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ADVANCED THERMAL-ENERGY-STORAGE CONCEPT-DEFINITION STUDY
FOR SOLAR BRAYTON POWER PLANTS

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Final Technical Report

Volume I

MASTER

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Prepared for

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ABSTRACT

This report presents the detailed results of a technical and economic assessment of phase change and thermochemical energy storage systems in a solar power plant employing a high temperature Brayton cycle thermal engine with helium as the heat transport fluid. The assessment included an examination of the storage system operation, efficiency, power plant interaction, design, materials, safety, maintenance, environmental impact, system life, and economics. These considerations are implemented in the conceptual design of three baseline storage systems and their components for use in a solar power plant module of 50 megawatt electrical power output. Rationale is provided to support the configuration, operation and material choices. A preliminary assessment of the technology development and experimental test program requirements are also included.

This report is an account of work sponsored by ERDA under contract EY-76-C-03-1300. The work is the second part of a two part cooperative EPRI/ERDA research program. The EPRI work was completed in June. A report on that effort was released at the conclusion of the first part of the program.

The report is contained in four separate volumes as follows:

- Volume I - Technical Report
- Volume II - Thermal Energy Storage Sizing Computer Program
- Volume III - Thermochemical TES Sizing Computer Program
- Volume IV - Solar Power Plant Operation Analysis Computer Program

The latter three volumes contain technical descriptions and operating instructions for the three computer programs developed as a part of this research program.

FOREWORD

Energy storage serves two major roles in electric power generating systems. One role is that of load leveling for non-uniform utility grid load profiles. The other is that of energy storage for deferred utilization in non-continuous energy sources such as wind power and solar energy. An application of advanced thermal energy storage (TES) systems in the latter role is the subject of this report.

The successful penetration of energy storage into the utility load leveling role is basically an economic and operational flexibility issue. The attractiveness of storage in this role has prompted major sponsoring organizations such as the Electric Power Research Institute (EPRI), the National Science Foundation (NSF), and the Energy Research and Development Administration (ERDA) to explore this potential. Early NSF sponsored system and subsystem technical feasibility studies, and most recently, the joint EPRI/ERDA sponsored Public Service Gas and Electric of New Jersey "Storage Technical and Economic Assessment" study for electric utility applications provide excellent background material for the study being reported here. Similar efforts are required to assess the potential of energy storage in the second role - deferred utilization or more commonly source leveling. ERDA has recently initiated Preliminary conceptual design studies for a 10 MW_e central receiver solar thermal power plant which includes the design and test demonstration of thermal energy storage systems for the steam turbine system.

In December 1974, EPRI awarded Boeing a contract (RP377-1-1) to examine the technical feasibility of a high temperature gas cooled central receiver for solar energy. In August 1975, that study was expanded to include the technical assessment and initial conceptual design of energy storage systems as a part of the overall solar power plant. The results of that study prompted further sponsorship on the part of both EPRI and ERDA. In February 1976, a cooperative EPRI/ERDA research program was initiated to expand the analytical base for high temperature TES concepts, and to enhance the technical base and

conceptual design work of the earlier EPRI study. Two advanced technology TES systems are to be investigated in depth as a part of this research program, and a third near term technology TES system is to be carried along as a "benchmark." The two advanced systems are phase change storage with molten salts and reversible thermochemical reaction energy storage systems. The near term technology TES system is a sensible heat device similar to the "checkerworks" used as air preheaters for blast furnaces in the steel industry.

The information developed through December, 1976, is presented in the four volumes of this ERDA Technical Report. The results of the first part of the research program were reported in June, 1976, in an interim EPRI Technical Report.

ACKNOWLEDGEMENTS

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Section 1.

INTRODUCTION AND SUMMARY

This report presents the results of a technical and economic assessment of phase change and thermochemical energy storage systems in a solar power plant utilizing a high temperature Brayton cycle thermal engine with helium as the heat transport fluid. The report encompasses the work performed for the Energy Research and Development Administration (ERDA) from August, 1976, through December, 1976.

1.1 BACKGROUND

Energy storage for the solar thermal power plant is required for plant control (i.e., thermal buffering) and for source leveling (i.e., capacity displacement). A half hour of direct storage of high temperature thermal energy on the upstream side of the turbine generator at a rating consistent with the full turbine output capability is expected to be sufficient to meet the plant control requirements. On the other hand, source leveling could be carried out on either side of the generator and, on the basis of the results of the Aerospace Corporation "Mission Analysis" studies ⁽¹⁾*, is normally taken as six (6) hours of storage.

A technology survey was conducted as a part of the RP377-1 ⁽²⁾ study in order to establish the available energy storage concepts. The design and development status of various conventional utility storage concepts, and the technology status of high temperature TES systems were reviewed. Although at least two of the conventional utility concepts offer near term technical solutions to the storage problem, thermal energy storage on the upstream end of the generator is still required for plant control. Consequently, an integral TES concept serving the dual role of source leveling and plant control has been selected as the preferred concept. In conclusion, BEC identified three promising TES concepts which are being further investigated and are the subject of this report. These three TES devices include:

---

*References are listed at the end of each section.

1. Sensible Heat (solid media)
2. Latent heat of fusion (inorganic salts)
3. Thermochemical reactions

The latter two devices offer as much as a four-fold increase in specific energy storage capacity over the sensible heat system. However, both will require significant advanced in materials and design technology. On the other hand, the sensible heat concept is near term technology and must therefore be considered "today's" solution to the solar power plant storage requirement.

In all cases, the major technical problems are similar.

1. Design and development time and cost
2. Availability of critical materials
3. Cost of fabrication, assembly, installation and maintenance
4. Safety and environmental considerations
5. Power plant performance and interface implications

To realize the potential economic and performance advantage of the phase change and thermochemical storage concepts, it will be necessary to arrive at practical solutions to each of these technical and economic barriers.

1.2 OBJECTIVES

In early FY 76 a program was undertaken by BEC that has as its long range objectives the development of a practical high temperature thermal energy storage system. A Phase 0 concept definition study supporting these objectives is currently in progress as a program coordination of EPRI and ERDA. The second part of that study, sponsored by ERDA, is the subject of this report. The results of the first part of the study sponsored by EPRI have been reported. (3)

The first part study objectives, established with EPRI at contract initiation, cover storage system conceptual design; consideration of the solar power plant interactions with the storage device; and initial analytical capability development. Specifically, the study was directed to:

- o Establish baseline system and operating requirements for a TES system in a gas cooled solar thermal electric power plant.
- o Provide storage system definition and system performance data for the preferred phase change and thermochemical energy storage system consistent with the above requirements.

- o Develop analytical methods and implementing computer programs for storage system sizing and integral solar power plant/storage system operation analysis.

Under the ERDA portion of the study, the objectives included 1) development of a technology base for the screening and selection of advanced thermal energy storage systems; 2) assessment, by analysis and survey, the technical and economic feasibility of the candidate storage systems; and 3) establishment of a realistic and orderly plan for the development and test verification of the advanced thermal energy storage systems. Requirements for the candidate storage systems were based on applications with the high temperature gas turbine solar thermal power plant concepts. Specifically, the study was directed to:

- o Continue the conceptual design work for the baseline TES systems with emphasis on material selection and other system configuration trades,
- o Extend and expand all three math models as required to support the continuing trade studies,
- o Expand the system level trade studies and comparative economic assessment studies to include broad variations in storage capacity and storage time.
- o Add an in-depth technical assessment task which includes a qualitative evaluation of the environmental, safety, and other operational characteristics of the TES devices.
- o Develop a test plan for an experimental verification program which will demonstrate the technical feasibility of the advanced TES concept alternatives.

1.3 STUDY GROUND RULES

The design requirements and ground rules were compiled at the outset of the study in coordination with EPRI and ERDA. A System Requirements Data Book, available from ERDA, was written and released at the end of the first month of the study. The data book contains a detailed description of the design and operating criteria summarized in the following text as study ground rules. An EPRI defined baseline solar power plant and the results of the EPRI

RP377-1 study⁽²⁾ serve as the principal data source for these criteria.

Two major ground rules have previously been cited in the requirements for direct storage of high temperature thermal energy and the use of a Brayton cycle utilizing helium as the heat transport fluid. Other initial ground rules include:

1. Size the storage unit to produce 50 MW_e at the generator for six hours duration.
2. Utilize high-temperature materials consistent with the state-of-the-art.
3. Design for 30-year life in accordance with standard power plant subsystem design codes.
4. Design the storage device and associated subsystems consistent with the operating pressure ($3.45 \times 10^6 \text{ N/m}^2 = 500 \text{ psi}$) and design temperature ($816^\circ\text{C} = 1500^\circ\text{F}$) of the solar power plant.
5. Size the storage unit for integral operations in the solar power plant thermodynamic loop as described in detail in Section 2.0 of Volume IV.
6. Size the helium heat exchanger in the TES device to a 4% pressure drop budget.
7. Design the TES device insulation system to limit heat loss to 2% per day.
8. State all costs in 1975 dollars and include fabrication and installation.

Solar power plant and reflector field descriptions were established as a part of the study ground rules in order to provide a consistent basis for the relative evaluation of storage concepts. The 100 MW_e power plant to be examined consists of 2-50MW_e modules each with six hours of storage. The

basic module consisted of a centrally located 260 meter tower and a collector field with characteristics as described on Figure 1-1.

Reflector field performance characteristics and representative insolation data for the four seasonal extremes were also established as study ground rules. The specific data and the source of that data are discussed in Section 2.0 of Volume IV. Data were also extracted directly from the RP377 program to describe the turbine generator and the gas cooled receiver performance. Finally, guidelines were established for the cost accounts for the 100 MW_e rated power plant. Figure 1-2 shows these cost accounts with baseline storage system costs.

1.4 SUMMARY OF RESULTS

Preliminary results show that direct storage of high temperature thermal energy for the gas cooled solar power plant is technically feasible with near term sensible heat TES technology. Two advanced TES concepts (i.e., phase change, and thermochemical) have also been assessed for this application. Although technology development favors the sensible heat device, cost considerations favor the phase change device and operational flexibility and cost favor the thermochemical system. Each concept, its operation, and the major technical considerations are summarized in this section.

Three major mathematical models (i.e., computer programs) have been successfully developed to support the technical and economic assessment objectives of the program. Several trade studies have been carried out using these computer programs. The results show, as expected, a significant interaction between the operating characteristic of the solar power plant and the storage device design.

100 MWe Plant

2 Modules
6 Hours storage

Characteristics

Tower height	260m
Collector area	0.5 km ² /module
Area utilization	38.6%
Total land area	1.3 km ² /module
No. of collectors	15,400/module
Size of collectors	32.4m ²

Figure 1-1. Plant/Field Concept

Collector area (km ²) 2 modules	1.0
Storage time (hour)	6
Account	
Land	2
Structures and facilities	44
Heliostats*	600
Central receiver/tower/heat exchanger	209
Storage/tanks**	180
Boiler plant (hybrid only)	0
Turbine plant equipment	119
Electric plant equipment	20
Misc plant equipment	28
Allowance for cooling towers	15
Total direct cost	1,217
Contingency and spare parts allowance (5%)	61
Indirect costs (10%)	122
Total capital investment (1975)	1,400
Interest during construction (15%)	210
Total cost at year of commercial operation	1,600

* Collector cost \$60/m²

** Storage cost \$30/kWh (actual TBD)

Figure 1-2. 100 MWe Solar Power Plant Cost Accounts (\$/kW)

1.4.1 Storage Concepts

Sensible Heat Concept. The preferred sensible heat storage system concept is summarized in Figure 1-3. A cascade manifold system distributes helium to three checkerwork containers. Magnesia firebrick has been selected for the checkerwork media because of its high temperature thermal and structural characteristics. Each heater is approximately 44 meters long, 6.2 meters in diameter, and contains over nine million kg of Magnesia brick. The major barrier in the sensible heat concept is the design, cost, and construction of the high pressure insulated checkerwork containment vessels.

Phase Change Concept. Figure 1-4 illustrates the phase change TES concept. Manifolds distribute the helium into approximately 26,250 straight superalloy tubes 1.0 cm in diameter and approximately 11.6 meters long. The salt is contained in a bath which immerses the 26,250 vertical tubes. A fluoride salt eutectic, $7 \text{ CaF}_2/54\text{KF}/39\text{NaF}$, has been selected as the preferred fusible salt media principally because of its acceptable economics combined with its potential for corrosion control. The container currently envisioned as the most economical solution is a buried insulated square concrete vessel. The insulation is lined with superalloy sheeting to avoid intimate contact between the salt and the insulation material, and a sealed truss supported, vapor relieved cover is used to separate the salt bath from the free environment.

Thermochemical Storage Concept. The reversible thermochemical decomposition and recombination of sulfur trioxide (SO_3) has been selected as the preferred thermochemical reaction for the high temperature solar power plant application. This particular reaction is catalytically controlled and most of the reaction constituents are stored at near ambient conditions as a liquid. A scale model of the storage system has been built and is shown with a quarter section of the base of the central tower in Figure 1-5. The integral reactor/helium heat exchanger is the key component in the system. Helium is distributed under control of the power plant to the reactor heat exchanger where reaction constituents are circulated at rates consistent with the heat exchange and temperature swing requirements. Products of the reaction are separated and stored in their respective storage containers for later use in the reverse reaction.

- Magnesia (Mg O) Brick Checkerwork
- Temperature Swing = 264°C (475°F)
- Critical Technical Problems
  - Brick Erosion
  - He Stream Contamination
  - Large Insulated Pressure Vessels

Figure 1-3. Sensible Heat Storage Concept

- Fusible Fluoride Salt Bath
- Temperature Swing 267°C (480°F)
- Key Thermophysical Data
  - $T_{\text{melt}} = 640^{\circ}\text{C}$
  - $\rho C_p = 0.672 \text{ cal/cm}^3\text{-}^{\circ}\text{C}$
  - $h_f = 143 \text{ cal/g}$
  - $k = 0.0103 \text{ cal/sec-cm}^{\circ}\text{C}$
  - Cost = 0.97\$/kg
- Critical Technical Problems
  - Material Compatibility

Figure 1-4. Phase Change Storage Concept

Figure 1-5. RCR Storage Model

The SO_3 reaction involves processes which are used commercially in the sulfuric acid industry and are also being considered by other investigators for storage and transport of heat ⁽⁴⁾ and for the production of hydrogen ⁽⁵⁾. Material compatibility is certainly a critical technical issue. The SO_3 dissociation reactor is also a new device and will require a significant development effort. Low cost catalysts to meet the temperature and pressure requirements associated with the high temperature solar application is also a critical technical issue. BEC and Rocket Research are confident that practical low cost catalysts for this application can be developed with an aggressive catalysts development program.

1.4.2 Storage/Solar Plant Integration and Performance

Figure 1-6 illustrates the approach to be used to integrate the thermal energy storage system into the thermodynamic loop of the solar power plant. This particular approach is used in view of the thermal behavior of the proposed TES devices and was selected on the basis of overall plant performance. During periods of high insolation, energy input to the helium stream in excess of that required to drive the turbine is used to charge storage. The high temperature gas flow from the receiver is transported in part to the turbine to meet the plant demand output and in part to a separate fluid circuit which includes the storage device and a high temperature helium pump. During periods of reduced or no insolation, thermal energy is withdrawn from storage to supplement the receiver input or to replace the receiver as a heat source in the absence of insolation.

Yearly average plant operation data for the baseline plant configuration with the three TES device alternatives are shown in Figure 1-7. These data, as indicated in the figure, are based on the 1.0 km^2 field and a plant capacity of 100 MW_e with 2 - 50 MW_e modules. The analysis shows, as expected, that the sensible heat storage device gives the best energy throughput for the power plant. This is a direct result of the round trip efficiency of the storage device. The phase change storage media is a fluoride salt with a melt temperature approximately 25% from the high end of the temperature swing of the receiver at its design point operation. A simple segregation of the molten salt heater with two or three properly selected melt temperatures will significantly improve the round trip efficiency of the phase change system.

State Point	Temp (°C)	Press (MN/m ²)
1	49	1.80
2	581	3.45
3	816	3.32

Figure 1-6. Storage Plant Schematic

	Overall Plant Conversion Efficiency (%)	Storage Round Trip Efficiency (%)	Peak Parasitic Power	Seasonally Adjusted Gross Capacity Factor (%)
Sensible Heat Concept	16.9	77.0	30.5	61.3
Phase Change Concept	15.9	64.8	24.3	61.3
Thermochemical Concept	16.2	68.5	24.0	53.6

- ④ Strawman field = 1.0 km²
- ④ Inyokern, California
- ④ Storage = 6 hours
- ④ Plant capacity = 100 MW_e (2 modules)

FIGURE 1-7 STORAGE/PLANT PERFORMANCE SUMMARY
(YEARLY AVERAGE DATA)

The sensible heat and phase change concepts are both designed to make use of the full turbine inlet temperature range capability. Consequently, both systems imply sufficient helium inventory capability to cover a demand range of 100% over nominal. The thermochemical system is designed to produce helium temperatures during discharge equal to the normal design point temperature of 816°C. In this case the helium inventory swing is approximately 50% over nominal which is just sufficient to handle the increased parasitic power load of the chemical process equipment during the charge cycle. This difference in helium inventory requirement is significant and represents a cost savings in the power plant for the thermochemical storage system that should be included in the overall system comparisons.

The data in Figure 1-7 show that the storage concept effects the performance of the solar power plant. There are also cost differences among the storage devices. Consequently, an evaluation of the total system cost per unit of throughput energy is required in the final system selection. Initial studies of this type have been carried out and the results are summarized in the following section.

1.4.3 Costs

Storage system costs for the 50 MW_e 6-hour discharge requirement have been estimated at 8-13 million dollars. Estimated costs by subsystem account are shown in Figure 1-8 for each of the preferred storage budget. This particular account includes the high temperature pump, flow control valves, filters, sensors, and helium flow lines from the downcomer to the riser. The remaining accounts in Figure 1-8 are related to the storage device itself. All costs are stated in 1975 dollars.

These costs are included in the total solar power plant cost account structure given earlier in Figure 1-2. The resultant plant capital costs are then combined with the energy throughput data summarized in the preceding paragraph to compute cost per unit electrical output (i.e., busbar energy cost) shown in Figure 1-9.

Account	Thermochemical	Phase Change	Sensible Heat
Storage media	.5	2.0	3.0
Storage container(s)	1.8	0.3	13.0
Reactor	4.9	-	-
Heat exchanger			
Tubes	-	3.1	-
Construction		0.3	0.5
Misc. plant equip.	3.4		
He circ. system	1.1	1.4	1.3
Total system	11.7	7.1	17.8

FIGURE 1-8 STORAGE SYSTEM COST SUMMARY
(MILLIONS OF DOLLARS)

	Storage Capital Cost*		Plant Cost (\$/kW)	Busbar Energy Cost (\$/kWh)
	(\$/kW)	(\$/kWh)		
Sensible Heat Concept	42	52.1	1841	63.0
Phase Change Concept	50	15.2	1558	54.4
Thermochemical Concept	217	7.8	1719	61.0

- Inyokern, California
- Strawman field = 1.0 km²
- Storage = 6 hours
- Plant capacity = 100 MW_e (2 modules)
- Seasonal average

*Storage capital cost = \$/kW + \$/kWh * hours

FIGURE 1-9 ENERGY COST COMPARISONS

1.4.4 Technology Development

The three major math models developed during this initial study period represent a significant analytical capability for the study of TES requirements and performance in a solar power plant. The two storage device sizing programs, one for the phase change concept and the other for the thermochemical concept, are capable of providing consistent trade study data representing a wide variety of design alternatives.

The plant performance program reported here is a complete revision of a similar computer program developed during the RP377-1 study program. Consequently, it is a second generation computer program and is significantly more mature than either of the other two. All three programs have been exercised in an extensive series of trade studies that are presented in this report.

System math models of the type reported here are essential to an integrated understanding of storage system application and design alternatives. In general, these models are less sophisticated tools than those generally required to support detailed system design studies and experimental data analysis studies. Advanced heat transfer and other subsystem design programs are required to support such studies. These kinds of tools are also essential to a complete understanding of the dominant heat transfer mechanism and other key technical issues.

Virtually every critical technical issue identified in the study of the three storage systems reported here involves materials or device behavior. Significant materials and device level research, supported by high reliability experimental data, are required in all cases. Many of the critical issues will involve some kind of accelerated life cycle testing which require an early test program commitment.

1.5 REPORT ORGANIZATION

Sections of this interim technical report are organized in response to the study objectives summarized at the end of Section 1.1. The basic operating requirements established in coordination with ERDA and a summary of the study

results have been included in this section. Sections 2.0, 3.0, and 4.0 define the preliminary storage concepts for each of the three TES devices included in the study. The storage/power plant integration approach currently envisioned for the high temperature solar power plant is presented in Section 5.0. Section 6.0 includes a summary description of the three major computer programs, while Section 7.0 summarizes the Phase I program plan. Finally, Section 8.0 presents the conclusions drawn from the results of the study to date.

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Section 2.

SENSIBLE HEAT CONCEPT

This section presents the results of the conceptual design of a sensible heat thermal energy storage system. The design described here is representative of a state-of-the-art high temperature thermal energy storage system. Included in this section are TES media constituent selection rationale, sensitivity and trade study results, design description, materials compatibility and availability, systems costs, critical technical problems, safety, maintenance, and ecological considerations, and related experience.

2.1 SENSIBLE HEAT STORAGE MEDIA CONSTITUENT SELECTION

The selection of a material for use in a sensible heat TES device is design dependent and must be based on a careful evaluation of the factors listed in Figure 2-1. Magnesia refractories have been chosen as the storage media for this study. The details of the design decision are presented in Reference (1). MgO brick was chosen over other refractories because of its high temperature thermal and structural characteristics. This choice has been confirmed by discussions with refractory manufacturers (see Related Experience, Section 2.8). Recently, there has been interest in evaluating cast iron bricks contained in prestressed cast iron pressure vessels as high temperature thermal storage devices⁽²⁾. A trade study between the MgO and cast iron concepts was conducted, and the results are presented in Section 2.2.

- o Maximize
  - o Heat capacity
  - o Density
  - o Thermal conductivity
- o Minimize
  - o Corrosivity
  - o Vapor pressure
  - o Thermal decomposition
  - o Cost
- o Working experience with media
- o Available in large quantities
- o Phase change transformations out of operating temperature range

Figure 2-1. Considerations for Selecting
Sensible Heat TES Media

2.2 SENSITIVITY/TRADE STUDIES

Preliminary trade studies have been carried out as part of the initial evaluation of the TES concept alternatives. The specific studies included in this task were selected on the basis of their significance to the solar power plant performance and to the design of the storage devices. The studies are grouped into areas of storage system operating condition trades and storage system configuration trades.

This section presents the results of initial trade studies for the sensible heat TES concept. The results reported here are initial conclusions which are indicative of the kinds of design decisions to be made.

2.2.1 Operating Condition Trades

The operating parameters included in this group of trade studies for the sensible heat device are (1) heat exchanger effectiveness; (2) storage media mass; (3) pressure loss criterion; (4) heat loss criterion, and (5) storage media thermal conductivity.

