat Pump Storage*	4/77	EIC
SO_2/SO_3 Catalyst Development*	4/77	RRC
Aquifier Characterization (Supports the H_2SO_4 program)	5/77	LBL
Ammonium Hydrogen Sulfate Decomposition**	5/77	UH
Heat Pipe/Solar Interface**	5/77	UH
The Chemical Heat Pump: A Simple Means to Conserve Energy*	5/77	CES
Thermal Decomposition Studies*	6/77	UCD
Extended Storage for Solar Power	7/77	RRC
Benzene/Cyclohexane Heat Pipe	9/77	GE/CRD

*Procurement has been initiated

**Procurement and funding from ERDA/Solar

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