Heat Exchanger Effectiveness and Storage Media Mass

The heat exchanger effectiveness is expressed as,

$$\epsilon = \frac{T_E - T_I}{T_M - T_I} = 1 - e^{-NTU} \quad (1)$$

where NTU - the number of thermal units - is given by,

$$NTU = \frac{UA}{\dot{m}C_p} \quad (2)$$

Equation (1) shows that heat exchanger effectiveness is directly related to the number of thermal units in the heat exchanger. NTU is affected by the unit thermal conductance (changing tube spacing, TES media thermal conductivity), the heat transfer surface area (long tubes, larger number of tubes, larger diameter tubes), the helium mass flow, and the working fluid heat capacity. Many of these parameters and the heat exchanger effectiveness itself are directly related to the

operation of the TES derived in the solar power plant. This relationship was evaluated by a series of TES performance studies using the plant operation computer program described in Section 6.0. The results of that trade study are presented in the following paragraphs.

The TES performance data presented below are based on the following plant and TES device operating characteristics.

- o Summer insolation
- o Turbine generator - baseline performance (See Section 1.2)
- o Heat loss criterion, 2% = 18 MW_th/day
- o Pressure loss criterion, 4% in storage device
3% in receiver
- o Pinch point temperature limit, 111°C (200°F)
- o System pressure ratio criterion (helium inventory ratio), 2.0
- o Sensible heat storage media - MgO brick
- o Number of thermal units in TES heat exchanger, 2-10

For the purpose of this trade study, the initial condition of the storage device is taken as a neutral thermocline. With the constraints defined above, the plant operation computer program was used to develop trade study data showing the effects of initial storage temperature, mass of storage media, and number of thermal units in the storage device.

For an assumed value of initial storage system temperature and a given mass of storage media, the plant operation program estimates the daily solar plant performance as a function of the NTU-value.

Figure 2-2 shows an example of trade study data for an initial storage temperature, $T_{wo} = 513^{\circ}\text{C}$ (955°F). These data are used to determine the sensible heat storage media mass required to meet the storage design requirement of 6 hours as a function of the heat exchanger size - NTU. The desired NTU is determined by considering the variation of the minimum turbine inlet temperature (i.e., the minimum TES system exit temperature) and system pressure ratio with NTU and initial storage temperature for the fixed storage times. Figure 2-3 shows those results in terms of the minimum turbine inlet temperature as a function of NTU for various initial storage temperatures. The intersections of the design system pressure ratio of 2.0 and the initial storage temperature curves give the required NTU. These

Figure 2-2. Sensible Heat System Performance

Figure 2-3. Sensible Heat Discharge Limits

NTU values correspond to specific media mass requirements as shown in Figure 2-1. Figure 2-4 shows the final results in terms of storage media mass as a function NTU for a system pressure ratio of 2.0. The specific design points shown in Table 2-1 for the sensible heat TES device were selected from these data.

Table 2-1 includes additional data from the plant operation results required to define the design point operating conditions. These data are used in the TES system sizing program to produce design data and cost estimates for each of the three design points. In an initial costing of the sensible heat device, it was determined that the vessel container cost account value by far dominates the total device cost. Therefore, choosing the design point with the largest energy density, i.e. lowest required media mass, will produce the lowest TES device cost. Table 2-1 shows for design point ③ (NTU = 10.63) the media mass is lowest. In principle, the required media mass could be decreased further with increased NTU-values, however this results in unpractical construction requirements, i.e., very small flow channels. The data presented in Section 2.2.2 for the sensible heat system configuration trades are based on design point ③ conditions.

Pressure Loss Criterion

A decrease in the pressure loss criterion will decrease the gas circulation pump size thereby decreasing this component of the system cost. However, a smaller pressure drop implies larger diameter flow channels which increases the void fraction (the ratio of flow channel volume to storage media volume). The increased void fraction requires an increase in vessel length to contain the required storage media mass. This increased vessel length increases the pressure vessel costs.

A trade study for design point ③ from Table 2-1 and for three vessels was performed considering the effects of changes in the pressure loss criterion. The results are presented in Figure 2-5. As can be seen, the gas pump component cost does decrease with decreasing pressure loss, however the increasing pressure vessel cost is more dominant, and the net effect on the total storage system cost is an increase with decreasing pressure loss. The baseline pressure loss value of 4% is seen to be favorable, whereas, losses on the order of 1-2% are seen to substantially increase the total system cost.

Also shown in Figure 2-5 is the effect of pressure loss criteria on flow channel diameter, d_H , flow channel half spacing, δ , vessel length, L , and gas pump

Figure 2-4. Sensible Heat Design Requirements

Table 2-1.
SENSIBLE HEAT DESIGN POINTS

	1	2	3
Heat exchanger NTU-value	5.00	7.88	10.63
Media mass (10^6 kg)	11.73	10.06	9.45
Initial storage temperature	533°C (990°F)	519°C (965°F)	513°C (955°F)
Temperature swing of media	219°C (395°F)	250°C (450°F)	264°C (475°F)
Average turbine efficiency	0.372	0.380	0.383
Design mass flowrate (kg/sec)	198	200	202
Minimum turbine inlet temperature	594°C (1,100°F)	594°C (1,100°F)	594°C (1,100°F)
Discharge power (MW_e)	50	50	50
Storage time (hours)	6	6	6
Pinch point mass flowrate (kg/sec)	146	151	145
Pinch point temperature difference	111°C (200°F)	111°C (200°F)	111°C (200°F)

Figure 2-5. Sensible Heat TES Pressure Loss Criterion Trade Study Results

size W_c . As can be seen, the channel diameter increases dramatically with decreasing pressure drop causing a lesser increase in vessel length.

Heat Loss Criterion

The heat loss criterion has an important effect on storage system cost. The lower the heat loss rate, the larger the interior insulation thickness required to maintain the vessel metal wall below 260°C (500°F). This results in an increase in pressure vessel length and cost to contain the required media mass.

A trade on the effects of heat loss rate on design point (3) with three tanks is shown in Figure 2-6. As can be seen, heat losses less than 2% result in substantial increases in insulation thickness. This effect results in dramatic increases in insulation, pressure vessel and total system cost. Since an increase in heat loss rate above 2% has an increasingly adverse effect on the storage system round trip efficiency, the baseline heat loss criterion of 2% is seen to be the most favorable combination storage cost and round trip efficiency.

Storage Media Thermal Conductivity

The effects of storage media thermal conductivity on design point (3) are shown in Figure 2-7. As can be seen, a change in media thermal conductivity from 5.0 to 0.5 $\text{W/m} - ^{\circ}\text{C}$ results in a substantial increase in system cost. However, an increase in thermal conductivity from 5.0 to 30.0 $\text{W/m} - ^{\circ}\text{C}$ has a very small effect on storage system cost. Also shown in Figure 2-7 is the relative values of thermal conductivity for NaOH, MgO and Cast Iron. Assuming all other factors are the same, e.g., storage media cost, density, heat capacity, etc., the results from Figure 2-7 show that on a thermal conductivity effect basis, using NaOH would tend to increase system cost over the baseline design whereas using cast iron will have a relatively small effect.

2.2.2 System Configuration Trades

The configuration parameters included in this set of trade studies for the sensible heat TES device include (1) pressure vessel wall thickness; (2) number of vessels; and (3) heat exchanger effectiveness (i.e., heat exchanger size). Also presented is a comparison between the baseline magnesite brick conceptual design and an alternative cast iron brick/pre-stressed cast iron pressure vessel conceptual design.

Figure 2-6. Sensible Heat TES Heat Loss Criterion Trade Study Results

Figure 2-7. Sensible Heat TES Storage Media Thermal Conductivity Trade Study Results

Vessel Wall Thickness and Number of Vessels

In the initial costing of the sensible heat TES device it was determined that a single pressure vessel designed to contain the storage media was either very large in length to diameter ratio (L/D) or the vessel wall thickness was beyond the present capability of field welding practice. Consequently a multiple vessel approach was adopted. The following trade study was made to determine the desired number of tanks.

The maximum vessel wall thickness that can be field fabricated is in the range of 7.62-12.7 cm (3-5 inches). For an internal pressure of 3.45 MN/m^2 (500 psi), ASME Boiler and Pressure Vessel Code, Section VIII, Division II relates the vessel wall thickness to the vessel diameter. By assuming the total storage media mass remains constant and is contained in the cylindrical portion of each tank, Figure 2-8 shows the variation in L/D for each vessel as a function of vessel wall thickness for 2, 3, and 4 tank TES device designs. Assuming design point ③ conditions, the effect of vessel wall thickness and vessel number on storage systems cost accounts is shown in Figure 2-9.

As can be seen, the pressure vessel cost account dominates the total system cost value. Each pressure vessel cost curve shows a broad minimum in the range of 7.62-8.89 cm (3.0 - 3.5 inches). The two vessel design is seen to produce the lowest system cost; however, the difference between the minimum cost values for the two and three vessel designs is well within the error bands associated with the cost estimates. The baseline design point choice is influenced not only by cost but also by operational flexibility and the length to diameter considerations. Based on these concerns, a baseline design point of three vessels with 7.62 cm (3.0 in.) vessel wall thickness was chosen. The three vessel design affords the operational flexibility of isolating one vessel for routine maintenance without shutdown of the entire storage system. The three vessel approach allows the use of lower length to diameter ratios implying a more compact system. Additional details of the baseline design point are described in Section 2.3.

Heat Exchanger Effectiveness

As was discussed in Section 2.2.1, it is expected that the largest heat exchanger, i.e., highest NTU value, will produce the highest energy density and the lowest system cost. To demonstrate this fact, the baseline design configuration was

Figure 2-8. Sensible Heat TES Multiple Vessel Sizing (MgO Storage Media)

Figure 2-9. Sensible Heat TES Multiple Vessel Systems Costs (MgO Storage Media)

sized for each of the three design points identified in Table 2-1. The resulting effects on the storage system cost accounts and required media mass are shown in Table 2-2. As can be seen, the larger NTU value makes more effective utilization of the storage media thereby requiring less media to store the required thermal energy. This in turn requires smaller pressure vessels and yields lower costs. This trend can be in principle extended to even larger NTU values, however, this requires more and smaller flow channels spaced closer together. This implies a smaller hydraulic diameter, d_H , for the flow channel. Assuming the flow channels are made of bricks with a height b , then the flow channel width c would be related to the hydraulic diameter by

$$\begin{aligned} d_H &= \frac{4 \times \text{crosssectional flow area}}{\text{Perimeter}} \\ &= 4 \times \frac{bc}{2(b+c)} \end{aligned}$$

Or

$$c = \frac{d_H b}{2b - d_H}$$

This implies for small values of d_H , c is approximately given by

$$c \approx \frac{d_H}{2}$$

For hydraulic diameters less than 3 cm, i.e., $c = 1.5$ cm, the problem of laying bricks accurately spaced becomes increasingly difficult. For this reason, NTU values larger than 10.63 were not investigated.

Cast Iron and Magnesia Comparison

During a recent discussion with a firm specializing in prestressed cast iron pressure vessels⁽²⁾, a suggestion was made to consider cast iron bricks as a possible thermal energy storage media contained in prestressed cast iron pressure vessels. Cast iron was used successfully in the past by a number of industries, e.g., glass manufacturers, as an energy storage medium up to temperatures of 900°C. As requirements for the glass furnaces exceeded this level, the cast iron was replaced with refractory materials such as magnesia. However, since the maximum temperature expected in the sensible heat TES system is 816°C (1500°F)

Table 2-2
EFFECT OF HEAT EXCHANGER NTU-VALUE ON
SENSIBLE HEAT TES BASELINE DESIGN

	DESIGN POINT		
	①	②	③
NTU	5.00	7.88	10.63
Required Media Mass (Mkg)	11.73	10.06	9.45
TES Media Cost (M\$)	3.75	3.22	3.02
Diffuser Cost (M\$)	0.25	0.26	0.26
Pressure Vessel Cost (M\$)	15.06	12.69	11.94
Brick Installation Cost (M\$)	0.66	0.56	0.53
Manifold Cost (M\$)	0.80	0.80	0.80
Gas Circulation System Cost (M\$)	1.29	1.31	1.28
Total System Cost (M\$)	21.89	18.84	17.84

cast iron may be applicable. Table 2-3 shows a comparison of properties for cast iron and magnesia brick (98% MgO manufactured by Kaiser Refractories). Cast iron demonstrates superior values of thermal conductivity and density implying smaller pressure vessels. Magnesia demonstrates a higher heat capacity and a lower cost. Also shown for an assumed temperature difference of 264°C is a comparison of the two medias on a capacity (energy per unit cost), density (energy per unit mass) and volume (energy per unit volume) basis. Magnesia is significantly higher on a storage capacity basis whereas cast iron is significantly higher on a storage volume basis. These trends indicate that the trade between magnesia and cast iron will involve lower storage media costs on one hand and lower pressure vessel costs on the other.

The TES system sizing program was used to develop a set of data for cast iron comparable to that presented for magnesia in Figures 2-8 and 2-9. The results for cast iron are shown in Figures 2-10 and 2-11. As can be seen, a cast iron media requires smaller pressure vessels and a reduced pressure vessel cost. However, the media cost is significantly increased so that the net effect is very similar total system costs for the two medias. Table 2-4 shows a comparison of the cost accounts for both medias for a 3 vessel, 7.62 cm vessel wall thickness conceptual design. The magnesia system is seen to have more expensive pressure vessels while the cast iron design requires more expensive media. The total cost favors the cast iron design slightly. These comparisons were made assuming all unit costs except storage media cost remained the same. There is some uncertainty in the value to be assumed for the prestressed cast iron pressure vessel unit cost. Should the unit cost value be discovered to be significantly different from the unit cost assumed for the welded steel pressure vessel (\$6.30/kg), then the cost comparison would become very different. At this time, there seems to be no clear cut reasoning for adopting the cast iron concept over the magnesia brick. The recent working experience with magnesia lends more reliability to the magnesia approach. The cast iron concept should be retained as an alternative until additional technical assessment can be performed to validate the potentials of this concept.

2.3 DESIGN DESCRIPTION

2.3.1 Conceptual Drawings

The conceptual design is based on the operating requirements listed in Section 1.2. The sensible heat TES system designed to meet the operating requirements

Table 2-3
COMPARISON OF PROPERTIES FOR CAST IRON
AND MAGNESIA BRICK

	<u>Cast Iron</u>	<u>Magnesia Brick</u>
Cost (\$/kg)	0.66	0.32
Thermal Conductivity (W/m-°C)	29.30	5.07
Heat Capacity (J/kg-°C)	837.00	1130.00
Linear Expansion	1.10%	1.09%
Density (kg/m ³)	7900.00	3000.00
For a $\Delta T = 264^{\circ}\text{C}$		
• Storage Capacity (kJ/\$)	334.8	932.2
• Storage Density (kJ/g)	220.9	298.3
• Storage Volume (MJ/m ³ m)	1746.0	894.9

Figure 2-10. Sensible Heat TES Multiple Vessel Sizing (Cast Iron Storage Media)

Figure 2-11. Sensible Heat TES Multiple Vessel Systems Costs (Cast Iron Storage Media)

Table 2-4

TES SYSTEM COMPARISON

	<u>Magnesia Brick</u>	<u>% of System Cost</u>	<u>Cast Iron</u>	<u>% of System Cost</u>
Required Storage Media Mass (Mkg)	9.45		12.76	
Media Cost (M\$)	3.02	16.9	8.42	49.6
Diffuser Cost (M\$)	0.26	1.5	0.29	1.7
Pressure Vessel Cost (M\$)	11.94	66.9	5.93	34.9
Brick Installation Cost (M\$)	0.53	3.0	0.27	1.6
Manifold Cost (M\$)	0.80	4.5	0.80	4.7
Gas Circulation System Cost (M\$)	<u>1.28</u>	<u>7.2</u>	<u>1.28</u>	<u>7.5</u>
Total System Cost (M\$)	17.84	100.0	16.99	100.0

is shown in Figure 2-12 and described in Table 2-5. The refractory brick is contained in three horizontally placed, insulated cylindrical pressure vessels (6.2 meters inside diameter x 44.2 meter length). The helium flow is distributed and collected to each vessel by an interior insulated cold steel manifold system. Valving allows each vessel to be isolated from the system for periodic routine maintenance. Allowance for thermal expansion is made by the use of expansion joints in manifold flow lines. The tank supports contain one fixed and three floating supports to allow for tank expansion/contraction. An overhead catwalk is included to provide access to two portals contained on each tank.

Details of a storage tank are also shown in Figure 2.12. Flow is distributed in each vessel by a packed bed of 1.9 cm (0.75 in.) diameter MgO refractory spheres. These are very similar to those used in the pebble bed heater described in Section 2.4.4. These pebbles are contained in the hemispherical domes of each vessel, and grates are used to assure the pebbles will not fall through the flow channels contained in the magnesia brick checkerwork. The inlet grating is inset a small amount to allow the working fluid to expand to a lower velocity before impinging the refractory pebbles. It is expected that the decreased velocity will eliminate any spalling of the pebbles. The pebbles will also contribute to the amount of stored energy for each vessel; however, this contribution has been ignored for this present design.

Two types of MgO bricks are shown -- a "standard" brick arrangement and a specialty brick arrangement. The standard brick concept uses 7.62 x 7.62 x 24.13 cm (3 x 3 x 9.5 in.) rectangular bricks individually placed so that 2.05 cm (0.81 in.) wide flow channels are contained. This 2.05 cm x 7.62 cm flow channel has a hydraulic diameter of 9.20 cm (3.62 in.). The specialty brick is a hexagonally shaped brick (Freyn type) with the flow channels contained at the desired spacing. The hexagonal shape can be a more easily laid, and interlocking can be provided to stop movement or ratcheting of the bricks. Both brick concepts can be made with a fine grain MgO to minimize brick erosion. However, the specialty brick will require an increase in the unit cost of the storage media to account for the increased fabrication costs. The exact magnitude of the increased cost has not as yet been determined, although it would be expected that for the number of bricks envisioned (1-2 million) the increase would be small. Because of the uncertainty in the specialty brick unit cost, the baseline conceptual design has assumed the "standard" brick approach.

STORAGE LIMITS		
	CHARGE	DISCHARGE
WORKING FLUID MAXIMUM MASS FLOW (kg/sec)	145	202
MAXIMUM INLET TEMPERATURE ($^{\circ}C$)	816	551
MINIMUM INLET TEMPERATURE ($^{\circ}C$)	816	432
MAXIMUM OUTLET TEMPERATURE ($^{\circ}C$)	705	816
MINIMUM OUTLET TEMPERATURE ($^{\circ}C$)	432	554

MATERIALS	
SENSIBLE HEAT STORAGE MATERIAL	98% U_2O_3 REFRACTORY BRICK
DIFFUSER	98% U_2O_3 REFRACTORY PEBBLES 1.9 cm DIA (15 IN)
VESSEL OUTER WALL	ASTM A516 GRADE 70 CARBON STEEL
INSULATION VESSEL-INTERNAL, END AND WALLS, FLOOR, VESSEL AND PIPING-EXTERNAL	KAOWOOL BLOCK, MINERAL WOOL BLOCK, KAOWOOL BLANKET

Table 2-5.
SENSIBLE HEAT TES CONCEPTUAL DESIGN SUMMARY

Number of cylindrical pressure tanks	3
Vessel diameter	6.22m (20.41 ft)
Vessel length	44.16m (144.88 ft)
L/D	7.10
Insulation thickness	19.9 cm (7.83 in)
Metal wall thickness	7.62 cm (3.0 in)
Flow channel number	3,457
Channel hydraulic diameter	3.23 cm (1.27 in)
Centerline to centerline channel spacing	9.20 cm (3.62 in)
Heat exchanger NTU-value	10.63
Required storage media mass	9.45 Mkg (20.8 Mlbm)
Material choices: TES media Diffuser Insulation Vessel outer wall	98% MgO refractory brick 1.9 cm (0.75 in) dia MgO refractory Kaowool ASTM A516 (grade 70) carbon steel

The brick is surrounded with a layer of insulation. Kaowool^R block is used on the bottom third of each tank to support the brick checkerwork because of its load bearing characteristics. Because of its lower cost, mineral wool is used in the remaining areas where loading stresses are much smaller. The insulation thickness was sized to allow a 2% maximum heat loss and maintain the carbon steel vessel at 260°C (500°F). The vessel wall is made of 7.6 centimeter carbon steel (ASTM 516). The vessel is designed in accordance with the ASME Boiler and Pressure Vessel Code, Section VIII, Division II. The thickness of material is consistent with field shop welding practices.⁽³⁾ The design wall thickness and vessel diameter allow the use of three vessels, each with a length to diameter ratio of about 7.10 to contain the required volume of solid thermal storage media.

The helium circulation system consists of a compressor sized to recoup the 7% pressure drop through the receiver plus the TES system while maintaining the design mass flow-rate. Also included in the circulation system is a filter or settling tank to remove any particles that may erode from the brick.

2.3.2 Systems Cost Summary

The systems costs for the baseline sensible heat TES conceptual design are presented in Figure 2-13. The refractory brick material cost is based on manufacturers' estimates. The assembly costs of the bricks into a heat exchanger form are listed in a separate account. The costs are based on data gained from 1976 Means

ACCOUNT	QUANTITY	UNIT COST	TOTAL COST (M\$)
BRICK (MgO)	9.45 Mkg	0.32 \$/kg	3.02
REFRACTORY DIFFUSER	0.79 Mkg	0.33 \$/kg	0.26
STORAGE CONTAINERS (3) (34 ATMS, 6.2 x 42.2 m)	1.7 Mkg	6.30 \$/kg	10.83
INSULATION	9.8×10^4 kg	11.30 \$/kg	1.11
HEAT EXCHANGER FABRICATION*	1.6×10^6 BRICKS	0.33 \$/BRICK	0.53
MANIFOLD	0.10 Mkg	7.70 \$/kg	0.80
HELIUM CIRCULATION SYSTEM	23.6 MW (PUMPING CAPACITY)	54,249 \$/MW	1.28
TOTAL SYSTEM			17.84

ESTIMATED SYSTEM MASS: 10×10^6 kg

*BRICK CONSTRUCTION COST 450 BRICKS PER
MAN-DAY/\$150 PER MAN-DAY

Figure 2-13. Sensible Heat TES Cost Summary

Cost Data Handbook for firebrick installation and from estimates from checkerwork contractors. The unit cost for the storage vessel is based on estimates given by Chicago Bridge and Iron for vessel dimensions of the design used. The helium circulation system costs were estimated by scaling up existing compressor costs to the power rating required.⁽⁴⁾

The costs listed in Figure 2-13 are revisions of costs presented at the end of the EPRI portion of the study⁽¹⁾. The revisions reflect the information gained under the technical assessment task of the present study. Included in this technical assessment are detail design calculations incorporated directly into the TES storage system sizing program. This allowed increased accuracy in estimating systems costs. Also revised was the brick installation unit cost. This reflects an increase in the number of bricks per man-day estimate but also an increase in the cost per man-day.

An additional cost account was added to reflect the cost of manifolding the three vessels together. The unit cost was estimated by assuming an interior insulated carbon steel wall piping system similar to that proposed for the riser and down-comer from the solar thermal power plant tower.

2.4 TECHNICAL ASSESSMENT

Additional information not related to systems costs was gathered under the technical assessment task accomplished under the present study. The results of this task are grouped into areas of materials compatibility, critical technical problems, safety, maintenance and ecological considerations and related experience.

2.4.1 Materials Compatibility

The main concern in the area of materials compatibility for the sensible heat TES conceptual design is the possibility of brick erosion and the subsequent contamination of the helium stream. By careful design of the manifold, it is expected that the helium flow velocity through each channel in the refractory will be low enough to minimize any brick erosion. The relatively high resistance to spalling exhibited by the MgO bricks minimizes this materials problem. Another materials problem could be introduced by thermal cycling stresses inherent in such a TES system. Again, the high strength of the MgO brick would alleviate this problem.

2.4.2 Critical Technical Problems

The main technical problem involved with this conceptual design is to ensure that the helium stream does not become contaminated with brick particles. The detailed design of the manifolds dictates a careful reduction of the inlet flow velocity to levels that will not induce brick erosion. This can be accomplished by inserting the diffuser refractory grate just inside the inlet to the vessel. This will allow the flow to expand to a lower velocity before impinging on the diffuser media. A filter system will be necessary to ensure particles do not enter and contaminate the compressor system.

2.4.3 Safety, Maintenance, and Ecological Considerations

Other areas that require consideration in the sensible heat TES conceptual design have been identified. The chief safety concern is the design of a pressure vessel for use at the expected temperature levels. Strict adherence to pressure vessel construction codes will be required to avoid this problem. The high temperature levels require that non-flammable materials be used in the construction and insulation of the container vessel. By using a solid media for thermal storage, there are no ecological hazards that could be released in the event of a leak in the container vessel. However, the specifics of a particular location and a particular design must be considered before a definitive statement on the ecological impact of a sensible heat TES system can be made.

In the area of maintenance, continuous monitoring of the system performance will be required. Also, periodic inspections for leaks or possible failures are needed. Continuous monitoring of the helium flow will allow the detection of any contaminating brick particles. The modular tank approach allows the shut-down of a portion of the system for repair or refurbishment at selected times during the lifetime of the TES system, with only a nominal reduction in storage system capacity.

2.4.4 Related Experience

The choice of a solid sensible heat storage media and the overall technical feasibility of a sensible heat TES device of the size envisioned in this study were the subjects of a discussion held with representatives of Kaiser Refractories. The choice of a high magnesia brick was verified. Specialty bricks with fine grain

MgO are available to reduce spalling concerns. It is also feasible to manufacture hexagonal interlocking MgO bricks with properly sized and spaced flow channels. The trade between increased brick costs and reduced brick installation costs remains to be made. The overall sensible heat TES device concept is not unlike installations in the glass and steel industries. In these installations high magnesia brick is used as a thermal energy storage media in what are essentially high temperature regenerative heat exchangers. The considerable working experience with these installations indicates that, while spalling of the flow channels is a concern, the present sensible heat TES concept is within current technology capability.

Boeing has operated a refractory/pressure vessel as an air preheating system for wind tunnel testing since 1964. The system consists of a packed bed of Al_2O_3 spheres contained in a 1.5 m ID x 4.6 m (5 ft. ID x 15 ft) steel tank lined with layers of insulating firebrick. Figure 2-14 shows a schematic of the heater. The tank shell is ASME code rated for $10.4 \times 10^6 \text{ N/m}^2$ (1500 psi) and 344°C (650°F). The heater is presently operated at maximum pressures of $9 \times 10^6 \text{ N/m}^2$ (1300 psi) and over a temperature range of 816°C – 1372°C (1500°F – 2500°F).

The alumina is contained in a 0.7 m x 2.9 m (28 in x 114 in) central core. The bed is comprised of 0.95 cm (0.375 in) diameter pebbles with a layer of 2.54 cm (1 in.) diameter pebbles on top and bottom to serve as diffusers for the gas flow and to restrain pebble movement. A super alloy grate supports the pebble bed.

A vertical flow arrangement is used. During the firing cycle, combustion products from a natural gas burner enter the top of the bed charging the storage media. The lower temperature combustion gases are exhausted to the atmosphere at the base. A water spray is used to cool the Hastelloy grate during charging of the bed. Figure 2-15 shows thermocline development in the packed bed during a typical charging cycle.

During discharge of the bed, high pressure air enters the bottom of the bed, flows upward and exits a side port into the wind tunnel plenum. Figure 2-16 shows the variation between pebble surface temperature and wind tunnel plenum stagnation temperature during a typical test. The test cycle is only a few minutes in duration and the two temperatures remain very nearly constant during this period. Losses due to the water cooled plenum and by-pass of air through the refractory brick insulation account for the difference between the

- Operational Since 1964
- Maximum Flow = 4.5 kg/sec (10 lb/sec)

Figure 2-14. Pebble Bed Heater Schematic

Figure 2-15. Thermocline Development in Packed Bed Heater During Charging Cycle

Figure 2-16. Typical Packed Bed Heater Performance Data During Discharge Cycle.

pebble bed surface temperature and the plenum stagnation temperature. During the discharge time, the pebble bed is transferring heat to the air at a rate of approximately 8 MW_{th} . The pebble bed contains approximately 0.1% of the volume of storage media contained in each of the three vessels of the sensible heat TES conceptual design described in this report.

Considerable experience has been gained on performance, heat transfer and refractory erosion as a function of temperature, mass flowrate and time through operation of this system. Although the pebble bed heater charge to discharge time ratio is several orders of magnitude larger than that envisioned for the sensible heat TES conceptual design, the technology is directly applicable in the development of system designs for this and subsequent studies. The long term operational status of the pebble bed heater is evidence that refractory TES is state-of-the-art.

As a result of the initial discussion with the West German pre-stressed cast iron specialists, Siempelkamp Giesserei K.G.⁽²⁾, a further technical interchange was made. Design requirements and operating conditions characteristic of the baseline sensible heat TES conceptual design were sent. Based on that data and Siempelkamp's own experience, cost estimates and conceptual design data comparing the welded steel and pre-stressed cast iron vessels and magnesia brick and cast iron brick medias were made. This data is presented in Appendix I.

2.5 REFERENCES FOR SECTION 2

1. Boeing Engineering and Construction, "Technical and Economic Assessment of Phase Change and Thermochemical Advanced Thermal Energy Storage (TES) Systems," RP-788, December, 1976.
2. Private communication with Mr. B. Beine, Siempelkamp Giesserei K.G., West Germany, October, 1976.
3. Private communication with Chicago Bridge and Iron
4. Boeing coordination sheet, "Turbomachinery Costs," K-6161-GLV-079

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Section 3

PHASE CHANGE TES SYSTEM

This section presents the results of the conceptual design of a phase change thermal energy storage system. Included in this section are TES media constituent selection rationale: sensitivity and trade study results; design and description; material compatibility and availability; systems costs; phase change thermal analysis; critical technical problems; and safety, maintenance and ecological considerations.

3.1 PHASE CHANGE STORAGE MEDIA CONSTITUENT SELECTION

The selection of a salt, or a salt mixture, for a particular application is design dependent and must be based on a careful evaluation of a number of technical and economic factors. Figure 3-1 presents a list of the considerations determined to be most important for selection of a phase change media. The first three main categories list the media thermophysical and cost properties. These properties largely determine the performance of the TES device. Since the TES device must meet a certain set of performance requirements, e.g., see Section 1.2, these three media selection considerations constitute an initial screening of the various media available. The remaining considerations when used in concert with the first three allow a second level media screening.

Based on these considerations, the salt type selected for phase change designs is the fluoride eutectics. Additional details of the salt type selection process is presented in Reference (1). It was concluded that fluoride salts are abundant and are characteristically higher than the other salts, and many melt temperatures fall in the 600°C - 800°C (1111°F - 1471°F) range. Fluorides have the highest heats of fusion and high thermal conductivities. Calculations made under this study have demonstrated that fluorides can meet the desired performance requirements. Based largely on data taken for the ORNL Molten Salt Reactor program, more reliable thermophysical data are available for fluorides than for other classes of salts. Working experience with molten fluorides is considerable. Fluorides have been shown to be compatible in actual long-term system testing with metals that exhibit good mechanical properties at 800°C (1471°F) and 3.45 MN/m^2 (500 psi); however, system testing of candidate metals

- Maximize values of:
  - Heat of Fusion
  - Heat capacity
  - Density
  - Thermal conductivity
- Minimize:
  - Vapor pressure
  - Thermal decomposition
  - Corrosion of vessel and tubing
  - Cost
- Melt temperature in desirable range
- Confidence level of thermophysical data and working experience with salt
- Available in large quantities
- Nonequilibrium thermodynamic effects (e.g., supercooling)
- Effect on environment
  - Toxicity
  - Physical hazard from contamination of salt

Figure 3-1. Considerations for Selecting Salt Mixture Type

at the 800°C and 3.45 MN/m² levels is required to establish materials compatibility. Pumps, valves, and field testing data on molten fluoride systems exist as part of the ORNL Molten Salt Reactor Program.

At the present, the primary source of fluoride salts is fluorspar or fluorite (CaF₂) which is mined and is available in large quantities. Fluorspar is decomposed with hydrogen to produce hydrogen fluoride which is then recombined with virtually any base metal combination to yield a wide variety of fluoride salts. The base metal, therefore, dominates the availability and thermophysical properties of the resultant salt. Mixtures of various salts provide a wide variation in cost, melt temperature and heat of fusion. The data from Reference (2) indicate a substantial reduction in current market price of the constituent fluoride salts if fluorosilicic acid (H₂SiF₆) is used as the fluorine source. Basing the cost of H₂SiF₆ on a market price of 0.359 \$/kg (0.163 \$/lbm) and in production quantities of 100 kilotons, Table 3-1 lists the current and projected prices of several constituent fluoride salts. Figure 3-2 shows several candidate fluoride eutectics with costs based on the data of Table 3-1. At the end of the EPRI portion of the study, the baseline fluoride eutectic was 63 NaF/37 ZnF₂. It was determined under the technical assessment task of the ERDA portion of the study that ZnF₂ was too reactive (See Section 3.5.1). Another baseline eutectic was sought. After comparing the properties of several eutectics and determining their projected effect on the system performance, the new choice for the baseline eutectic salt is 7 CaF₂ - 54 KF - 39 NaF. A comparison of thermophysical properties for 7 CaF₂ - 54 KF - 39 NaF and 63 NaF/37 ZnF₂ is shown in Table 3-2. The higher melt temperature for the new baseline eutectic will cause a decrease in storage system round trip efficiency. A trade study was performed to determine the best compromise in storage media mass and system performance. The results are presented in Section 3.2. The remaining thermophysical properties are nearly the same for the two eutectic salts. The 7 CaF₂ - 54 KF - 39 NaF has a significant cost advantage on a per unit mass basis; however, 63 NaF/37 ZnF₂ has an advantage in higher density.

3.2 SENSITIVITY/TRADE STUDIES

This section presents the results of trade study for the phase change TES concept. The studies are grouped into areas of storage system operating condition and configuration trades. The specific studies were selected on the basis of their significance to the solar thermal power plant performance and to the

Table 3-1
CURRENT AND PROJECTED PRICES
OF METAL FLUORIDES

<u>Compound</u>	<u>Current Price (\$/kg)</u>	<u>Projected Price (\$/kg)</u>
NaF	0.730	0.331
KF	1.444	0.573
MgF ₂	0.860-1.700	0.463
CaF ₂	0.117	-
LiF	5.335	2.910
ZnF ₂	35.0	0.926

Table 3-2
COMPARISON OF FLUORIDE EUTECTIC THERMOPHYSICAL PROPERTIES

	<u>7 CaF₂-54 KF-39 NaF</u>	<u>63 NaF/37 ZnF₂</u>
Melt Temperature (°C)	682	640
Cost (\$/kg)	0.45	0.68
Heat of Fusion (cal/g)	133.7	128.82
Heat Capacity (cal/g-°C)		
Solid	0.277	0.204
Liquid	0.314	0.224
Thermal Conductivity (W/m-°C)*	4.5	4.3
Density (kg/m ³)	1993.	2339.

*estimated values

<u>MELT</u>	<u>SALT (MOLE PERCENT)</u>	<u>T_{melt} (°C)</u>	<u>h_f (cal/g)</u>	<u>Cost (\$/kg)</u>	<u>h_f/cost (kcal/\$)</u>
1	67 LiF/33MgF ₂	746	217	1.58	137.3
2	65NaF/23CaF ₂ /12MgF ₂	745	137	0.28	489.3
3	5.6KF/64.4LiF/30MgF ₂	713	212	1.53	138.6
4	40NaF/60KF	710	133	0.49	271.4
5	59KF/34.5NaF/6.5MgF ₂	685	136	0.50	272.0
6	7CaF ₂ /54KF/39NaF	682	134	0.45	297.8
7	60LiF/40NaF	652	190	1.57	121.0
8	46LiF/44NaF/10MgF ₂	632	205	1.19	172.3
9	52LiF/35NaF/13CaF ₂	615	145	1.18	122.9

Figure 3-2 Candidate Fluoride Salts

design of the storage devices. The results reported here are initial conclusions which are indicative of the kind of decisions to be made.

3.2.1 Operating Condition Trades

The operating parameters included in this group of trade studies for the phase change TES device are (1) heat exchanger effectiveness; (2) storage media mass; (3) pinch point temperature limit; (4) storage media thermal conductivity; (5) pressure loss criterion, and (6) heat loss criterion. Because of the importance of their interaction, the first three parameters must be considered together, whereas, the last three can be treated more independently.

Heat Exchanger Effectiveness, Storage Media Mass, and Pinch Point Temperature Limit

In a fashion analagous to the sensible heat TES device, a series of design points were established for the phase change device using the 7 CaF₂ - 54 KF - 39 NaF eutectic. After an initial investigation, it became apparent that because of the high melt temperature (682°C = 1259°F) and the assumed pinch point temperature limit of 111°C (200°F), considerably more media mass would be required to meet the charge condition requirements. Therefore, in investigating the heat exchanger effectiveness relationship with storage media mass, the pinch point temperature limit value was also considered.

Figure 3-3 shows system performance data for an initial storage temperature of 532°C (990°F) and a pinch point temperature difference of 83.3°C (150°F). Figure 3-4 shows the discharge limits in terms of minimum turbine inlet temperature as a function on NTU for various initial storage temperatures and pinch point temperature limits. Figure 3-5 shows the final results in terms of phase change salt mass as a function of NTU for system pressure ratios of 1.8 and 2.0 for pinch point temperature limits of 83.3°C (150°F), 97.2°C (175°F) and 111°C (200°F). The indicated design points selected from these data for subsequent use in the configuration trades (Section 3.2.2) are shown in Table 3-3. As is shown in Figure 3-5, the pinch point temperature limit value has a significant effect on the required amount of storage media mass and subsequently on system cost.

Figure 3-3. Phase Change TES System Performance

Figure 3-4. Phase Change TES Discharge Limits

Figure 3-5. Phase Change TES Design Requirements

Table 3-3

PHASE CHANGE DESIGN POINTS

	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪
Heat exchanger NTU-value	3.75	4.55	8.25	5.00	6.85	3.90	4.75	6.20	5.10	7.15	5.00
Media mass (Mkg)	4.51	3.95	3.39	4.10	3.65	6.60	5.28	4.38	5.64	4.29	8.15
Initial storage temperature ($^{\circ}\text{C}$)	532	504	477	532	504	532	504	491	532	504	504
Temperature swing of media ($^{\circ}\text{C}$)	222	259	310	231	273	185	227	261	197	218	194
Effective heat of fusion (10^5 J/kg)	4.347	4.579	5.021	4.533	4.835	2.650	3.138	3.812	3.092	3.882	1.650
Average turbine efficiency	0.341	0.355	0.365	0.359	0.363	0.338	0.350	0.356	0.352	0.367	0.338
3-6 Design mass flowrate (kg/sec)	197	197	197	177	177	197	197	197	177	177	197
Minimum turbine inlet temperature ($^{\circ}\text{C}$)	593	593	593	616	616	593	593	593	616	616	593
Discharge power (MW_e)	50	50	50	50	50	50	50	50	50	50	50
Storage time (hr.)	6	6	6	6	6	6	6	6	6	6	6
Pinch point mass flowrate (kg/sec)	173	173	173	173	173	163	163	163	163	163	150
Pinch point temperature difference ($^{\circ}\text{C}$)	83.3	83.3	83.3	83.3	83.3	97.2	97.2	97.2	97.2	97.2	111
System inventory ratio	2.0	2.0	2.0	1.8	1.8	2.0	2.0	2.0	1.8	1.8	2.0
Average heater temperature ($^{\circ}\text{C}$)	513	513	513	533	533	513	513	513	533	533	513

Storage Media Thermal Conductivity

The value of the phase change eutectic thermal conductivity is the least well defined media property. There is a great paucity of thermal conductivity data on not only fluorides but all inorganic salts. This is caused in part by the difficulty of accurately measuring the thermal conductivity at high temperatures while accounting for the thermal radiation and convective effects within the molten salt. There is also some concern that differences in thermal conductivity between the solid and molten salt will significantly affect the sizing of the TES device heat exchanger. While significant differences in thermal conductivity between solid and liquid salt components may exist for certain types of salts, it is not clear at all that this is the situation for fluoride eutectics. Data from Reference (3) indicate that only a 4% difference in thermal conductivity exists between the solid and liquid components of the eutectic 46.5 LiF - 11.5 NaF - 42 KF. This trend is consistent with information gathered from the personnel at ORNL and Philips Labs. Because of these findings, the thermal sizing of the phase change TES device has proceeded assuming an "average" thermal conductivity estimated from values for the constituent fluoride salts.

A trade study was performed to explore the sensitivity of the storage system costs to the value assumed for the phase change media thermal conductivity. The study was performed assuming design point (1) conditions from Table 3-3. The results of the study are presented in Figure 3-6. As can be seen, the systems costs are extremely sensitive to the value of media thermal conductivity. Although relatively small gains are made by increases in thermal conductivity over the baseline salt value of $4.5 \text{ W/m} \cdot ^\circ\text{C}$, lowering the thermal conductivity by an order of magnitude is seen to nearly triple the total system cost. This increase is caused by the requirement of more heat transfer surface area to deposit/retrieve energy into the media at the rates desired. This results in larger numbers of tubes spaced closer together which is seen to raise all costs associated with the tube-in-bath heat exchanger. These effects demonstrate the necessity of determining accurate thermal conductivity measurements on candidate phase change salts.

Finally, it is important to note that the above thermal conductivity trade has been made off one design point, i.e., an $\text{NTU} = 3.75$. If a phase change storage media with low thermal conductivity was being used, it is possible that an even lower NTU value (i.e., smaller heat exchanger) would be chosen. To make this design decision would involve a trade between heat exchanger size (NTU value)

Figure 3-6. Phase Change Media Thermal Conductivity Trade Study Results

and media mass as demonstrated earlier in this section and later in Section 3.2.2 under system configuration trades. The result of such a trade may be a system cost penalty from thermal conductivity considerations less than that indicated in Figure 3-6.

Pressure Loss Criterion

As was the case for the sensible heat TES device, a lower pressure drop criterion will decrease the gas circulation pump size thereby decreasing the cost component of the total storage system. However, the larger heat exchanger tubes implied by a lower pressure drop criterion necessarily increases the heat exchanger cost. A trade study was performed assuming design point (1) conditions to determine the effects of pressure loss criterion on total storage system costs. The results of the study are presented in Table 3-4. A very small difference between the total costs is noted for value of pressure loss from 1% to 4%. This results from the cancelling effect of gas pump costs and heat exchanger costs. Table 3-4 also shows that the baseline 4% pressure loss criterion is a reasonable compromise in heat exchanger and gas pump costs.

Heat Loss Criterion

The heat loss criterion has a less serious impact on the phase change TES design as compared to the sensible heat TES device. The heat loss is regulated by the thickness of insulating brick between the vessel liner and the vessel reinforced concrete wall. Increasing the insulation thickness of the vessel is decoupled from the sizing calculations which assume a given inside vessel dimension. A trade study was performed to explore the effect of the assumed heat loss criterion on the container costs via the insulation. The results of the trade study are shown in Table 3-5. Although the insulation mass increases dramatically from 4% to 1% heat loss, its effect on the total container cost and subsequently on the total system cost is minimal.

3.2.2 System Configuration Trades

The type of configuration trades considered for the phase change TES device are (1) vessel cross section shape; (2) tubing spacing pattern; (3) vessel characteristic dimension; (4) heat exchanger effectiveness; (5) pinch point temperature difference; and (6) discharge rate and storage time. The first two trades were considered in Reference 1 and will not be repeated here. The results of those trades indicate a square vessel cross section and a square tubing spacing pattern is preferred. The trades presented in this section assume this configuration.

Table 3-4
PRESSURE LOSS CRITERION TRADE
STUDY RESULTS

Pressure Loss Criterion	1%	2%	3%	4%	5%	6%
Gas Pump Size (MW)	16.41	20.58	24.66	28.84	33.04	37.23
Gas Pump Cost (M\$)	1.03	1.18	1.31	1.44	1.57	1.68
Heat Exchanger Cost (M\$)	3.61	3.40	3.32	3.26	3.25	3.23
Total System Cost (M\$)	7.02	6.95	7.00	7.08	7.18	7.28

Table 3-5
HEAT LOSS CRITERION TRADE
STUDY RESULTS

Heat Loss Criterion	1%	2%	3%	4%
Average Heat Loss Rate (MW)	0.375	0.75	1.125	1.50
Insulation Mass (Mkg)	0.348	0.168	0.111	0.082
Container Cost (M\$)	0.41	0.34	0.31	0.29
Total System Cost (M\$)	7.17	7.08	7.05	7.04

Vessel Characteristic Dimension

The phase change design point list shown in Table 3-5 includes the data from the plant operation results required to define a set of consistent operating conditions. These data were used in the phase change sizing program to produce design data and cost estimates for each of the design points. The key physical parameter in the phase change sizing program is the characteristic vessel dimension D . Figure 3-7 shows for design point (1) the variation in TES costs as a function of the characteristic dimension D for a square vessel cross section. The costs presented assume the vessel container design consists of a reinforced concrete wall refractory brick insulation, metal liner, and a truss roof. The heat exchange tubes were placed on a square spacing pattern.

Changes in D produce significant changes in components costs. As D increases, the number of tubes that can be placed in the vessel increases. This provides more flow area and allows a decrease in tubing diameter and wall thickness for a given pressure drop criterion. These effects are recognized in the heat exchanger tubing costs. The increasing tube number is reflected in increased tubing fabrication costs. A decreasing tube diameter and wall thickness yield a decreasing tubing metal cost with increasing vessel dimension. The cost of welding the tubes to provide the desired heat exchanger length is dependent on the longest tubing length manufactured H_t . The number of welds is given by

$$n_w = n_t \cdot \text{Integer} \left(\frac{H}{H_t} \right)$$

The number of welds required increases with the tube number. However, as D increases, a smaller vessel height H is required to contain the same salt volume. Points are reached where the height is an exact multiple of H_t . The weld number drops as each of these points is passed. This behavior is represented in the step function behavior of the tubing welding cost. As the vessel height H passes an exact multiple of H_t , the welding cost drops appropriately, e.g., in going from $H = 4 H_t$ to $3 H_t$ the welding cost drops by $\frac{1}{4}$. After the step behavior, the welding cost continues to rise reflecting the increasing number of tubes with increasing vessel dimension D . The step function behavior is also evident in the total system cost shown in Figure 3-7.

The manifold costs shown in Figure 3-6 were estimated from a point design for a manifold system. Included were costs for welding, tubing fabrication and tubing metal.

Figure 3-7. Phase Change TES Configuration Synthesis

Heat Exchanger Effectiveness

The total system cost curve shows a minimum point of 7.03 M\$ at about $D = 13.7$ m. Similar other minimum points exist for design points (2) - (11). Plotting these minimum cost points against NTU-value allows a representation of the effect of heat exchanger effectiveness on TES costs. These data are presented in Figure 3-8. The quantity of TES media decreases as the thermal size of the heat exchanger increases. This demonstrates the media is being used more effectively with a larger heat exchanger. The increasing NTU-value requires more heat exchanger surface area causing tubing costs to increase.

Pinch Point Temperature Differences

The effect of variations in pinch point temperature difference on storage costs are shown in Figure 3-9. This figure displays the data from the minimum cost points for design points (2), (7) and (11). Table 3-3 shows that these three design points have a common initial storage temperature of 504°C , system inventory ratio of 2.0 and a nearly constant NTU-value (4.55-5.00).

As can be seen from both Table 3-3 and Figure 3-9, the amount of media mass required is significantly affected by the pinch point temperature difference. This is caused by the relationship between the salt melt temperature, the pinch point temperature and the amount of energy stored in the media as latent heat versus sensible heat. This relationship can be displayed by the representation shown in Figure 3-10. This figure represents the time variation of the outlet fluid temperature of a phase change TES device for a charging cycle assuming a constant inlet fluid temperature and mass flowrate and a uniform initial device temperature. The outlet temperature for two salts with differing melt temperatures are shown. Also given are three pinch point temperature differences. As the charging cycle begins, the outlet temperature rises rapidly to the salt melt temperature. The energy is deposited as sensible heat. As a considerable portion of the salt becomes temperature remains constant at the salt melt temperature with energy deposited as latent heat of fusion. The outlet temperature again begins to rise as energy is again deposited as sensible heat. As a considerable portion of the salt becomes molten, the outlet temperature begins to rise rapidly. Eventually, the outlet temperature passes through the pinch point temperature which is defined as the device inlet temperature less the pinch point temperature difference. Since the

Figure 3-8. Phase Change TES NTU Selection

Figure 3-9. Phase Change TES Pinch Point Effects

Figure 3-10. Phase Change TES Device Characteristic Thermal Behavior

charge rate of the TES device is proportional to the working fluid mass flowrate times the difference in inlet and outlet temperature, maintaining a constant charge rate of energy into storage would require an ever-increasing mass flowrate as the outlet temperature approaches the inlet temperature. The increasing mass flowrate increases friction losses and gas pump requirements. The pinch point temperature represents the desirable upper limit in charge mass flowrate. However, the selection of the pinch point temperature cannot be made without due consideration of the salt melt temperature. For a salt melt temperature considerably lower than the pinch point temperature, e.g., salt 1 in Figure 3-10, a considerable portion, i.e., 70-80% of the total energy deposited in storage is deposited as latent heat of fusion. This implies that the energy density advantage of a phase change media is being fully exploited. For a salt with a high melting temperature, e.g., salt 2 of Figure 3-10, considerably less of the total energy deposited is deposited as latent heat when the lower pinch point temperature is reached. This implies that to store the same thermal energy much more media mass is required, i.e., the device functions more as a sensible heat device and less as a phase change device. This significant increase in mass results in a high media cost increase. Figures 3-5 and 3-9 and Table 3-3 demonstrates that a reduction in pinch point temperature difference, i.e., an increase in pinch point temperature, significantly decreases the required media mass through an increase in the effective heat of fusion. Figure 3-5 shows that a significant advantage in required media mass is obtained through a reduction of pinch point temperature difference, ΔT_{pp} , from 111°C (200°F) to 97.2°C (175°F). A much less advantage is gained by going to $\Delta T_{pp} = 83.3^{\circ}\text{C}$ (150°F). This implies that at $\Delta T_{pp} = 83.3^{\circ}\text{C}$ (150°F), the portion of energy stored as latent heat is again in the 70-80% range.

The above discussion demonstrates that the selection of pinch point temperature limit involves a careful compromise between the salt media mass and the mass flowrate. Because of the large cost advantage gained, the baseline pinch point temperature difference for the $7\text{CaF}_2 - 54\text{KF} - 39\text{NaF}$ eutectic salt has been decreased to $\Delta T_{pp} = 83.3^{\circ}\text{C}$ (150°F).

Consideration of both heat exchanger effectiveness (NTU-value) and pinch point temperature difference, ΔT_{pp} , allows the selection of design point ① from Table 3-3 as the baseline design point for the phase change device using the $7\text{CaF}_2 - 54\text{KF} - 39\text{NaF}$ eutectic. The design details of the phase change baseline conceptual TES device are shown in Section 3.3.

Discharge Rate and Storage Time

A trade study was performed to explore the sensitivity of the phase change storage system capital energy costs expressed in \$/kW as a function of storage time, t , and discharge power level, P_D .

Figure 3-11 shows the results of the trade study. The capital cost is seen to increase nearly linearly with storage time for power levels of 5, 50, and 100 MW_e . The nearly equal slope for each power level indicates the costs related to the storage system energy (\$/kWh) remain relatively insensitive to power level. The costs related to storage capacity (\$/kW), i.e., the intercept of each power storage system capital cost curve, are seen to be a function of the power level. For the baseline TES value of $t = 6h$ and $P_D = 50 MW_e$, the energy cost was found to be 15.2 \$/kWh and the capacity cost was 50 \$/kW. The phase change storage system capital cost was assumed to be given by

$$\text{capital cost} = 50 + 15.2 t$$

The results of this trade study serve as input to the power plant economics studies described in Section 5.

3.3 DESIGN DESCRIPTION

3.3.1 Conceptual Drawings

The conceptual design is based on the operating requirements listed in Section 1.2 and the design point (1) conditions given in Table 3-3. The baseline phase change TES system designed to these requirements and conditions is shown in Figure 3-12 and described in Table 3-6. The phase change material and heat exchanger is contained in a concrete, insulated cubic vessel (14.05 m x 14.05 m x 11.58 m height). The helium flow is dispersed and collected by manifolds into 26244 tubes (1.049 cm outside diameter x 0.070 cm wall) placed vertically on a square spacing pattern (centerline to centerline tube spacing - 8.54 cm). The fluoride eutectic salt is contained as a bath between the helium tubes. The vertical flow arrangement with the hot helium entering the top manifold during charging and the cold helium entering the bottom manifold during discharging will maintain the solidified salt below the liquified portion. This arrangement will assure that the salt will remain in intimate contact with the helium tubes by avoiding the formation of voids during salt solidification. The baseline fluoride eutectic is 7 CaF_2 - 54KF - 39 NaF. Thermophysical data on the eutectic

Figure 3-11. Phase Change TES Point Design Matrix Trade Results

Table 3-6.
PHASE CHANGE TES CONCEPTUAL DESIGN SUMMARY

Vessel cross section shape	Square
Tube spacing pattern	Square
Vessel width, D	14.05m (46.10 ft)
Vessel height, H	11.58m (37.99 ft)
H/D	0.82
Tube number	26,244
Tube outer diameter	1.049 cm (0.413 in)
Centerline to centerline intertube spacing	8.54 cm (3.362 in)
Tube wall thickness	0.070 cm (0.028 in)
Heat exchanger NTU-value	3.75
Unit thermal conductance	386 W/m ² -°C
Required TES media mass	4.508 Mkg (9.94 Mlbm)
Material choices:	
TES media	7CaF ₂ /54KF/39NaF Eutectic salt
Tubing metal	Inconel 617
Vessel outer wall	Reinforced concrete
Insulation	Refractory brick
Liner metal	Hastelloy-N

are given in Table 3-2. Inconel 617 is the present choice for the heat exchanger tubing metal because of demonstrated stress rupture life and because it is also the choice for the receiver heat exchanger system. There is concern that the chromium content of the Inconel 617 will be attacked by the fluoride eutectic. However, the work of Philips Labs in the Aachen, Germany (See Section 3.5.1) indicates the fluoride attack can be controlled by small quantities of elemental aluminum. The container vessel wall has an inner layer of Hastelloy-N, a middle insulating layer of refractory brick, and an outer layer of reinforced concrete. The helium circulation system consists of a compressor sized to recoup the 7% pressure drop through the receiver and the TES system while maintaining the design mass flow rate. Also included in the circulation system is a filter to remove any fluoride that may enter the helium system via a leak.

The conceptual layout of the phase change TES system shown in Figure 3-12 allows the visualization of the scale of the system and the assessment of a number of technical design details that could influence the overall design of the TES device. A number of areas addressed in this study are represented in the drawing. A salt expansion space will allow the TES media to expand and contract without immersing the top manifold. Although not shown explicitly, a vapor relief system in the truss roof will maintain a slight constant inert gas pressure over the salt thereby insuring air and moisture do not enter the container device.

The manifold system for the phase change TES system is complex, and its design certainly affects the whole TES device. The manifold is broken down into several levels of branching; i.e., levels A through G. Interior insulated, cold steel piping will be used for the A through E levels; Inconel 617 will be used for F and G. A thermal barrier will lower heat transfer losses from the top of the hot salt while also allowing the exterior of the cold steel piping to be maintained lower than 260°C (500°F). Expansion joints will be utilized throughout the manifold to reduce the effect of differential thermal expansion. The heat exchanger will be supported both on top and bottom, and will be maintained in slight tension to lessen the tendency of the heat exchanger tubes to deflect into a serpentine shape as the salt melts and solidifies. Access will be maintained to both top and bottom manifolds for inspection and maintenance purposes. The lower manifold will be contained in a chamber beneath the storage vessel. The support for the storage vessel will be provided by post-supported I-beams. Should a leak occur in the portion of the heat exchange immersed by the salt media, the leaking portion can be sealed off at top and bottom. This will require a slight overdesign in the

number of heat exchanger tubes to reflect the estimated loss in heat exchanger tubes by leaking. The most likely place to seal off the leak would be at the E level of the heat exchanger just after it penetrates the lower vessel floor. This will result in the loss of 253 tubes which represents approximately 1% of the total 26,244 tubes.

The choice of the number of heat exchanger tubes to be used requires an interaction between the trade study results and the manifold design. As was shown in Figure 3-7, the minimum cost vessel dimension occurred at $D = 13.7\text{m}$. Because of the square cross-sectional shape of the system and the square tubing spacing pattern, logic would indicate the total number of tubes should be a perfect square. An increase in vessel dimension to $D = 14.05\text{m}$ results in a slight increase in cost but yields 26,244 tubes - $(162)^2$. Detail II and III of Figure 3-12 show full-scale and isometric views of the last branch of the heat exchanger manifold. With the use of numbers of heat exchanger tubes like 26,244, it became apparent that the handling of such number of closely spaced tubes would be cumbersome. The ganging of nine tubes together as shown allows the creation of a more workable unit which could be welded outside the vessel and then dropped into place via a crane. The choice of the 26,244 number is convenient in that 26,244 divided by 9 yields 2,916, which is also a perfect square ($2916 = 54^2$). This process of choosing branching to produce perfect squares is continued through the largest size, $D_A = 1.219\text{m}$ (4 ft.). This approach utilizes the natural geometrical advantage afforded by the square vessel cross section and square tubing spacing.

3.3.2 Cost Summary

The systems costs for the baseline phase change TES conceptual design are presented in Figure 3-13. The fluoride eutectic salt costs are based on the projected costs of the constituent salts given in Table 3-1. These costs are based on using fluorosilic acid (H_2SiF_6) as the fluorine source and in production quantities of 100,000 tons.⁽²⁾ The metal costs were based on 11.02 \$/kg (5.00 \$/lb) of base metal plus 4.92 \$/m (1.50 \$/ft) fabricating costs. The gas circulation systems costs were estimated by scaling up existing compressor costs to the power rating required.⁽⁴⁾ The cost estimate for the Hastelloy N inner liner is 16.53 \$/kg (7.50 \$/lb), for the refractory insulation 0.33 \$/kg (0.15 \$/lb), and for the reinforced concrete poured in place 0.11 \$/kg (0.05 \$/lb or approximately 200 \$/cu yd).

The costs listed in Figure 3-13 are revisions of costs presented at the end of the EPRI portion of the study⁽¹⁾. The revisions reflect the information gained under the technical assessment task of the present study. This technical assessment has included a selection of a new baseline eutectic salt, the incorporation of detail design calculations for the storage vessel container, and a detail manifold design and cost estimate. The costs have been expressed on a per unit mass basis rather than a per unit volume basis as was done in the EPRI study. This is done to facilitate comparison with other energy storage concept designs being developed by other contractors.

Account	Quantity	Unit cost	Total cost (M\$)
Salt (fluoride eutectic)	4.508 Mkg	0.45 \$/kg	2.04
Storage container			
Vessel outer wall	1.167 Mkg	0.11 \$/kg	0.13
Insulation	0.168 Mkg	0.33 \$/kg	0.06
Liner	0.006 Mkg	16.53 \$/kg	0.10
Roof	0.032 Mkg	1.54 \$/kg	0.05
Heat exchanger			
Metal mass	0.054 Mkg	11.02 \$/kg	0.60
Tubing fabrication	3.03 x 10 ⁵ m	4.92 \$/m	1.49
Tubing welding	26,244 welds	12.0 \$/welds	0.31
Manifold			0.86
Gas circulation system	28.8 MWe	50,057 \$/MW	1.44
Total			7.08

Figure 3-13. Phase Change TES Cost Summary

3.4 THERMAL ANALYSIS

Under the technology assessment task the methodology used in the plant operation and TES device sizing models for determining the heat transfer in and out of the phase change storage media was reviewed. The most crucial portion of the calculation used to describe the heat exchanger effectiveness is the unit thermal conductance calculation. As described in Volume II, Section 2.0, the unit thermal conductance is calculated based on a one-dimensional nodal approach. Assumed in this approach is that the thermal conductivity is constant, i.e. that the difference between solid and liquid thermal conductivity is small. Also, the change of phase effects on the unit thermal conductance were assumed to be small variations from the nominal value obtained from the one-dimensional nodal approach.

Significant uncertainty remained in the phase change heater thermal behavior when melting and freezing of the salt occurs. A study of the transient thermal behavior of the phase change TES device was initiated. The purpose of the study is two fold: (1) develop an accurate model of the phase change storage transient thermal behavior; and (2) develop an accurate but simplified algorithm simulating phase change effects for plant operation math models.

3.4.1 Method of Analysis

The methodology used for this study involved the following:

1. Develop a thermal nodal model of the problem.
2. Modify an existing computer program to represent the thermal model.
3. Add additional heat transfer mechanisms not found in the existing program.
4. Include state and temperature dependent properties of salt and working fluid.
5. Compare results between detailed analysis and the transient analysis used in the plant operation program
6. Develop an updated algorithm for the plant operation program.

Thermal Nodal Model

Figure 3-14 shows a portion of the tube-in-bath heat exchanger. Recognizing that an adiabatic surface exists halfway between each tube, the thermal model

Thermal Nodal Model (Cont'd)

was simplified to consider the thermal behavior of a single tube surrounded by an annular ring of salt with a thickness equal to the intertube half spacing, δ . Figure 3-15 shows a section view of the tube and salt. The radial dimension has been nondimensionalized by the parameter $1/2 (d + 2\delta)$, and the tube length direction nondimensionalized by the total length L . The physical system was sectional into an array of discrete volumes, and the mass of each volume element was "lumped" at a point within the volume which it represented. The paths for heat transfer from one node to another were represented by conductors joining the appropriate nodes. The heat exchanger tube and phase change salt were broken into 300 nodes containing ten annular rings and thirty wafers. The dimensions of the 290 salt nodal volumes were chosen so that every node has equal volume. Thirty heat sources incident on the tube wall model the convective heat transfer between the working fluid and the heat exchanger tubing. The boundaries are assumed perfectly insulating. The inlet (always defined as $\delta = 0$) temperature and mass flowrate are assumed to be available and expressed as functions of time. During a change of phase, each salt node must receive or release a quantity of energy equal to its latent heat of fusion. This process was simulated by an energy exchange accounting numerical process. Each node is surveyed to determine if the node is at or undergoing a change of phase. If the node is undergoing a phase change, the accounting system keeps the nodal temperature at the melt temperature until the energy exchange matches the latent heat of fusion.

Computer Program

The thermal nodal model were input into the Boeing Engineering Thermal Analyzer (BETA) computer program. This program solves an electrical analogy network system using an iterative forward differencing numerical method. BETA is a generalized computer program developed for the solution of heat transfer problems. BETA's capabilities include (1) steady-state or transient analysis; (2) arbitrary geometrical shape; (3) heat transfer by conduction, convection and radiation; (4) internal heat generation; and (5) varying physical properties.

Figure 3-14. Phase Change TES
Thermal Model Schematic

Figure 3-15. Thermal Nodal Model

Computer Program (Cont'd)

An existing BETA program was modified to simulate the thermal model. The existing program modeled a cylindrical crystal melting under the action of an external heat source.⁽⁵⁾ As such, a subroutine was available to provide the phase change energy exchange accounting system. By using the same numbering scheme and total number of nodes as the existing thermal model, the existing program was easily modified by redefining the dimensions of the nodes to allow for the heat exchanger tube and gas flow along the centerline of the phase change media and by transferring the energy sources to the tube wall.

Additional Heat Transfer Mechanisms

The convective heat transfer between the gas stream and the tube wall was modeled in the same manner as for the TES sizing math model. The methodology used in determining the convective heat transfer film coefficient is described in Volume II, Section 2. For the preliminary analysis results described in Section 3.4.2, a constant convective heat transfer coefficient was assumed. As the analysis progresses, the film coefficient will be evaluated as a function of the average fluid temperature along the direction of flow.

Other heat transfer mechanisms which may prove to be important include natural convection within the molten salt and radiation heat transfer within the salt. At present, neither mechanism has been included in the thermal model. This is caused in large part by the lack of reliable properties data on eutectic salts, e.g. viscosity, bulk expansion coefficient, and infrared transmission.

It is expected that each of these mechanisms, assuming property data were available, can be modeled by adding an "effective" thermal conductivity to the normal value. If this approach proves invalid, an order of magnitude more complexity is required to accurately model the thermal radiation portion of the heat transfer. It should be noted, however, that both mechanisms, natural convection and radiation, increase the heat transfer rate, i.e. the existing model provides a conservative approach to the heat transfer rates. One of the most important pieces of information to be gained from a device demonstration as described in Section 8.0 is how well the model without natural convection and radiation heat transfer effects can predict the actual experimental results.

Additional Heat Transfer Mechanisms (Cont'd)

If the predictions are successful, the additional complexity caused by the additional heat transfer mechanisms will not be necessary.

State and Temperature Dependent Properties

The important properties of the eutectic salt that may be state or temperature dependent include heat capacity, density and thermal conductivity. The solid salt heat capacity is characteristically linear with temperature. The liquid salt heat capacity is characteristically constant. Most eutectic salts expand 15-20% upon melting so that liquid and solid salt densities are different. The salt thermal conductivity is the least well understood of the salt properties. The data that does exist for fluorides indicates little difference between liquid and solid thermal conductivity.⁽³⁾ However, to establish the effect of such a difference if present, it is desirable to include in the thermal model differing liquid and solid salt thermal conductivities. Temperature dependent properties are straight forward to enter into the model. However, state dependent properties i.e. liquid or solid, require more sophisticated logic. Also, if the state changes are very significant, numerical stability problems may be encountered.

For the preliminary analysis presented in Section 3.4.2, constant properties were assumed. In a later version of the analysis, the state and temperature dependent properties will be incorporated.

The temperature dependence of the working fluid properties affects mainly the convective heat transfer coefficient. As was discussed earlier, the preliminary analysis assumes a constant convective heat transfer coefficient, i.e. constant working fluid properties. In later analyses, the working fluid properties will be reevaluated at each station along the heat exchanger tube and the appropriate convection heat transfer coefficient calculated.

3.4.2 Preliminary Analysis Results

A preliminary version of the phase change transient thermal model was completed. The preliminary model included constant inlet fluid temperatures and mass flowrates, constant convective heat transfer coefficient, constant salt pro-

3.4.2 Preliminary Analysis Results (Cont'd)

perties and uniform initial salt temperatures. The assumed values are given in Table 3-7. The salt properties and device geometry are representative of the baseline phase change TES conceptual design as it existed at the end of the EPRI portion of the study.

As a means of comparison, the transient analysis routine used by the plant operation math model which assumes a constant unit thermal conductance was formed into a separate program. This constant unit thermal conductance routine is described in detail in Appendix I of Volume IV. The routine was used to analyze the same case input listed in Table 3-7.

The overall effects on the heat exchanger performance for the charge and discharge cases are shown in Figures 3-16 and 3-17 respectively. For the charge case, the outlet temperature rises rapidly from the initial salt temperature to the salt melt temperature where it remains for a significant period before again increasing. The charge rate is dependent on the mass flowrate times the difference in inlet and outlet temperatures. Since the mass flowrate is fixed for this case, the charge rate drops to a nearly constant value and then again drops as the outlet temperature again increases. In a real plant operation, the mass flowrate would be increased to maintain the charge rate at the desired level. Both the models predict nearly the same results indicating the approximate 1-D nodal solution does provide essentially the correct performance.

The discharge performance shown in Figure 3-17 shows analogous behavior. Again the outlet temperature remains constant at the salt melt temperature for a considerable portion of the discharge cycle. This also causes the discharge rate to remain fairly constant during this period. Also, the two models give good agreement. This comparison again shows that on a macroscopic basis, the constant unit thermal conductance model gives satisfactory thermal behavior for this case input.

Table 3-7
PHASE CHANGE TES TRANSIENT THERMAL
ANALYSIS PRELIMINARY CASE INPUT

- Charge Case
  - $T_{\text{salt}} = 505^{\circ}\text{C}$
  - Helium inlet temperature = 816°C
  - Helium mass flowrate = 5.8g/sec
- Discharge Case
  - $T_{\text{salt}} = 816^{\circ}\text{C}$
  - Helium inlet temperature = 505°C
  - Helium mass flowrate = 5.8g/sec
- Device Geometry
  - Tube diameter = 0.96cm
  - Tube length = 12m
  - Intertube half spacing = 2.84cm
- Assumed salt properties
  - Salt thermal conductivity = $4.3\text{W/m}^{\circ}\text{C}$
  - Salt heat capacity = $937\text{ J/kg}^{\circ}\text{C}$
  - Salt heat of fusion = 598,000 J/kg
  - Salt melt temperature = 640°C
  - Salt density = $2,339\text{ kg/m}^3$
- Convective heat transfer coefficient = $1905\text{W/m}^2\text{-}^{\circ}\text{C}$

Figure 3-16. Phase Change TES Overall Transient Thermal Behavior (Charge Cycle)

Figure 3-17. Phase Change TES Overall Transient Thermal Behavior (Discharge Cycle)

The instantaneous values of the unit thermal conductance can also be displayed. Choosing 1.2 hours into both the charge and discharge cycles as characteristic of a large segment of each cycle, details of the thermal behavior were investigated. Figure 3-18 shows for the charge case isotherms for the thermal model. As can be seen, the large majority of the thermal gradient along the phase change salt is located between 10% and 50% of the distance down the heat exchanger. Very small temperature differences occur from 0-10% and 50-100% of the heat exchanger length. The melt face is shown where the isotherm equals 640°C. It should be noted that the non-dimensioning of the radial and axial dimensions removes the relative scale between the axial and radial dimensions. In reality the radial dimension is expanded 218 times the axial dimension.

Figure 3-19 shows for the charge condition the source values, adiabatic boundary temperature, tube wall temperature, and fluid temperature as functions of the non-dimensional distance along the heat exchanger tube. This set of curves also demonstrates that the significant heat transfer is occurring over a small region of the tube length. Defining the unit thermal conductance, U , by the source per unit area divided by the temperature difference between the adiabatic boundary and the fluid,

$$U = \frac{S/A}{T_{ADB} - T_f}$$

$$\text{or} \quad UA = \frac{S}{\Delta T}$$

Figure 3-20 shows the value of UA plotted against the non-dimensional tube length, ξ . Also shown is the approximate 1-D nodal solution value assumed in the TES sizing math model and plant operation math model. As can be seen, significant numerical error exists in places where small temperature differences exist. However, the heat transfer accomplished in those regions is small so that the net effect of the numerical error bands on the overall performance is small. The maximum percent difference between the detailed analysis results and the approximate 1-D nodal solution is seen to be 27%. However, the approximate solution is seen to be a fair average of the detailed behavior.

Figure 3-18. Phase Change TES Isotherms
(1.2 Hours into Charge Cycle)

Figure 3-19. Thermal Profile (Charge Cycle) Flow Direction →

Figure 3-20. Unit Thermal Conductance Comparison (Charge Cycle)

In a similar manner, Figure 3-21 shows the source and temperature data for the discharge case. Figure 3-22 shows the UA results and comparisons. As was seen for the charge case, the approximate 1-D nodal solution gives reasonable agreement to the detailed analysis results.

The results of the preliminary analysis indicate that for the case input of Table 3-7, the detailed and approximate 1-D nodal thermal analyses are in good agreement both on the macroscopic and microscopic scales. Using another case input with varying salt and fluid properties and inlet temperature and mass flowrate may significantly change the above conclusion. One of the tasks proposed under Section 8, Phase I Program Plan is to extend the preliminary analysis to investigate the effect of state and temperature dependent properties. If needed, an updated version of the approximate 1-D nodal solution will be sought which will more closely model the expected thermal behavior.

3.5 TECHNICAL ASSESSMENT

Additional information not related to systems costs was gathered under the technical assessment task accomplished under the present study. The results of this task are grouped into areas of materials compatibility and availability, critical technical problems, and safety, maintenance, and ecological considerations.

Figure 3-21. Thermal Profile (Discharge Cycle)

Figure 3-22. Unit Thermal Conductance Comparison (Discharge Cycle)

3.5.1 Materials Compatibility and Availability

The heat exchanger tubing and container wall must be compatible with either helium or air as the working fluid and with the fluoride eutectic salt. The expected temperature range extends from a maximum of 816°C (1500°F) to a minimum of 432°C (810°F). The tubing will encounter internal pressures of 3.45 MN/m^2 (500 psi). The required service life is 30 years. Within these design requirements, the major materials compatibility concern is with possible corrosive action of metal fluoride salts on tubing metal and vessel container wall. Other equally important materials concerns include stress-rupture strength, oxidation resistance, fabricability, repairability, availability, specification control and material cost. The selection of a metal that would meet the compatibility concerns cannot be made without considering the other materials concerns especially creep-rupture and oxidation resistance.

The free energy of formation is commonly used as a figure of merit to measure the stability of a compound. A compound is stable if the free energy is negative, and the stability increases with decreasing free energy. Table 3-8 shows the relative stabilities of a number of metal fluorides. As can be seen, the fluoride eutectic constituent salts, NaF, KF, etc., are more stable than the fluorides of the structural metals, Cr, Fe, Ni & Mo. On this basis, corrosion rates should be low. However, of the structural metals, Cr has the greatest affinity for fluorine. This indicates that metals with nickel and molybdenum are preferred, while the chromium and iron content should be held to a minimum. However, both nickel and molybdenum oxidize rapidly at high temperatures requiring alloying with chromium.

The mechanism of corrosion attack on chromium containing alloys is thought to proceed by the formation of subsurface voids initiated by the oxidation of chromium along exposed surfaces through oxidation - reduction reactions with impurities or constituents of the molten fluoride eutectic. As the surface is depleted in chromium, chromium from the interior diffuses down the concentration gradient toward the surface. The chromium vacancies precipitate to form voids, principally at grain boundaries and impurities. The depth of void formation depends strongly on operating temperature of the system and on the composition of the salt mixture.

Table 3-8

RELATIVE THERMODYNAMIC STABILITIES OF SELECTED
FLUORINE COMPOUNDS

<u>Element</u>	<u>Most Stable Fluorine Compound</u>	<u>Stability</u>	<u>Ref.</u>
Aluminium	AlF_3	268	1
Calcium	CaF_2	250	1
Magnesium	MgF_2	222	1
Lithium	LiF	123	1
Sodium	NaF	112	1
Potassium	KF	110	1
Chromium	CrF_2	72	2
Iron	FeF_2	66	2
Nickel	NiF_2	59	2
Zinc	ZnF_2	59	1
Molybdenum	MoF_2	57	2

- Reference: 1. Bureau of Mines Bulletin 605, 1963, $T=1000^\circ\text{K}$
 2. McCoy, H.E. "The INOR-8 Story", ORNL Review
 V.3, N.2, 1969 p. 35 - 48.

3.5.1 Materials Compatibility and Availability (Cont'd)

Two approaches to control the molten fluoride attack on metal alloys have been identified: (1) develop an alloy with enough Cr to provide oxidation resistance while still not being especially susceptible to fluoride attack; or (2) add inhibiting agents to the salt mixture to eliminate impurities and control corrosion.

The first approach was adopted by the Oak Ridge National Labs for their Molten Salt Reactor Program.⁽⁶⁾ This led to the development of Hastelloy N, a low chromium alloy which exhibits excellent corrosion resistance after lengthy exposure to molten fluoride eutectics at 600⁰-700⁰C temperatures. Hastelloy N was developed with the idea that the alloy base should be nickel, with molybdenum (<20%) for strengthening, and some chromium for oxidation resistance. Figure 3-23 shows for the variation in the rate of oxidation of several 80%Ni-20%Mo alloys with varying Cr content. As can be seen, the oxidation rate decreases sharply at chromium levels of 5 to 7%. 6% chromium was required to obtain an adherent oxide protective layer. Operation of the Molten Salt Reactor Experiment for almost four years showed very low corrosion of the Hastelloy N by molten fluoride eutectics. Corrosion rates on the order of 2×10^{-5} m/yr (0.8 mil/yr) (uniform corrosion) were measured after 3500 hours of testing with the eutectic NaF-NaBF₄ at maximum temperatures of 607⁰C (1124⁰F). The attack from similar mixtures at temperatures as high as 705⁰C (1300⁰F) is barely observable in tests as long as 12,000 hours. Attack was estimated at 0.5 mil/year.⁽⁸⁾

Although specific conclusions on corrosion rates for a specific fluoride eutectic are dangerous to make without experimental data for the eutectic in question, in general, the results gained by ORNL in their Molten Salt Reactor Program indicates that control of fluoride corrosion is feasible at temperature levels approximately 100⁰C less than those envisioned in the present thermal energy storage design. It is known that corrosion attack and oxidation rate are very sensitive to temperature. There is some feeling that the Hastelloy N may not have acceptable corrosion and oxidation resistance at 816⁰C (1500⁰F).⁽⁹⁾

Very little corrosion and oxidation rate data exists on Hastelloy N except for very short exposure times at these temperatures. Additional technical assessment is required in this area. The testing proposed for Phase I Material Compatibility Tests described in Section 8 will address this area.

Figure 3-23. Oxidation Rate of 80%Ni-20%Mo Alloys for Varying Chromium Contents (data from Reference 6).

The second approach to controlling molten fluoride attack by the addition of inhibiting agents was investigated by Philips Labs in Aachen, Germany.⁽¹⁰⁾

Elemental aluminum is used as a getter material for impurities in the salt such as H_2O and $NaOH$. Equilibrium constants with and without aluminum gettering in NaF at $827^{\circ}C$ ($1520^{\circ}F$) were calculated by Philips and are shown in Figure 3-24. As can be seen, the addition of the aluminum is seen to reduce the impurity levels. Corrosion experiments with 0.1-0.2% Al added by weight to $65NaF/23CaF_2/12MgF_2$ contained in No. 321 stainless steel at temperatures of $780^{\circ}C$ ($1435^{\circ}F$) for 14000 hours indicate no corrosion occurring.

The effects of adding aluminum to the salt mixture is demonstrated in Figure 3-25. The top specimen shows the results of testing with aluminum added whereas the bottom specimen demonstrates results without aluminum added. In both cases technical grade (95% pure) salts were used. The top specimen was sealed with air included. The bottom specimen was back filled with argon. The discoloration of the bottom salt is caused by the chromium removal from the wall material. Photomicrographs of the two wall specimens show clear intergranular attack for the bottom sample and no attack at all on the top sample. These data and figures demonstrate that the use of an aluminum inhibiting agent has considerable potential. The exact quantity of aluminum to be added depends upon the impurity level in the salt mixture, more Al required for more impurities.

A preliminary fluoride salt/metal compatibility evaluation has been initiated under BEC's IR&D program. The objective of these tests is to confirm the compatibility of the baseline salt media and heat exchanger metal. Metal coupons of the baseline and alternative metals are exposed to selected molten fluorides. Analysis of salt and metal before and after exposure determines changes. To date the major conclusion is that the zinc component of the $63NaF/37ZnF_2$ eutectic was too reactive and made this fluoride mixture unsatisfactory for use as a TES media. Additional testing with other fluoride mixtures is continuing.

Figure 3-24. Calculated Equilibrium Constants With and Without Aluminum Gettering at 827°C in NaF. (data from Reference 10)

With Al Inhibitor

D4

152x

Without Al Inhibitor

152x

4B

Figure 3-25. Comparison of Fluoride Salt/Metal Compatibility Tests (photo courtesy of Philips Labs, Acchen, Germany)

3.5.1 (Cont'd)

The availability of heat exchanger metal and container structural materials is not of great concern, although a certain amount of lead time is required to produce the quantities needed. The availability of metal fluorides for heat storage applications has been considered in detail in Reference 2. Fluorine occurs widely in nature and more fluorine exists than does chlorine, zinc and copper. The two commercial sources of fluorine are calcium fluoride or fluorspar (CaF_2) and fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$).

The resources of CaF_2 are 86182 Mkg (95 million tons) and represent approximately 11% of world resources. Production of fluorspar has decreased over the last few years indicating production far below capacity. The U.S. government has examined the fluorspar supply carefully because of its strategic importance in the steel, aluminium, oil and nuclear industries. Even though the U.S. currently imports 85% of its CaF_2 (mainly from Mexico), the government has concluded that the economic impact of attempts at cartel-like action would be small because of the large number of CaF_2 sources. Additional details on fluoride availability are contained in Reference 2. Based on the data of that reference, the availability of metal fluorides in the quantities envisioned is certain.

3.5.2 Critical Technical Problems

The main critical technical problem for the phase change TES concept is in the area of materials compatibility. The corrosion data now available indicates that the Inconel 617 will be severely attacked by the molten fluoride unless the Al inhibitor is added to the salt. The results from the Philips Labs indicate considerable potential for this approach. Experimental verification will be necessary to validate the compatibility of Inconel 617 with the 7CaF_2 -54KF-39NaF baseline fluoride eutectic. Use of the alternate tubing metal, Hastelloy-N, will require extrapolation of the corrosion and oxidation rate data now available to the temperature and pressure ranges for the proposed design. Again, experimental investigation will be necessary to validate the Hastelloy N compatibility with the baseline salt.

3.5.3 Safety, Maintenance, and Ecological Considerations

The chief safety concern is the containment of the salt. The safety problems associated with high-temperature thermal-energy storage systems have been reported by the Philips Labs.⁽¹⁰⁾ As explained in that report, the high chemical stability of the fluorides indicates that it is unlikely that reducing reactions would take place if the fluorides were released accidentally. However, because of its high temperature, a leak in the molten salt would pose a fire hazard to any flammable substance it contacts. This will require the use of non-flammable insulation materials. For above-ground construction, a catch basin may become necessary to contain any molten salt release. Below ground storage has safety advantages for this application. Careful consideration for the safety of maintenance personnel must be planned. This will require development of protective clothing and safety procedures to be used in routine maintenance and inspection of the bottom manifold system. Special safety procedures to be used by repair teams for use in the event of minor leaks in the heat exchanger system will be required.

It should be noted, however, that a leak of the salt is "self-healing;" that is, the leaking salt will solidify and tend to plug any leak. Release of large quantities of salt will require a massive structural failure. Again, because of the fluoride salts' chemical stability, it is unlikely that a release of the salts will pose a hazard to the environment. A number of fluoride salts occur naturally in the environment; e.g., NaF (villiaumite), CaF_2 (fluorite), MgF_2 (sellaite), Na_3AlF_6 (cryolite), $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (fluorapatite) and $\text{Al}_2(\text{F,OH})_2\text{SiO}_4$ (topaz). However, the specifics of a particular location and a particular system design must be considered before a definitive statement on the ecological impact of a phase change TES system can be made.

In the area of maintenance, continuous monitoring of the system performance will be required. Also, periodic inspection for leaks or possible failures is needed. A means of sampling the salt at various levels will allow determination of any corrosion or sedimentation occurring. As discussed under the critical technical problems, the methodology used to seal off leaking portions of the heat exchanger tubing is an important concern. This will require the installation of support equipment, i.e., electrical, gas supplies, etc., at both top and bottom manifolds. The helium stream must be constantly monitored to insure that leaks into the helium flow will not foul the helium circulation system. A filter used in conjunction with the compressor should allow the helium flow to

remain uncontaminated. A drain/fill system for removing/filling the molten salt will allow inspection and/or repair of the system at various times during the lifetime of the plant.

The TES system materials may be recoverable, except possibly the tubing metal. Operation of the Molten Salt Reactor Experiment by the AEC showed very low corrosion over a period of four years at maximum temperatures on the order of 600°C.⁽⁷⁾ Assuming the fluoride eutectic chosen for the phase change TES system design demonstrates at the 800°C temperature levels a similar low corrosive attack of tubing and vessel metals and a similar resistance to thermal decomposition, the salt would not be expended and could be reprocessed and purified if necessary. The metal liner and refractory insulating brick can also be repaired and/or replaced. This affords the potential of refurbishing of a given TES system at a substantial savings of the cost of a replacement.

3.6 REFERENCES FOR SECTION 3

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Section 4

THERMOCHEMICAL CONCEPT

This section presents the results of the initial conceptual sizing of the reversible chemical reaction (RCR) storage system integrated with the solar power plant. The work was performed by Rocket Research Corporation as a subcontractor to Boeing. Their earlier results are presented in a similar context in the RP788-1⁽²⁾ and RP377-1⁽¹⁾ technical reports. A summary of the major technical issues and conceptual design results are presented here.

The thermochemical storage concept involves the storage of thermal energy in the heat of decomposition and recombination of reversible chemical reactions. A large number of chemical reactions were evaluated for use in this application. Most of those investigated, involve solid or entirely gaseous constituents which are difficult to manipulate and difficult to store. Although a purely liquid CES system is highly desirable, no purely liquid system with high temperature capabilities has been identified. The best compromise in terms of energy storage density and high temperature capability is the sulfur dioxide/oxygen system, even though one of the reactants has to be stored as a gas.

The sulfur dioxide/oxygen system is readily reversible and was first proposed by T. A. Chubb. As far as is known, the study presented here and in the RP788-1 and RP377-1 technical reports is the first systematic attempt to evaluate the SO_2/O_2 reaction on a system level, to determine the storage efficiency, and to establish a computer code capable of carrying out the system conceptual design and estimating system cost.

This section includes a description of the storage system and its operation, and presents the results of the Phase 0 Conceptual Design Study. A conceptual drawing of the RCR storage plant layout is presented and finally the results of the technical assessment are discussed.

4.1 RCR STORAGE SYSTEM DESCRIPTION

4.1.1 System Process Chemistry

4.1.1 System Process Chemistry (Cont'd)

The chemical energy storage system is based on the reversibility of the dissociation of sulfur trioxide:

In the reactant generating mode, sulfur trioxide is decomposed to sulfur dioxide and oxygen:

This process is endothermic and consumes energy at the rate of 295.3 cal/g SO_3 (531.5 BTU/lb SO_3). Conversely, the same amount of energy is released when SO_2 and O_2 recombine in the heat generation mode to form SO_3 :

The theoretical evaluation of the thermodynamic conversion efficiency is the basis of the system chemistry. In addition, kinetic calculations determine if the reaction will proceed to completion within a reasonable time. Both thermodynamic and kinetic results determine the conversion efficiency achieved in a given piece of hardware which in turn determines the round trip storage efficiency of the overall system.

An existing generalized thermochemical equilibrium computer program, CEC 72, developed by the NASA Lewis Research Center in Cleveland, Ohio, has been used to calculate dissociation as well as synthesis equilibria under a wide range of conditions. Data were developed throughout the range of temperatures and pressures expected in the CES reactor. The results show, as expected, that temperature and pressure can both be used independently to shift the equilibrium conditions.

Since heat is required to dissociate SO_3 higher temperatures will increase the dissociation rate and consequently shift the reaction in the direction of the SO_2/O_2 constituents. Conversely, the SO_2/O_2 constituents involve a larger molar volume than the SO_3 constituent (i.e., lower density). Since an increase in pressure will shift the reaction in the direction of the higher density constituents, it follows the higher pressures will improve the recombination rate

and thus shift the reaction in the direction of the SO_3 constituent. These are precisely the results obtained from the CEC 72 computer program. A summary of those results are given in Figure 4-1 in terms of the equilibrium reaction conversion fraction as a function of reactor temperature and pressure.

Figure 4-1. *Equilibrium Dissociation of Sulfur Trioxide*

As currently envisioned, the CES reactor will operate with the same helium temperature swing in both the dissociation and heat generation modes. Consequently, feed gas pressure becomes the primary determinant of the equilibrium conditions. The feed gas pressure in the dissociation mode is constrained at something just greater than 1 atmosphere. On the other end, the practical constraints of reactor design at high pressures set the equilibrium recombination fraction. A reactor feed gas pressure 10 atmospheres has been chosen for the baseline reactor design work. Obviously, this selected pressure level is the result of a system trade and design optimization study, which is presented in Section 4.2.

Although the reaction constituents are stored and transported at near ambient conditions, the feed gas will enter the reactor at higher than ambient temperature because it will have exchanged heat with the hot reaction products leaving the reactor. The reaction products will leave the reactor at a temperature slightly above 500°C, the helium inlet temperature. Consequently, the reactants can be preheated to temperatures in excess of 400°C significantly improving the average reactant temperatures. These higher feed gas temperatures will lower the recombination rates at least in the inlet portion of the reactor. However, the overall conversion which can be achieved in the reactor is more determined by the helium inlet temperature than by the reactant feed gas temperature.

The kinetics of the dissociation and formation reactions are a very important selection criterion in the design of an RCR system. It is very important to select a reaction which can be turned on and off by contact with a catalyst. If this was not possible and the equilibrium was not frozen at the high temperature condition, the dissociation reaction would revert itself while the dissociation products are cooling off.

Kinetic rates must be determined for both the catalyzed and the uncatalyzed reaction. A preliminary literature search has provided some literature references on SO_2/SO_3 kinetics, but additional work is required, especially on the dissociation of sulfur trioxide which is not a useful industrial process. Consequently, very little work has been done on sulfur trioxide dissociation other than the recent catalysts development work of Westinghouse. (4)

The kinetics of sulfur dioxide oxidation have been extensively studied because this reaction constitutes an important industrial process in the production of sulfuric acid. Even though sulfur monoxide or atomic oxygen do not show up as reaction products in the equilibrium calculations, they may play an important role in the kinetics and may be involved in rate-determining steps of the reaction.

The results of these initial investigations confirm the results of T. A. Chubb⁽³⁾

- o The purely gas phase decomposition time is longer than the residence time of the gas in a practical size noncatalyzed reaction chamber.
- o Hence, surface reactions must be employed to achieve chemical equilibrium.
- o Purely gas phase recombination rates are too slow to cause significant heat evolution in the regeneration heat exchanger.

These are precisely the results needed for practical application of a reversible thermochemical reaction in a controlled closed loop CES system.

4.1.2 System Description

A system design description and a summary of the corresponding cost estimates are presented in this section. Cost estimates and major operating parameters are presented in conjunction with the RP788-1 results for comparison purposes. As a part of the RCR storage system design effort, a conceptual design drawing was developed. This drawing serves as the focal point of the design description presented in this section.

System Operation

The basic requirements for the RCR storage system operation and interface with the STC power plant are presented in Section 1.3. The single characteristic that is unique to the CES system is that through proper design of the chemical process system, helium outlet temperature can be controlled in both the charge and discharge mode of operation.

The system operating schematics for both operational modes are presented in Figures 4-2 and 4-3. The reactant flow lines which are operational in a particular mode are drawn in bold lines. Partial flow is designated by dashed

Figure 4-2. Chemical Energy Storage System—Heat Generation Cycle

Figure 4-3. Chemical Energy Storage System—Reactant Generation Cycle

lines, and the light lines show inoperational paths in the particular mode of operation.

During the heat generation cycle, Figure 4-2, liquid SO_2 is withdrawn from storage and vaporized. Oxygen is concurrently withdrawn from storage and combined with the gaseous SO_2 . This mixture is then transported to the recuperator where it is heated by the reaction products to the operating temperature of the reactor.

After leaving the reactor, these hot reaction products give up their sensible heat to the unheated gas stream in the regenerative heat exchanger. The cool gaseous products are then transported to the fractionation column where they are separated by condensation. The separated constituents are then transported for storage to their respective storage containers. The reactant generation mode is simply the reverse procedure with high pressure oxygen and liquid SO_2 as the stored reaction products.

Plant Description

The physical plant layout for the baseline RCR storage system is presented in the conceptual drawing shown in Figure 4-4. The following paragraphs describe the major components and the sizing requirements for those components. The drawing and descriptive paragraphs are based on the final results of the many conceptual design trades presented in Section 4.2 and therefore represent the "selected" plant subsystems and operating conditions.

Six hours of operation at the design discharge rate of $113 \text{ NW}_{\text{th}}$ require approximately 5.6×10^6 lbm of reactants to be stored. This storage plus the holdup allowance consists of 1.7×10^6 kg (3.7×10^6 pounds) sulfur dioxide and 0.43×10^6 kg (1.9×10^6 pounds) oxygen.

Sulfur dioxide is commonly shipped in 35,000 gallon tank cars, and stationary storage tanks can hold up to 40,000 gallons (151 meters³). Mild steel can be used in the construction of sulfur dioxide storage tanks as long as the liquid is kept dry. At ambient temperature ($25^\circ\text{C} = 77^\circ\text{F}$), the vapor pressure in a liquid sulfur dioxide tank is 3.78 bar (55 psia). The SO_2 will be stored at these conditions in six mild steel tanks 5.65 m in diameter and 11.3 m long.

Sulfur dioxide storage poses no problem and is existing technology. However, compressed oxygen storage of the dimensions proposed here has never been attempted. Oxygen storage has to comply with very strict safety authority requirements with regard to system cleanliness and quantity-distance relationships. The formation of hot spots during high flow rates through curved tubing or discharge orifices must be avoided because it may lead to ignition of the metal. Oxygen will be stored as a compressed gas in 157 heavy-walled compressed gas cylinders which are manifolded together to form the storage bank.

The sizing of the reactor in the exothermic mode depends on the thermal-to-electric conversion efficiency. With the 816°C turbine inlet temperature the conversion efficiency is .442. Thus, to provide 50 MW_e , the reactor has to deliver 113 MW_{th} . The corresponding helium mass flow requirement is 92 kg/sec (201 lbm/sec). On the reactant side the conversion of SO_2 and O_2 to SO_3 is not 100 percent efficient. As discussed in the preceding paragraph, a maximum theoretical conversion efficiency of 96.2 percent by weight would be achieved at 495°C (922°F) and 10.13 bar (147 psia). However, the conversion efficiency is also limited by kinetic rates and mass transfer to and from the catalyst surface, and 96.2 percent by weight efficiency could only be achieved with a very long reactor.

For the baseline reactor the exothermic conversion efficiency is 74.5% by weight for a single pass through the complete reactor stack. The corresponding reactant mass flow rate is 135.9 kg/sec (299 lbm/sec). This consists of 108.7 kg/sec SO_2 and 27.2 kg/sec O_2 .

For the reactant generation cycle, the key specification is the charge-to-discharge power ratio. The charge-to-discharge ratio is set by the integrated operation of the STC power plant and storage system, the results of which are presented in Section 5. Figure 5-5 shows the results of this integration study as a function of heliostat field area. For the baseline plant (i.e. $.5 \text{ km}^2$ collector area) the design charge to discharge ratio is .9.

For the $\text{Cr} = .9$ design condition, the system will have a peak charging load of 104 MW_{th} . With this much thermal energy available 186 lbm/sec SO_3 can be

dissociated. However, dissociation efficiency at the selected reactor operating conditions is only 28.5 percent by weight. The SO_3 will therefore have to be separated from the dissociation products and recycled repeatedly to achieve complete dissociation of all SO_3 . The corresponding SO_3 flow rate at the peak charging condition is 167.5 kg/sec (368.5 lbm/sec).

For the reactant generation mode, SO_3 storage requirements are comparatively easy. A maximum of 2.2×10^6 kilograms (4.8×10^6 pounds) SO_3 will have to be stored when the system is in the completely depleted condition. This will most likely be the start-up condition after the system has been filled with chemicals for the first time. The same filling level will never again be achieved during later operation because of SO_2 and O_2 holdup in the system.

A significant simplification of the overall system was made possible by using joint storage tanks for sulfur trioxide and sulfur dioxide. In the fully charged or discharged condition, only one or the other has to be stored. SO_2 and SO_3 are completely miscible over the entire range of compositions. Inevitably, some contamination will occur if liquid SO_3 is filled into a tank which has previously contained SO_2 and vice versa. However, the ingredients in the CES system are not expected to remain in the chemically pure state, and the fractionation column will not be designed to achieve 100 percent separation. The contamination caused by liquid adhering to the walls and vapor absorbed may not be higher than that already existing in the incoming product.

Based on information obtained from Stauffer Chemicals, all materials proved to be compatible with sulfur trioxide (the more aggressive of the two oxides) can also be used for sulfur dioxide service. The tanks have to be designed for the higher vapor pressure of sulfur dioxide.

A small amount of SO_2 in SO_3 may actually be beneficial in lowering its melting point, widening the liquid range, and preventing accidental freezing. If no SO_2 is added, the sulfur trioxide tanks have to be kept above 38°C (100°F) all the time to prevent solidification of the tank contents.

System Costs

A preliminary system cost statement is presented in Figure 4-5. In this figure

Figure 4-5. COMPARISON OF CES PLANT COST
AND ROUND-TRIP EFFICIENCY

Case Input/Output	Nonoptimized CESTOR Baseline, EPRI-788-1	Optimized CESTOR, E(04-3)-1300
<u>Operating Parameter</u>		
Endo reactor pressure, bar	1.7	10.0
Endo column pressure, bar	12.1	10.3
Oxygen storage pressure, bar	151.7	208.1
<u>Components</u>		
Oxygen tanks	2,453,760	1,808,640
Pump, SO ₂	4,939	16,637
Pump, SO ₃	31,133	31,042
Mixer	12,546	12,707
Filters	33,220	31,042
Reactor	10,010,843	4,860,671
External heat exchanger	1,106,173	1,117,503
Separation column	891,184	858,989
Vaporizer	29,145	31,562
Cooler	12,663	12,792
Compressor, product	3,260,490	452,070
Compressor, oxygen	793,016	791,791
Compressor, helium	1,111,314	1,111,314
Chemicals and SO _x tanks	517,254	517,254
Total cost, \$	20,267,678	11,654,251
Round trip efficiency	0.44	0.71

System Costs (Cont'd)

component costs and major operating parameters are shown on a side by side basis with the prior results presented in the EPRI RP788-1 documentation. A 43% reduction in cost has been achieved as a result of the current conceptual design and process optimization effort. The corresponding round trip efficiency has been increased by 61%.

As much cost data as possible were assembled on the various components that constitute the system. Most of this data and the corresponding scaling equations were taken from "Process Plant Cost Estimating" by V. M. Gulhrie. The data are 1969 costs and have to be expanded by the chemical equipment plant cost index, which is published weekly in Chemical Engineering. The factor to be applied to convert 1969 estimates to 1976 dollars is 1.45. The costs do not include installation labor except for field-fabricated items.

All of the cost estimating relationships have been incorporated in the RCR storage system computer model. The actual equations used in the program are presented in the program listings in Volume III of this report.

4.2 CONCEPTUAL DESIGN STUDIES

The conceptual design studies conducted during this program were aimed at identifying possible system simplifications with associated cost savings. The studies included a careful evaluation of each of the major components in the RCR system, as well as a parametric design study and system sensitivity studies.

The catalyst in the RCR reactor has been identified as a key to realization of the SO_2/SO_3 RCR storage system. Before embarking on an ambitious and time-consuming catalyst development program, a survey of catalyst manufacturers was conducted to see if current technology readily available catalysts would meet the RCR requirements. Alternate catalyst concepts were then reviewed for their applicability to the RCR system.

The compressed oxygen storage and the dissociation product compressor have been identified during previous studies as major cost items and parasitic power consumers. Alternate modes of oxygen storage and dissociation product separa-

tion are sought which would reduce installation and operating cost of the CES system. A modular reactor design is being proposed which would move fabrication of reactor/heat exchanger modules into the reach of current manufacturing technology and facilitate maintenance by replacing single modules as opposed to shutting down the entire plant for repair or maintenance.

The RCR computer model was used to study the effect of reactor pressure and separation column pressure on round trip efficiency and parasitic power requirements. This study is not yet equivalent with an optimization since many other variables are also involved. However, cost and performance trends have been identified and significant improvements in cost and performance have been realized. Finally, a parametric sizing study was carried out. Size, cost and round trip efficiency were calculated for three power levels, two storage capacities and two charge to discharge power ratios. The results of all of the above work is presented in this section.

4.2.1 Catalyst Durability Review

Preliminary Discussion

The work performed during this phase of the SO_2/SO_3 program was the continuation of a previous effort to contact catalyst suppliers which was carried out during the early phase of Contract EPRI 377-1 (Reference 1). Several catalyst manufacturers, some of which were known sulfuric acid catalyst producers, were contacted to obtain information pertaining to their catalyst and to obtain catalyst samples. The survey conducted was not limited to vanadium pentoxide catalyst; however, these catalysts were found to be the only commercially available catalysts for the SO_2/SO_3 reaction. The catalyst producers contacted are listed below; however, it should be noted that Kerr-McGee is a vanadium pentoxide producer rather than a catalyst manufacturer and was contacted in order to establish if anyone was producing a sulfuric acid catalyst that might otherwise have been overlooked. Kerr-McGee information identifies the principal catalyst manufacturers for sulfur trioxide production as Monsanto, BASF, Catalyst and Chemicals, American Cyanamid, Stauffer, Catalyst Development, Fairmount Chemical, Girdler Chemical, and Thompson-Hayward. The questions submitted to the catalyst manufacturers are listed on Table 4.1.

POTENTIAL SULFURIC ACID CATALYST SUPPLIER

Catalyst and Chemicals Inc.	Fairmount Chemical Company
American Cyanamid Company	Catalyst Development
Monsanto Enviro-Chem Systems, Inc.	Thompson-Hayward Chemical Company
Stauffer Chemical Company	Hooker Chemical Company
BASF Wyandotte Corporation	Air Products and Chemicals
Girdler Chemical Company	(Houdry Division)
Davison Chemical Company	Kerr-McGee Chemical Corporation*
Harshaw Chemical Company	

*Vanadium pentoxide producer rather than a catalyst manufacturer.

Table 4-1
LIST OF QUESTIONS SUBMITTED TO CATALYST SUPPLIERS

1. What is the upper temperature limitation of their catalyst? What is the correlation between operating temperature and useful lifetime?
2. What activity test do they use? Could they provide a copy of their testing procedure or is it described in the open literature? If so, could a reference be obtained?
3. What is the activity cutoff point for commercial utilization in sulfuric acid production?
4. What is the likely degradation mechanism if the catalyst is exposed to above nominal temperatures?
5. Is anybody considering the use of oxygen instead of air for commercial sulfuric acid production? Does the benefit of zero tail-gas cleanup outweigh the extra cost for oxygen?
6. Are they aware of efforts to use the waste energy generated in burning sulfur or oxidizing SO_2 to SO_3 to generate steam or electric power?
7. Do they have experience with this catalyst being used to decompose SO_3 ?

Survey Results

The results of the survey conducted are described below with the reply of each manufacturer treated separately. It should be noted that some of the manufacturers have not yet replied with the technical information requested.

Catalyst and Chemicals, Inc. replied that the lifetime of their catalyst at 773⁰K (932⁰F) would be years in the absence of poisons, but that at 1,090⁰K (1,508⁰F) the lifetime would be measured in hours due to V₂O₅ losses by sublimation. Their activity test procedure is proprietary but it actually simulates a small sulfuric acid manufacturing plant. The activity cutoff point depends upon the plant design so no absolute activity values are available.

The degradation mechanism of the catalyst observed at higher than normal temperatures is the volatilization of the vanadium. There are apparently no problems associated with heating the catalyst carrier. Catalysts and Chemicals, Inc. stated that their catalyst would oxidize sulfur dioxide with oxygen rather than air and that the heat generated in burning sulfur and oxidizing the SO₂ is almost always used to generate steam in sulfuric acid manufacturing plants. They stated that their catalyst has not been used for the endothermic dissociation of sulfur trioxide but that it should work.

American Cyanamid stated that their catalyst should not be operated higher than 894 to 900⁰K (1,150 to 1,160⁰F) or the vanadium active metal would be sublime. They intended to send a copy of their activity testing procedure if at all possible; however, at the time of report preparation, the procedure was not received. The actual activity cutoff point for commercial sulfuric acid production was explained to be a very subjective number depending upon the plant design in which the catalyst is employed. Also, other tests are performed which aid in the determination of the utility of the catalyst. American Cyanamid replies that the degradation mechanisms of their catalyst when exposed to high temperatures would be the sublimation of vanadium and the actual melting of the catalyst carrier at 977 to 1,033⁰K (1,300 to 1,400⁰F). They were not aware of anybody considering the utilization of oxygen instead of air for commercial sulfuric acid production, and they did not know if their catalyst would decompose sulfuric trioxide. They were aware of efforts to utilize the waste heat generated during sulfuric acid production; however, the heat recovered was solely intended for internal consumption. They were

unable to assist in identifying other catalysts or active metals which would oxidize sulfur dioxide.

Monsanto Enviro-Chem Systems, Inc. replied that in normal commercial use, their catalyst temperatures do not exceed 883 to 893⁰K (1,130 to 1,140⁰F) and increased temperature results in decreased expected lifetime because of partial sintering and loss of pore structure. They said that volatilization of catalyst components does not occur to any significant degree but could not say categorically that it was zero. They were not able to provide a detailed description of their catalyst activity test unit but did state that it is a high temperature, differential conversion unit in which a reasonable approach to isothermal conditions is achieved. An activity cutoff point for commercial sulfuric acid manufacture is not available since the specific type of system used determines the cutoff point. Monsanto stated that the utilization of oxygen instead of air is being investigated because of the advantage of building a smaller plant, but apparently there is a problem with the cost of oxygen outweighing the capital equipment costs. Waste heat generated is currently recovering 3,900 Btu's of steam per pound of sulfur burned. Their catalysts have not been employed commercially for the endothermic dissociation of sulfur trioxide, but this has been found to work in the laboratory so long as the catalyst is maintained above a lower threshold temperature of approximately 683 to 703⁰K.

Stauffer Chemicals replied that much above 888⁰K (1,140⁰F), their catalyst loses vanadium by volatilization; and as the temperature increases, the useful lifetime of the catalyst decreases. They said that for an activity measurement, they performed the Reich test and would send relevant literature; however, the actual activity cutoff point depends on which type of system is employed. The degradation mechanism appears to be primarily the volatilization of vanadium, but Stauffer Chemicals has also found that the catalyst becomes sensitized to certain temperatures resulting in a more narrow temperature band for optimum sulfur dioxide conversion. For this reason, fluctuation of bed temperature, which does not happen in commercial sulfuric acid production, could cause serious problems. They stated that oxygen has been used instead of air in commercial sulfuric acid production, but now it would be too expensive due to rising oxygen costs. The zero tailgas clean-up does not justify the cost of oxygen. Also, removing the nitrogen from the feed gas would

cause a tremendous heat rise in the reactor bed and destroy the catalyst. They replied that is common practice in all sulfuric acid plants to route the hot gases through a boiler to generate steam, thereby utilizing the waste heat generated. Stauffer Chemicals stated that their catalyst would not decompose sulfur trioxide. They also promised to send a sample of spent catalyst but stated that documentation of use history was impossible to obtain. They also suggested using platinum or ferric oxide as active metals for the oxidation of sulfur dioxide.

Both BASF Wyandotte Corporation and Girdler Chemical Company were contacted to obtain samples and request information; however, prior to the cutoff date for report preparation, the information was not received.

Davison Chemical Company replies that their vanadium pentoxide catalyst is used in the production of phthalic anhydride from naphthalene in a fluidized bed reactor rather than sulfuric acid production in a fixed bed reactor. Their catalyst is a 50 to 300 mesh powder and not in pellet form as are commercial sulfur dioxide oxidation catalysts.

Harshaw Chemical Company also produces a vanadium pentoxide catalyst but stated that theirs is not utilized in commercial sulfuric acid production. They were unable to answer the questions presented but indicated they would respond at a later date; however, the information was not obtained prior to report preparation.

Fairmount Chemical Company, Catalyst Development, Thompson-Hayward Chemical Company, and Hooker Chemical Company stated that they do not manufacture catalysts for the oxidation of sulfur dioxide.

Air Products and Chemicals also do not market a catalyst for sulfuric acid production, but they have done developmental work with vanadium pentoxide, platinum, and platinum/palladium combinations.

4.2.2 Advanced Catalyst Concepts

As previously discussed and again confirmed during the catalyst durability review conducted as a part of the current contract, existing sulfuric acid production catalysts are not expected to satisfy the 30-year RCR storage system operating life requirements.

Advanced catalyst concepts are outlined in this section with regard to their mechanical mode of operation.

Packed Bed Reactor Catalysts

Pelletized, spherical or extruded catalysts constitute current technology in sulfur dioxide oxidation catalyst. The development of a high-temperature resistant catalyst of this form would constitute a low-risk approach. However, heat transfer problems are not easily solved with this relatively coarse material if it is desirable to transfer heat directly from the catalyst material to the working fluid heat exchanger tubes. Some RCR reactor designs envision that the heat exchanger tubes would be embedded in the catalyst bed for intimate heat transfer. However, catalyst replacement would be difficult. In particular, if the catalyst sinters and forms a solid mass between the heat exchanger tubes; this mass is difficult to remove without damaging the tubes.

During an analytical study of RCR reactors, the reactor and heat exchanger have been subdivided into numerous small subsequent reactors and heat exchangers as a matter of convenience for computer modeling by the method of finite differences. This arrangement may be useful not only for modeling, but also as an engineering approach. A modular unit consisting of flanged reactor and heat exchanger units will make reactor and catalyst or heat exchanger replacement easier, and has been adopted as the baseline reactor.

Fluidized Bed Reactors

In a fluidized catalyst bed, very fine catalyst particles (approximately 150 to 200 mesh equal 100 to 75 μm) are placed on a porous disc or screen in a funnel-shaped reactor. As the gases stream upward, their flow velocity decreases to a point where catalyst particles are suspended in a dynamic recirculation pattern. The mass of suspended particles behaves like a fluid. The geometric surface area of contact between catalyst and reactant medium is larger than in supported catalysts. Because more geometric surface area is exposed, less attention need be paid to granule porosity and internal surface area. Because the catalyst is in motion most of the time, it is easy to remove a small fraction of the catalyst continuously for reactivation or replacement. Most of the units of this

type are used with catalyst that deactivates rapidly, and the catalyst is removed continuously, regenerated, and returned to the reactor.

The temperature distribution in a fluidized catalyst bed is very uniform, and the high degree of turbulence avoids hot spots in the bed. The heat can be removed by heat exchanger coils in direct contact with the fluidized bed.

The system has the disadvantage that the catalyst powder tends to be carried out of the reactor and must be trapped in some way. In the laboratory, this can be accomplished by using sintered discs. In the plant, it is done with cyclone separators and electric precipitators.

Fluidized bed catalytic reactors are used extensively in the petroleum refining industry. Fluidized bed reactors have been considered but are not currently used for the production of sulfuric acid by the contact process. Accordingly, fluidized bed catalysts for the SO_x conversion reaction are not available on the market.

It has been observed that the active phase, at the operating temperature of current technology sulfuric acid catalysts, is a viscous melt of vanadium pentoxide and potassium pyrosulfate. The viscous material would be very sticky, and it is not possible to convert to a fluidized bed with a vanadium pentoxide/potassium pyrosulfate catalyst by simply pulverizing the extruded or pelletized material. A new catalyst would have to be developed which has a higher abrasion resistance and will not melt at the operating temperature.

Skeleton Catalysts

Skeleton catalysts are also frequently referred to as Raney catalysts, named after the inventor of this type of catalysts. Skeleton catalysts in powder or sheet form are prepared by leaching aluminum (or any other easily dissolved metal) from an alloy with the active metal. The skeleton of undissolved active metal which is left behind after the aluminum has been dissolved and rinsed out has a high surface area. Some of the Raney metal powders prepared by this method are so active that they ignite spontaneously when brought in contact with air. Skeleton catalysts can be deposited directly on the heat exchanger

tubes such as in the tube wall reactors used for methanation studies.

In the tubewall reactor, very high heat fluxes up to 10,000 Btu/h sq. ft. have been achieved in bench-scale and pilot-scale methanators. However, demonstrated life of the plasma-sprayed Raney nickel coating does not yet exceed 5,500 hours. The catalyst can be sprayed on the inside of the reactor tubes, but it is very difficult to replace.

Monolithic Catalysts

Monolithic catalysts consisting of ceramic bodies with a multitude of channels are currently in use in catalytic mufflers in automobiles. Monolithic catalysts are more durable than pelletized or granular catalysts in high temperature applications with dynamic loads (pressure pulsations and vehicle vibrations). However, monolithic catalyst resulting from the proposed program will be of the monolithic type.

In contrast to the plasma-sprayed Raney nickel coating, a monolithic catalyst insert is easily replaced after it has exceeded its useful life. The cartridge-shaped insert could slide in and out of the reactor with a minimum of downtime of the RCR storage plant for catalyst replacement.

The heat transfer from a monolithic catalyst insert to the wall of the reactor depends on convection, radiation, and point contact. Maximum heat flux is below that possible with a tube wall reactor.

Molten Catalysts

It has been observed that the vanadium sulfate/potassium pyrosulfate active material on current technology supported catalysts is actually molten at reactor operating temperatures. The molten material is expected to fill all small pores of the catalyst carrier by capillary action, and the actual surface area of exposed vanadium must consequently be quite small. The function of the catalyst carrier, in particular at very high temperatures, is thus degraded to that of a sponge to hold the molten catalytic material and to prevent it from flowing away. It has been suggested (Reference 5) that molten catalyst be used for the oxidation of sulfur dioxide. While this may not be attractive to

the sulfuric acid industry, it may hold the key to success of reversible reactions in RCR systems.

There are no other known applications of a molten catalyst in industry. The reactant gases could be bubbled through a bath of molten catalyst in which the heat exchanger tubes are submerged or the molten catalyst could be pumped to the top of a tower from where it flows down along the walls and the heat exchanger tube, maintaining a thin film of active material on the heat exchanger tube at all times. Potential problems with this concept are the hydrostatic pressure which the reactants must overcome in the bubble bath and the need to keep the catalyst molten all the time. The melting point of the catalyst could be of the order of 500°K (440°F).

Advanced Catalyst Concepts -- Conclusions

When reviewing the various advanced catalyst concepts, the evaluation criteria summarized in Table 4-2 can be used to select a most promising approach. For the 30-year operation at $1,144^{\circ}\text{K}$ ($1,600^{\circ}\text{F}$) for delivering $1,089^{\circ}\text{K}$ ($1,500^{\circ}\text{F}$) helium or air, a molten catalyst seems to be most promising. Applications with lower operating temperature interfacing with a steam power plant may be able to operate with supported bed catalysts. A supported catalyst reactor would be a lower risk approach compared to the molten catalyst reactor for which technology does not yet exist.

Table 4-2
REACTOR/CATALYST EVALUATION CRITERIA

Reactor/ Catalyst Type Evaluation Criterion	Packed Bed/ Supported Catalyst	Fluidized Bed/ Supported Catalyst	Pumped Molten Catalyst
Pressure drop	High	Low	Low
Reactivity	Medium	High	Unknown
Space velocity	Good	High	Unknown
Ease of replacement	Poor	Good	Good
Heat transfer	Poor	Medium	Excellent
Potential for scale-up	Good	Good	Good
Initial reactor cost	Low	High	Higher
Initial catalyst cost	High	Medium	Low

and it was thought to be desirable that the catalyst be in close proximity or in intimate contact with the heat exchanger tubes. At a later time, during the development of a mathematical model for the reactor, the reactor was subdivided into a large number of alternating adiabatic catalyst beds and heat exchangers for convenience of expressing temperature and conversion profiles by the method of finite difference. While this was done initially only as a mathematical exercise, it became apparent that it would also constitute a desirable design from a standpoint of practicality and maintainability.

The initial concept would have required a single large pressure shell to house the catalyst with numerous penetrations for the heat exchanger tubes. A large single pressure shell of these dimensions for a 50-MW_e power plant would be beyond current technology. Furthermore, if the catalyst was filled between the heat exchanger tubes and inadvertently sintered in place during use, it would be very difficult to remove the catalyst without damage to the heat exchanger tubes. From a standpoint of catalyst replacement and maintenance, it would be better to separate catalyst beds and heat exchangers. The reactor sizing model assumes that the reactants react (oxidize or dissociate) adiabatically in each segment of the bed, followed by a frozen equilibrium purely convective heat exchange with the helium working fluid. Actual conversion rates may be higher because it will be inevitable that some catalyst dust is deposited on the heat exchanger tubes, causing desirable shift of equilibrium during heat transfer (without blocking heat transfer by depositing a layer of insulating material). Required dimensions may also be smaller than those printed out by the computer model because small contributions by radiation and conduction between bed sections and tube sections were neglected.

A design study was performed to investigate the feasibility of reducing the cost involved in erecting the catalytic reactor/heat exchanger section of the RCR system. Certain problems immediately became apparent in the construction of a 30-foot diameter pressure vessel/heat exchanger both in the physical operation of the initial concept and the complexity of on-site fabrication and testing of the hardware.

An obvious solution is to reduce the physical size of the hardware to a point where more standard in-shop manufacturing techniques can be utilized. This, of course, requires multiple reactor segments manifolded

4.2.3. Cursory Design Concept Trade Studies

The process flow diagram of the RCR system developed during EPRI-RP-377-1 which formed the basis for the CESTOR computer model, was based on certain assumptions with regard to the means of product separation and reactant storage. While this approach was very useful in obtaining investment cost and performance efficiency data, time did not permit a thorough evaluation of all alternatives or an optimization of operating parameters. The majority of the time during the current effort was therefore devoted to a critical re-evaluation of the initial system design.

Virtually all components in the RCR system have undergone re-evaluation, and new design concepts have been worked out for some of the components, in particular the reactor. A more detailed analysis has been conducted of the vaporizer/condenser, for which design data were not yet available and gross assumptions had to be made in sizing and costing this unit. Alternate separation techniques were evaluated as a replacement for distillation. Alternate oxygen storage methods were studied in more detail than was previously possible. In particular, this included a discussion of the open air cycle, in which oxygen is replaced by ambient air and only sulfur oxides have to be stored.

Finally, using the CESTOR math model, the effect of a number of operating parameters on round trip efficiency and plant cost was studied. The parameters included endothermic and exothermic reactor pressure, charging cycle separation column pressure and oxygen storage pressure. While these point checks do not yet constitute a full-fledged optimization study, they have identified trends which should be followed in an effort to improve round trip efficiency and minimize RCR storage plant cost.

Reactor Design Trade Study

The initial concept as illustrated in the final reports of RPRI RP-3771-1 and RP-788-1 and repeated in the System Requirements Data Book released as a part of this contract envisioned a packed bed reactor with a tube and shell type heat exchanger for the helium flow. The granular or pelletized catalyst would be located between the heat exchanger tubes,

together. As the size of the components decreases and the number of identical components increases, moderate to high volume production techniques can be utilized with significant savings realized in the area of rework and repair of deviations.

As a starting point, the reactor has been broken down into 13 reactor groups each consisting of 7 reactor stacks with each stack containing 10 reactor modules, two concepts of which are shown in Figures 4-6 and 4-7. These reactor modules, 910 in all, reduce to a size (2 x 3 feet), which is readily handled by most available fabrication equipment. Further, the quantities for a single system have reached the point where, for a single CES facility, moderate to high production manufacturing techniques can be utilized with no significant difference in material quantities required when compared to a one-piece field fabrication reactor.

Each reactor module consists of an outer pressure shell, a catalyst bed, and a heat exchanger. Prior to the availability of material compatibility test results, the assumption was made that CRES 316, the material selected for the outer shell, would become degraded after long exposure to hot scrubbing SO_3 . It is known that hot SO_2 will degrade some stainless alloys. For these reasons, two module concepts were considered. The first, shown in Figure 4-6, utilizes a catalyst bed liner fabricated from Haynes alloy 188 which is felt to have a better chance of resisting the corrosive attack of hot scrubbing SO_3 . The second, shown in Figure 4-7, utilizes a cast alumina ceramic catalyst bucket to achieve the same end. The heat exchanger is assumed to be fabricated from Haynes 188 alloy tubing, furnace brazed into a manifold simultaneously with the manifold being brazed to the inner shell. Conoseal (Marmon Division, Aeroquip Corporation) flanges are utilized for module mating as well as all helium and SO_x system plumbing.

Material selections described above are tentative, awaiting compatibility test data with various oxides of sulfur. Final selection criteria will be compatibility, low cost, and acceptable mechanical properties at elevated temperatures. Due to the large quantities of material involved, a special alloy with properties tailored to the task will be considered a viable alternative.

Figure 4-6. REACTOR MODULE (LINED)

- 1 CONOSEAL FLANGE
- 2 BED PLATE (HAYNES 188)
- 3 BED LINER (HAYNES 188)
- 4 He INLET
- 5 He OUTLET
- 6 MODULE BODY (316 L RES)

Figure 4-7. SO₂/SO₃ REACTOR MODULE (INSULATED)

- (1) CONDENSATE FLANGE
- (2) CATALYST BED COVER - ALUMINA
- (3) CATALYST BED RETAINER - ALUMINA
- (4) H₂ INLET
- (5) H₂ OUTLET
- (6) MODULE BODY - 316 S.S.

The module stack is shown in the cutaway view of the reactor building in the conceptual drawing, Figure 4-4. The 10 modules are secured to one another and the end caps utilizing Marmon 3-bolt pipe clamps to minimize large numbers of bolts and provide angular indexing for manifolding the helium system, which is interconnected module-to-module in series. Seven stacks are manifolded into a group, and each group is provided with isolation valves for both helium and reactant systems. The groups form the building blocks of the modular reactor.

The complete reactor facility contains 13 reactor groups housed in an insulated structure to maintain system temperature. Operationally, this type of system offers several advantages over a single large reactor. First, operation during periods of non-peak demand can be handled incrementally at peak reactor efficiency by selective utilization of reactor groups. Second, the status of all modules can be monitored and maintenance and repair functions can be carried out without total shutdown of the reactor by removing only reactor groups requiring maintenance or repair. This could be accomplished by utilizing spare reactor groups to maintain peak power capability or operating the reactor at a reduced level.

A preliminary cost estimate indicates that using ceramic insulated CRES 316 reactor modules and Haynes 188 heat exchanger modules, the reactor plus internal heat exchanger cost would be \$5 M (1976 dollars). This is within 4% of reactor/internal heat exchanger cost printed out by the computer model.

Vaporizer/Condenser Sizing Study

Design information in the literature on a vaporizer/condenser with two-phase flow on both sides of the heat transfer surface is extremely scarce. The condensation/vaporization process is made more complex by the multicomponent nature of the process product stream on the condensing side. Most published design cases involve only boiling or condensing heat transfer

on one side with the heat source or heat sink on the opposite side being flowing water, steam, or air.

Fundamental physical properties for the vaporizing and condensing components had to be used to extrapolate heat fluxes and heat transfer coefficients. It appears that additional laboratory work is required to determine all the heat transfer properties needed in the design of the vaporizer/condenser. A test plan outlined to fill this data gap is described the Phase I Statement of Work.

Prior to embarking on calculating the required heat transfer areas, a survey was conducted of several companies known to be involved with sulfur oxide processes. The objective of this survey was to obtain design information on SO_2 and SO_3 vaporizers. Both Asarco, Tacoma and Chemithon, Seattle recommended to contact Armstrong Corporation in West Chester, Pennsylvania, for design information on SO_2 vaporizers. However, Armstrong Corporation considers the heat transfer coefficients used in their designs as proprietary data and no information could be obtained.

Lacking more accurate heat transfer data, the Zuber equation (Reference 6) was used to identify the film boiling regime of SO_2 and SO_3 . This equation applies to vaporizing liquid on a horizontal plate without forced convection. It thus represents a conservative approach if this equation is used for sizing a heat exchanger with forced convection of liquid flowing through tubes. The minimum heat flux is expressed by:

$$\left(\frac{q}{A}\right)_{\min} = \frac{\pi^2 \lambda \rho_v}{60} \left[\frac{1.35 g_c g (\rho_L - \rho_v)}{3(\rho_L + \rho_v)^2} \right]^{1/4}$$

where:

$\frac{q}{A}$ = Heat flux, Btu/hr ft²

λ = Heat of vaporization, Btu/lb (232 Btu/lb)

σ = Interfacial tension, lb/ft (0.00185 lb/ft)

ρ_v = Vapor density (0.1914 lb/ft³)

ρ_L = Liquid density (111 lb/ft³)

g_c = Newton's law conversion factor (4.17×10^8 ft lbm/lbf h²)

$$g = \text{Gravitational acceleration } (4.17 \times 10^8 \text{ ft/h}^2)$$

Using this equation, a heat flux of $10,228 \text{ Btu/ft}^2\text{h}$ ($32,268 \text{ W/m}^2$) was obtained for SO_3 vaporization and a heat flux of $43,838 \text{ Btu/ft}^2\text{h}$ ($138,305 \text{ W/m}^2$) was obtained for SO_2 vaporization.

To obtain the surface area required in the vaporizer, it was assumed that the heat flux for heating the liquid to the boiling point is the same as that for film boiling heat transfer. The energy required to heat the liquid constitutes only a small fraction (4 percent) of the latent heat of vaporization; thus the error in this assumption is very small. For an SO_3 flow of 219.4 lb/s (50 MW_e , CR = 0.6 baseline case), the required area would be:

$$A_{\text{max}} = \frac{52,917 \times 3,600}{10,228} = 18,626 \text{ ft}^2 = 1,721 \text{ m}^2$$

The sizing factor for the SO_3 vaporizer is then

$$84.9 \frac{\text{ft}^2}{\text{lb/s}} = 17.4 \frac{\text{m}^2}{\text{kg/s}}$$

An analogous equation for the SO_2 vaporizer yields a

$$\frac{q}{A}_{\text{min}} = 43,838 \text{ Btu/ft}^2\text{h} = 138,305 \text{ W/m}^2$$

and a sizing factor of $11.96 \text{ ft}^2/\text{lb/s} = 2.45 \text{ m}^2\text{s/kg}$. This number is considerably smaller than the SO_3 sizing factor because SO_2 is vaporized at comparatively high pressure while the SO_3 is vaporized at ambient pressure. The low pressure evaporation requires more bulky equipment. The baseline design SO_2 vaporizer requires a surface area of 263 m^2 ($2,833 \text{ sq ft}$).

Up to this point in the calculation, it is not yet evident if the heat transfer on the vapor or the liquid side of the tube will become size determining. For all cases calculated so far, the vaporizer/condenser has added cooling requirements, and the total energy removed from the condensate is higher than the energy needed to vaporize the reactants. It is necessary to get a better understanding of the design variables which will result in a better heat balance in the vaporizer/condenser.

The next step then is to calculate heat transfer coefficients on the

condensing side of the system using a Nusselt form equation from Reference 7 :

$$h_o = 0.725 \left(\frac{K_f^3 \rho_f g \lambda}{\Delta T_o D_o \mu_f} \right)^{1/4}$$

for one horizontal tube, where:

K_f = Thermal conductivity of fluid (0.35 Btu/h ft °F) Btu/(ft hr °F)

ρ_f = Density of fluid, lb/ft³ (101 lb/ft³ = 1.625 g/cm³)

g = Gravitational acceleration, ft/hr² (4.17×10^8 ft/h²)

λ = Heat of vaporization, Btu/lb (205 Btu/lb)

D_o = Outside diameter of tube, ft (0.75 in. = 1.9 cm)

μ_f = Absolute viscosity of fluid lb/ft-hr (0.869 lb/ft h)

ΔT_o = Temperature drop across condensate film, $T_h - T_w$ (212 - 135 = 77°F = 430K)

For condensing calculations in the exothermic mode, it is assumed that all condensate is SO₃. Thus, in order to vaporize 107.4 kg/s (236.5 lb/s) SO₂, assuming no fouling or wall resistance with a film transfer coefficient of $h = 1,255$ Btu/h ft² °F, an area of 1,047 ft² = 13.5 m²/lb/s = 2.76 m²s/kg is required for the vapor side-heat transfer. This area is larger than the liquid side and becomes therefore size determining.

In calculating K_f in the above equation, the expression

$$K_f = \frac{0.869 C_p \rho^{4/3}}{M^{1/3}}$$

from Reference 8 was used where:

C_p = Heat capacity, Btu/lb°F

ρ_p = Density, g/cc

M = Molecular weight

Based on information from Pizer Laboratories/Stauffer Chemicals (Reference 9), a heat transfer coefficient of 65 Btu/h ft²°F is used when vaporizing SO₃ with steam on the inside of horizontal hairpin tubes.

Assuming an average temperature difference of 237°F (132°K) and using the equation

$$Q = U A \Delta T \quad h_i \equiv U$$

a heat transfer coefficient of 43 Btu/h ft² °F is obtained from approximate assumptions which compare well with the reported industry value above. Currently a liquid flow velocity of 0.15 ft/s (4.5 cm/s) is assumed which is very low. The heat transfer can be improved significantly by increasing the flow speed. Using 3/4-inch (1.9 cm) BWG = 12 tubes in 15-foot lengths with an internal diameter of 0.532 inch (1.35 cm), 8,916 tubes would be required for the SO₃ vaporizer coil. A similar calculation shows that only 1,876 tubes are required for the SO₂ vaporizer.

A different set of equations is used to size the oxygen warmup coil. In the case of oxygen warmup, it must be assumed that the internal heat transfer coefficient is the limiting criterion because oxygen is all gaseous while the outside flow is partially condensing liquid.

Equation 12-37 from Reference 10

$$\frac{h_i}{C_p G} \left(\frac{C_p u}{K} \right)_f^{2/3} = \frac{0.023 \left[1 + \left(\frac{D}{L} \right)^{.7} \right]}{\left(\frac{D G}{u_f} \right)^{.2}}$$

gives the required dimensions, where:

h_i = Individual heat-transfer coefficient, Btu/ft² hr°F based on the inside of tube

C_p = Specific heat, Btu/lb°F

G = Mass velocity, lb/ft² sec

D = Inside diameter, ft

L = Length of tubing, ft

μ = Absolute viscosity, lb/ft-hr

The Reynolds number

$$N_{RE} = \frac{D G}{\mu}$$

for this equation must be larger than 10,000. A Reynolds number of 50,000 was assumed for the subsequent calculations:

$$G = \frac{50,000 \mu}{D} = 46,241 \text{ lb/ft}^2 \text{ h (for each tube)}$$

This corresponds to a heat transfer coefficient of

$$h_i = 2.78 \text{ Btu/ft}^2 \text{ h } ^\circ\text{F} \text{ (15.8 W/m}^2 \text{ } ^\circ\text{K)}$$

With a temperature increase of 245°F (136°K), it is apparent that the heat transfer objectives cannot be achieved in a single pass with 15-foot (4.5 m) long tubes. Instead, four passes are required. For an oxygen flow of 59 lb/s (26.8 kg/s), a total surface area of $2,289 \text{ m}^2$ provided by 12,018 tubes is required. The scaling factor is $417 \text{ ft}^2/\text{lb/s} = 85.4 \text{ m}^2/\text{s/kg oxygen}$. The oxygen tubing is thus the most bulky component in the baseline design vaporizer/condenser. However, in terms of energy transferred, the oxygen ranks lowest.

The oxygen coil requires close scrutiny with regard to cost benefit. The cool gas available during the initial blowdown of the compressed oxygen storage constitutes a valuable source of cooling for the separation column. However, its temperature changes with operating time, and the load on the auxiliary cooling unit increases as the oxygen storage pressure drops to the reactant feed pressure. As an alternate, the cold oxygen could be mixed with the superheated sulfur dioxide vapor in the mixer, completely eliminating the need for an oxygen coil. The cooling unit would have to be sized large enough to satisfy cooling requirements without additional cold supplied by the expanding oxygen stream.

The more detailed analysis of the vaporizer/condenser and the ability to calculate (and eventually minimize) cooling requirements using the CESTOR program have resulted in some recommended design changes to the distillation column and its interface with the condenser/vaporizer.

It is now proposed to combine the vaporizer/condenser with the top stages ("plates") of the fractionating column as opposed to making the condenser a separate unit on top of the separation column. In this arrangement, the temperature differential between the column feed and the vaporizing liquid is used to its full extent. Otherwise, thermal losses of the condensing vapors on the way from the feed state to the top of the column would reduce the available energy and the useful temperature difference ΔT . The ΔT , the liquid feed pressure, and the flow speed should be selected such that most of the heat transfer occurs in the nucleate boiling regime. It may actually be advisable to insert a heat exchanger between the dissociation product compressor and the fractionation column to cool the gases before they enter the column. This will recover useful energy by preheating the SO_3 vapors before they enter the external heat exchanger on their way to the dissociating reactor.

Using the same equations for costing carbon steel heat exchangers as used for calculating the cost of the external heat exchanger and not taking credit for three heat exchangers housed in one common shell, the cost of the baseline design vaporizer/condenser would be \$190,000. The major part of this cost (\$92,000) is attributable to the oxygen coil. If the oxygen coil is omitted, which can be done without major system changes as discussed above, the cost of the vaporizer/condenser is reduced to \$98,000. This number is higher than the original preliminary estimate used in the CESTOR program (\$29,145). Now that a more reliable sizing equation has become available, the more detailed data can be substituted during future CESTOR program revisions.

As a result of the foregoing studies, the following recommendations are made:

1. Remove the bulky oxygen warmup coil from the condenser pressure shell and feed cold oxygen directly into the mixer.
2. Intersperse heat exchanger/condenser coils with column sections in the upper part of the column.

3. Insert a heat exchanger between compressor and column (if compressor is still required at all).
4. Upgrade CESTOR model to incorporate more detailed vaporizer/condenser sizing and costing equations.

Alternate Separation Techniques

The task of separating reaction products and unreacted reactants of the SO_2/SO_3 system can be satisfied by more than one method. The advantages of a fractionated distillation seemed to be so overwhelming that very little effort had previously been spent on considering alternate separation techniques. The need to consider alternate separation techniques became more urgent after the dissociation product compressor in the charging cycle was identified as the major parasitic power consumer. However, all separation techniques will have to compress the dissociation products to a pressure high enough to overcome the vapor pressure in the sulfur dioxide storage tank.

Alternate separation techniques considered include membrane diffusion, freeze-thaw cycles, selective absorption, magnetic moment separation, and Clusius-Dickel diffusion. Freeze-thaw cycles require that the melting points of the compounds be more than 10°K apart and that no eutectic compounds are formed. The melting point of SO_2 is 200°K (-99°F) and that of $\alpha\text{-SO}_3$ is 290°K (62.2°F). Judged by the melting points above, a separation by freeze-thaw cycles may be possible. However, no information about the liquidus-solidus diagram of the binary system SO_2/SO_3 could be obtained. Sparse comments in the literature (Reference 11) state that liquid SO_2 and SO_3 are miscible in all proportions. If an excess of SO_2 is present, nothing separates out on cooling, but a mixture of equal parts deposits the beta-trioxide which redissolves at ordinary temperature. This mixture boils at 278°K . Depending on the amount of SO_3 present, it may be possible to separate the two oxides by cooling close to the freezing point and filtering of the precipitate of SO_3 . Additional studies of the phase diagram SO_2/SO_3 .

are required to evaluate this method. Traces of H_2SO_4 may enhance phase separation. The melting point and phase diagram of the ternary system $\text{SO}_2/\text{SO}_3/\text{H}_2\text{SO}_4$ should be studied as well.

Selective absorption will be aimed at selectively absorbing SO_2 or SO_3 or both, leaving only oxygen behind. Because this can be done at ambient pressure, the oxygen does not have to pass through a dissociation product compressor if it does not have to be stored.

Both SO_2 and SO_3 form Lewis-type adducts with organic amines, preferably tertiary amines or pyridine. The stability constants of these complexes may be sufficiently different that the gases can be stripped at different temperatures and the absorbent recycled. The reaction between the sulfur oxides and the amine (electron donor) is very exothermic. On the other hand, additional heat is required to separate the sulfur oxide from the absorbing agent. Ideally, the absorbing agent and the adducts should be all liquid.

SO_3 can be selectively washed out of an SO_2/SO_3 mixture by concentrated sulfuric acid. SO_3 dissolves in sulfuric acid at up to 40 percent at ambient temperature and pressure forming a fuming sulfuric acid called "oleum". SO_3 can be distilled from oleum by heating the mixture.

Besides sulfuric acid, alkali metal sulfates can also be used to selectively absorb SO_3 from a process stream. The normal reaction between alkali sulfates and SO_3 proceeds according to

M = alkali metal

forming pyrosulfates. Potassium and the higher alkali metal sulfates have the ability to form multiple adducts with gross formulas of $\text{M}_2\text{O} \cdot 8\text{SO}_3$. Potassium sulfate could be used to selectively absorb SO_3 from a process stream. It is not known if SO_2 will interfere in this reaction. The SO_3 could then be stored as the solid sulfate adduct rather than a liquid under pressure. If the inconvenience of solid material handling can be overcome, this would constitute a safe method for storing SO_3 . Besides elimination of the leakage and spillage hazard, the undesirable transformation to the asbestos-type modification of SO_3 is also avoided by forming adducts. The adducts no longer have to be stored hot as the liquid SO_3 does.

As indicated in the above equation, the formation of $\text{XSO}_3 \cdot \text{M}_2\text{SO}_4$ adducts is exothermic. Additional energy is required during the charging cycle to break the adduct bond and evaporate the SO_3 . However, this thermal energy requirement may be smaller than the parasitic power requirement of the dissociation product compressor and condenser coolers of the current design concept.

With regard to the use of potassium sulfate as an SO_3 absorber, it has been observed that when SO_3 and K_2SO_4 are heated together in a sealed tube at 380°K , two liquids are formed. The upper one is free SO_3 ; the lower one, when cooled, forms a solid adduct $\text{K}_2\text{SO}_4 \cdot 7\text{SO}_3$. Similar results are obtained with the sulfates of ammonium, rubidium, cesium, and thallium but not with the sulfates of sodium or lithium.

Paramagnetic and diamagnetic gases can be separated by passing them through a magnetic field and skimming off that part of the flow which has been deflected. This principle has been used for the measurement of (paramagnetic) oxygen in diamagnetic gases. The magnetic susceptibility of oxygen is $+3.449 \times 10^{-3}$ cgs units (paramagnetic) while the susceptibility of sulfur dioxide is -1.82×10^{-5} cgs units (diamagnetic). This difference may be sufficient to design a machine which will separate the two gases. There is no design experience with a separator of this kind.

The magnetic susceptibility of SO_3 is -3×10^{-7} (diamagnetic). Its magnetic properties are too close to those of SO_2 to allow a separation by magnetic fields.

The Clusius-Dickel technique couples thermal diffusion to a countercurrent natural convective flow to effect separation in liquid and gaseous mixtures (Reference 12). The technique has been demonstrated in the separation of gaseous HCl , UF_6 , and N_2 isotopes but is not yet finding large-scale industrial application. Because the technique is so effective in the separation of molecules of very similar molecular weights, it should be comparatively easy to separate gases with molecular weights of 32, 64, and 80 such as oxygen, sulfur dioxide, and sulfur trioxide.

In summary, it may be concluded that none of the alternate separation techniques known to date offers performance or cost advantages over a common distillation/fractionation technique such as the one currently proposed in the baseline design.

Alternate Oxygen Storage Methods

Alternate oxygen storage methods considered here as a replacement for compressed gas storage are liquefied oxygen cryogenic storage, underground cavern dry oxygen storage, and underground aquifer wet oxygen storage. While a large amount of operating data exists on air separation plants, no data could be obtained on liquid oxygen plants operating on gaseous oxygen as a feedstock.

Compressed gases, such as air or oxygen, can be stored very economically in underground caverns leached from salt deposits. This method of compressed air storage is currently being tested in West Germany as a means of load leveling energy storage. The same method can be applied to the storage of compressed oxygen. However, suitable salt formations are not ubiquitous, and the selection of a RCR/STC plant would be restricted to sites with suitable underlying geological formations.

In addition to oxygen, the sulfur oxides could also be stored in underground tanks. Because the storage pressure is minimal compared to compressed air or compressed oxygen storage, restrictions with regard to plasticity of the geologic formation no longer apply. Instead, the formation should be impermeable to gases, free from ground water, and must not react with either sulfur dioxide or sulfur trioxide. Caverns excavated from basaltic deposits and flame sprayed with a glass liner would satisfy these requirements.

In several locations, underground depleted natural gas fields are used to store natural gas pumped from other sources. Storage of this type is used to level out the seasonal demand fluctuations. The storage volume is typically contained in a bubble at the top of a dome formed by impervious material (clay) and pressure in the reservoir is exerted by hydrostatic pressure from surrounding ground water in porous strata. After a reservoir of this kind is thoroughly purged from remaining natural gas, it could be used for the storage of oxygen for an RCR plant. The main disadvantage is that the oxygen withdrawn after storage will be wet and will have to be thoroughly dried before using it in a SO_2/SO_3 reactor.

Similar to the underground compressed oxygen storage in salt caverns, the site selection is very limited if a solar power plant with RCR storage has to depend on aquifer storage of part of its reactants.

Alternate Oxygen Supply Methods

An alternate oxygen supply from air is considered here to replace the closed-loop oxygen supply proposed in the RCR system. The baseline design case of 50 MW_e requires an oxygen flow of 26,853 g/s (59 lb/sec). A CR = 0.6 (charge ratio) implies that the total amount of oxygen to be supplied during a 6.0-hour period is 5.78×10^8 g (1.27×10^6 lb) of air.

Using oxygen from ambient air can be done by separating oxygen from nitrogen and argon and using the oxygen only or by using air instead of oxygen as an oxidizer during the exothermic mode of operation. Both possibilities will be considered here.

There are two cryogenic methods to be considered as a substitute for compressed oxygen storage: oxygen liquefaction and air separation. The former retains the closed-loop feature while the latter converts the system to an open-loop operation and will be discussed in a later paragraph.

Two companies were contacted to obtain information on the separation of oxygen from air by using membrane materials. The companies involved are General Electric (Reference 13) and Dow Chemical (Reference 14). Both have stated that they are in the preliminary development of membranes and that the membrane process would not be available for large-scale operations in the near future. Both companies did give some information regarding costs and purity of oxygen produced. It appears from this information that Dow Chemical has done more work on the scaled up process of oxygen manufacture using membrane materials. The following paragraphs will summarize the information received on each type of material. Both companies use a different form of membrane material.

General Electric is presently engaged in producing a semipermeable membrane material that can increase the oxygen content of air up to 50 percent. Power and cost figures were obtained for a process stream of 28,320 l/min (1,000 CFM) of air at standard conditions. They are as follows:

<u>O₂ Vol. Conc. (Percent)</u>	<u>Membrane Cost \$</u>	<u>Power Consumption (kW)</u>
30	200,000	112
35	250,000	291
50	500,000	298

Extrapolating this for a flow rate of 1.13×10^6 l/min (39,728 CFM) of oxygen at standard conditions, the following is obtained:

<u>O₂ Vol. Conc. (Percent)</u>	<u>Membrane Cost (1976) (\$)</u>	<u>Power Consumption (kW h/kg O₂)</u>
30	2.66×10^7	0.15
35	2.85×10^7	0.34
50	3.99×10^7	0.25

Where the power consumed is for gaseous O₂ at standard conditions of 0°C and 1.01 bar.

It is noted here that the data obtained may be uncertain since General Electric did not optimize the cost nor the power consumption. The cost of the membrane material may be reduced due to the future quantity involved and manufacturing techniques. The power consumption may also be reduced if other than a two-stage vacuum pump to pull the product through the membrane were used.

Even with these considerations, the cost to store oxygen and the power to compress oxygen into storage is still considerably less for the RCR baseline case. Power consumption is 0.06 kW/kg O₂ for the compressor and the cost of the oxygen compressor and storage tanks is 3.2×10^6 dollars (1976). With this information, the closed-loop oxygen system is better for the RCR storage system.

Dow Chemical is presently engaged in producing a hollow-fiber permeable membrane material that can separate oxygen from air. Through a series of these membranes, they claim a 98 percent oxygen product (gas) at reasonably high pressure (about 120 psig). The cost to operate this system is estimated to be able to compete with cryogenic gaseous oxygen manufacture. The reason for this is that the compressed waste gas (mainly nitrogen) is used to drive a turbine, and much of the energy is recovered that was used to push the air through

the membrane material. Actual figures were not given for power consumption or plant cost, but it was admitted that at present the membrane plant would cost more than the cryogenic plant. The next paragraph will cover cryogenic oxygen.

There is much data available on cryogenic oxygen manufacture for both the liquid and the gas. To replace the closed-loop oxygen network of the RCR system with a cryogenic oxygen plant, two methods are possible. The first method would be to use the gaseous oxygen output of the cryogenic plant as the oxygen feed into the O_2/SO_2 mixer. This would involve an oxygen output of 26,853 g/s (59 lbs) for a 6-hour period at CR = 0.6 (charge ratio). The second method would still employ a storage system for oxygen, but the oxygen output would be less for a longer period of time. Output during a charging period of 10 hours would be 16,112 g/s (35.5 lbs).

For direct feed from the cryogenic oxygen plant, a flow rate of 26,853 g/s of gaseous oxygen is required at 147 psia. A practical figure for power consumption (Reference 15) depending on the process involved is about 0.20 hp h/lb. Studies have indicated a range of values from 0.272 to 0.462 hp h/lb. These figures are given for producing essentially pure oxygen at atmospheric pressure. For SI units, the practical figure of energy consumption is 0.329 kW h/kg and the studies range would be 0.447 to 0.760 kW h/kg. These values are uncorrected for compression of oxygen to 10.1 bar (147 psia) and would be slightly higher, depending on the reactor pressure. The cost of the plant would be about 18 million dollars (Reference 16). Other sources estimated the capital cost of such a large air separation plant at 30 to 35 million dollars.

Major disadvantages of this system are the startup energy consumption and time. The power requirement for air separation is much larger than the parasitic power saved during the charging cycle by eliminating the oxygen compressor (5.6 MW_e). It is very doubtful that credit which can eventually be derived from the sale of by-product argon and nitrogen can offset this discrepancy. Similarly, the oxygen produced in the endothermic mode would be hard to sell because it may be contaminated with traces of sulfur oxides.

The air separation plant introduces a time delay in the startup time of the

RCR storage plant in the exothermic mode. It may take 30 minutes for an air separation plant to come on stream. During this time, the RCR system would depend on gaseous or liquid oxygen stored from the previous operation.

In summary, air separation producing pure oxygen for the SO_2 oxidation is not economically attractive for a RCR plant.

For liquid oxygen to be manufactured and stored for RCR use, a flow rate of 16,112 g/s for 10 hours is required. The largest liquid oxygen plants currently in operation produce 400 tons/day (4,200 g/s) and cost approximately \$15 M. The capacity for the baseline design is at least four times higher and would require four such plants. Obviously, the capital cost is much higher than that of the oxygen compressor and compressed oxygen storage tanks it replaces. The energy consumption for liquid oxygen manufacture from air was given as 0.6 hp-hr/lb (Reference 15) as a practical figure. For SI units, this is 0.986 kW h/kg, considerably higher than for gaseous oxygen manufacture. With these figures, it is evident that the closed-loop oxygen system for CES is more economical.

Open Cycle Air

Existing sulfuric acid factories use air instead of oxygen for the oxidation of sulfur dioxide. Because air contains only 20.9 percent by volume oxygen and the remaining nitrogen acts as an inert diluent, exothermic adiabatic flame temperatures are lower than with pure oxygen. In the case of sulfuric acid production, the lower reactor temperature and dilution by nitrogen is desirable because it improves conversion to SO_3 and eliminates hot spots in the reactor. For the RCR applications, it is desirable to deliver heat at as high a temperature as possible.

The dilution of oxygen by nitrogen is tantamount to lowering the partial pressure of oxygen in the reactor. Correspondingly, the dilution effect can be compensated by increasing the reactor pressure. Also, preheating the feed gases before they enter the reactor will allow the system to provide 1,089⁰K (1,500⁰F) helium.

Thermochemical equilibrium calculations using the NASA Lewis CECS 70 computer program have shown that adiabatic reactor temperatures with air are not significantly below those with oxygen as oxidizer (Figure 4-8). The reactor pressure may be increased even beyond 10 bar if higher temperatures are desired. If the

Figure 4-8. EFFECT OF FEED GAS TEMPERATURE, COMPOSITION, AND PRESSURE ON ADIABATIC REACTOR TEMPERATURE

power plant is operated in an open-air cycle instead of closed helium cycle, hot air which leaves the STC power plant can be used as feed for the RCR reactor. Cooling air from various places in the RCR or solar plant can be used for the same purpose.

Operating the SO_2/SO_3 RCR plant with an open air instead of closed oxygen cycle will require some added components. A trade-off analysis will have to be conducted to determine the cost benefit of open air versus stored oxygen operation.

The major added expense is the tailgas cleanup of the oxygen-depleted air leaving the separation column. This gas is mainly nitrogen with some remaining oxygen, but it is contaminated with traces of sulfur dioxide and some sulfur trioxide. In addition, nitrogen oxides may form at the higher temperatures on the catalyst surface. The tailgas cleanup would be similar to that of sulfuric acid factories and sufficient design experience exists with this type of equipment. NO_x contamination of the SO_3 product would also be very undesirable. An additional piece of equipment is the air compressor which compresses air to the exothermic reactor operating pressure.

During the charging mode, SO_3 dissociates into SO_2 and oxygen. In the open air cycle, the oxygen can be discarded or sold to industrial users after purification and liquefaction. Coal gasification plants will require large amounts of oxygen, and geographic proximity to a coal gasification plant might allow additional profit from the sale of solar-generated oxygen. In this mode, the RCR plant becomes an air separation plant by chemical means rather than by physical means. The nitrogen generated in the exothermic mode is not as pure as the oxygen derived from SO_3 dissociation. The nitrogen contains residual oxygen. It is very doubtful that an industrial use, such as for ammonia production, can be found for the nitrogen by-product of the plant.

In trying to obtain a preliminary cost estimate of an open air cycle RCR plant in comparison to the current baseline closed oxygen cycle plant cost, one may assume that all flow components (i.e., reactor, internal heat exchanger, external heat exchanger, distillation column, and mixer) will increase by a factor of five. However, cost of these components does not increase linearly with size. In order to obtain cost of these components, a 250 MW_e case has been calculated using the CESTOR computer program. Because only components

in the exothermic mode have to be resized, a very low charge to discharge ratio of 0.2 was chosen to make sure that the exothermic mode becomes size determining.

The components obtained from this calculation were then added up separately and oxygen compressor, filter, and storage tanks were omitted from the compilation. The results in Table 4-3 show that an air open cycle system would cost approximately twice as much as the basic oxygen system (both systems operating at the improved endothermic reactor pressure of 10 bar).

The air open cycle is not very suitable for the high temperature requirements of a Brayton cycle power plant. The high reactor pressure requires large amounts ($116 \text{ kg/s} = 256 \text{ lb/s}$) of air to be compressed from ambient pressure to reactor pressure ($12.7 \text{ bar} = 183 \text{ psia}$). The parasitic power requirement for this task would be approximately 50 MW_e . It would be desirable to lower the reactor pressure and the working fluid (helium or air) outlet temperature requirements for the open air cycle. However, lowering the output temperature would subsequently reduce the conversion efficiency during turbine operation from storage and thus reduce the round trip efficiency of the CES system.

In summary, it may be concluded that cryogenic oxygen storage or air separation are not economically viable alternates to compressed oxygen storage for the 6-to 24-hour operation on storage regime. Operating the system with air instead of stored oxygen will lower the possible output temperature and round trip efficiency for short-term storage (24 hours). However, the open air cycle has promising potential for long term storage capacity (100 hours) when delivering heat to a lower temperature energy conversion cycle.

Operating Parameter Study

The CESTOR computer program was used to study the effect of exothermic reactor pressure, endothermic reactor pressure, endothermic fractionation column pressure, and oxygen storage pressure on system performance and cost. The study was performed by varying only one parameter at a time, and the results were combined for the purpose of establishing the revised baseline RCR storage plant presented in Section 4.1.

The effect of exothermic reactor pressure, separation column pressure, or oxygen storage pressure on round trip efficiency was only minimal; the round trip efficiency remained in the neighborhood of 44%. The small changes in fractional percents helped to identify trends but did not result in a sub-

Table 4-3
COST COMPARISON -- AIR OPEN CYCLE VERSUS
COMPRESSED OXYGEN CES PLANT*

Item	Cost, \$ (1976)	
	Air	Oxygen
Reactant, SO_3	0.289	0.289
Pumps, SO_2	0.017	0.017
SO_3	0.031	0.031
Reactant tanks, SO_2/SO_3	0.228	0.228
O_2	0	2.449
Mixer	0.052	0.013
Filters	0	0.031
Reactor	11.892	4.861
Separation column	1.720	0.877
External heat exchanger	3.227	1.117
Vaporizer	0.316	0.316
Cooler	0.064	0.013
Compressor, product	0.788	0.760
Air/Oxygen	1.057	0.700
Helium	1.111	1.111
Tailgas cleanup (est.)	<u>1.000</u>	<u>0</u>
Total	21.79	12.92

*50 MW_e , 6-hour storage, CR = 0.6, ENPRI = 10 bar

stantial improvement. However, the dramatic improvement of round trip efficiency by increasing the endothermic reactor pressure strengthens the competitive position of the SO_2/SO_3 RCR storage device.

The effect of reactor pressure on equilibrium composition during the exothermic operation was discussed in Section 4.1.1. As predicted by the principle of Le Chatelier, an increase in reactor pressure results in improved conversion and higher adiabatic reaction temperature. Improved conversion means less recirculation and lower parasitic power loss for compressors and cooling fans. Higher reaction temperature allows the design of a more compact reactor, unless its dimensions are dictated by the endothermic mode. For the original baseline system the endothermic operation sizes the reactor, consequently reducing the exothermic pressure effect. The system was sized and performance calculated for the four different pressures shown in Table 4-4. Reactor dimensions remained unchanged because the endothermic mode is size determining. System cost increases because the reactor and other components need heavier walls in order to withstand the higher pressures.

Table 4-4
EFFECT OF EXOTHERMIC REACTOR PRESSURE

Pressure		Maximum Reactant Exit Temperature (°K)	Product Composition (% by Weight)			Parasitic Power (kW)	Reactor		Round Trip Efficiency (%)	System Cost (M \$)
MN/m ²	psia		SO ₃	SO ₂	O ₂		Diameter (m)	Length (m)		
1.01	147	1,182	73.1	21.5	5.4	102.7	9.15	9.15	43.9	19.08
1.27	183	1,191	72.1	22.3	5.6	101.2	9.15	9.15	43.9	19.62
1.52	220	1,199	76.9	18.5	4.6	108.1	9.15	9.15	43.9	20.19
2.03	294	1,212	79.9	16.1	4.0	139.4	9.15	9.15	43.9	21.38

In general the endothermic reactor pressure should be as low as possible in order to achieve complete dissociation of sulfur trioxide. However, other factors are more dominating on round trip efficiency and system cost than dissociation product decomposition. If the endothermic reactor is operated at higher pressure, less energy has to be spent to compress dissociation products to the condensation pressure. All equipment is less bulky, and heat transfer is much better at higher pressures.

The results summarized in Table 4-5 clearly demonstrate the advantage of higher dissociation reactor pressure both with regard to round trip efficiency and system cost.

Table 4-5
EFFECT OF ENDOTHERMIC REACTOR PRESSURE

Pressure		Dissociation Product Composition (% by Weight)			Dissociation Product Compressor Power (MW _e)	Cost (\$)			Round Trip Efficiency (%)
MN/m ²	psia	SO ₃	SO ₂	O ₂		Dissociation Product Compressor	Reactor	Total	
0.172	25	57.64	33.90	8.46	32.9	3.26	10.01	19.62	43.7
0.25	36	60.87	31.31	7.80	29.7	2.99	8.52	17.92	45.3
0.50	72	66.27	26.99	6.74	20.9	2.24	6.53	15.12	51.3
1.00	145	71.50	22.81	5.70	5.36	0.77	4.86	11.96	67.2

Further improvement may be possible by increasing the dissociation reactor pressure beyond 10 bar. The limit is reached when the reactor outlet pressure approaches the operating pressure of the separation column.

Throughout the stepwise increase of endothermic reactor pressure, the charging mode remained size determining for the reactor. The reactor became more narrow, but longer. If the endothermic reactor pressure is increased beyond 10 bar, a point will be reached where the exothermic mode becomes size determining. It would be desirable to have similar reactor size for either mode of operation. One way of optimizing the system would be to select an exothermic pressure, then gradually increase the endothermic pressure and/or the charge-to-

discharge ratio until the reactor dimensions match.

The endothermic fractionation column pressure is determined by the compression ratio in the dissociation product compressor. It has to be optimized in the narrow regime above the dew point of sulfur dioxide and below the critical pressure of 84 bar (1,230 psia).

The results of the fractionation column pressure study summarized in Table 4-6 indicate that the separation column pressure should be kept as low as possible. Increasing the separation column pressure increases the cost and lowers the round trip efficiency. The dissociation product parasitic power requirements increase faster than the decrease in corresponding oxygen compressor power requirements. The column diameter remains constant with varying pressure, but the column height increases with pressure. This is caused by poor separation efficiency as the pressure approaches the critical pressure of one of the components. At the critical pressure, separation becomes impossible. The results in Table 4-7 show that the round trip efficiency improves if the oxygen storage pressure is lowered. However, the cost for extra oxygen storage tanks increases faster than the benefit derived from a smaller oxygen compressor. Therefore, the overall system cost increases if the oxygen storage pressure is lowered. If the oxygen storage pressure is decreased below 3.5 MN/m^2 (500 psig), the holdup volume of the tanks in relation to the useful storage capacity becomes excessive. A booster pump may then be needed to boost the oxygen pressure to the reactor feed pressure. Capital cost data indicate that it is more economical to operate at the higher pressure.

Process Optimization

As a result of the previous parametric studies, the operating conditions can now be chosen to represent an optimum combination. In the previous cases only one parameter at a time was varied. These results were combined and one set of calculations was conducted wherein three important parameters were varied at the same time. The exothermic reactor pressure was left unchanged at 12.7 bar; but the endothermic reactor pressure was increased to 10 bar, the endothermic column pressure was increased to 10.3 bar, and the oxygen storage pressure was increased to 208.1 bar.

The improvement in system cost and system performance which became possible by optimizing these parameters is illustrated in the baseline system cost

Table 4-6
EFFECT OF ENDOTHERMIC SEPARATION COLUMN PRESSURE

Column Pressure		Separation Column		Compressor Parasitic Power (MW _e)		Cooling Requirement (MW _t)	Round Trip Efficiency (%)	System Cost (M \$)
MN/m ²	psia	Diameter (m)	Height (m)	Dissociation Product	Oxygen			
1.03	150	3.64	12.30	32.3	5.9	-11.15	44.1	19.59
				38.2				
1.21	175	3.64	12.62	32.9	5.6	-11.47	43.89	19.62
				38.5				
1.38	200	3.64	12.93	35.0	5.4	-11.76	42.9	19.79
				40.4				

Table 4-7
EFFECT OF OXYGEN STORAGE PRESSURE

Oxygen Pressure		Number of Tanks	Oxygen Compressor Endo Power (MW _e)	Oxygen Compressor Cost (M \$)	Oxygen Tank Cost (M \$)	Total System Cost (M \$)	Round Trip Efficiency (%)
MN/m ²	psia						
3.5	500	971	2.40	0.43	11.19	28.63	45.61
7.00	1,000	471	4.52	0.67	5.25	23.12	44.31
15.17	2,215	213	5.60	0.79	2.45	20.26	43.89
20.81	3,015	157	6.29	0.87	1.81	19.70	43.31

description at the end of Section 4.1. Using the optimization conditions, the effect of charge to discharge ratio on system cost and round trip efficiency has been studied in one final set of calculations. As shown in Table 4-8, cost increases slightly and round trip efficiency remains quite high until a charge to discharge ratio of 0.8 is exceeded. Below this point, the exothermic mode was size determining and reactor dimensions remained unchanged (Table 4-9). This means that if a higher charge to discharge ratio is dictated by the interface with the solar power plant, this change is easily accommodated without significant cost increases or performance losses compared to the baseline case with a charge to discharge ratio 0.6. The charge to discharge ratio can be increased beyond .8; however, the endothermic mode will become size determining and system cost will begin to rise more rapidly as shown in the accompanying tables.

Since the parasitic power effects the power available in the solar plant for storage, the selection of the proper charge to discharge ration becomes an interactive analysis requiring the repetitive use of the CESTOR and the solar power plant operation programs. This relationship and its effect on the sizing of the RCR storage device and the solar plant is discussed in depth in Section 5.

4.2.4. Ces System Design Matrix

The CESTOR computer program was used to develop RCR storage system conceptual designs for combinations of three different power levels, two storage capacities, and two charge to discharge power ratios as outlined in Table 4-10. The results shown in the table and in Figure 4-9 are based on the new optimized process parameters described in the preceeding paragrapsh. Figure 4-9 shows that RCR plant costs increase nearly linearly with storage time and power level. The most significant result of the study as illustrated in Table 4-10 and again in Figure 4-9 is that for a factor of four increase in the time of operation from storage, the RCR plant cost increased by less than a factor of two.

Table 4-10
DESIGN MATRIX USING OPTIMIZED
OPERATING PARAMETERS

Power output, MW _e	5	50	100	5	50	100	5	50	100	5	50	100
Discharge time, h	6	6	6	6	6	6	24	24	24	24	24	24
Charge:discharge ratio	0.6	0.6	0.6	1.0	1.0	1.0	0.6	0.6	0.6	1.0	1.0	1.0
Round-trip efficiency	0.71	0.71	0.71	0.65	0.65	0.64	0.71	0.71	0.71	0.65	0.65	0.64
Storage plant cost, MS	3.0	11.7	18.5	4.0	15.7	25.0	3.7	18.5	32.1	4.7	22.5	38.5

Table 4-8
OPTIMIZED OPERATING PARAMETERS,
EFFECT OF CR VARIATION, BASELINE
50 MW_e, 6 h STORAGE

Charge-to-Discharge Ratio	System cost (M \$)	Round-Trip Efficiency
0.5	11.296	0.72
0.6	11.654	0.71
0.7	12.105	0.70
0.8	12.717	0.68
1.0	15.655	0.65
2.0	22.590	0.65
3.0	28.420	0.65
4.0	33.797	0.65
5.0	38.852	0.65

Table 4-9
EFFECT OF CHARGE:DISCHARGE RATIO ON
SYSTEM DIMENSIONS, CLOSED OXYGEN CYCLE

CR	Reactor, m		Column, m		Total Cost (M \$)
	Diameter	Length	Diameter	Length	
0.5	5.03	11.00	3.70	11.84	11.3
0.6	5.03	11.00	3.70	11.84	11.7
0.7	5.03	11.00	3.84	11.84	12.1
0.8	5.03	11.00	4.11	11.84	12.7
1.0	5.43	12.92	4.52	11.81	15.7
2.0	7.67	16.16	6.38	11.99	22.6
3.0	9.39	18.66	7.80	11.97	28.4
4.0	10.84	20.74	9.01	11.94	33.8
5.0	12.12	22.63	10.07	11.93	38.9

Figure 4-9. ADVANCED TES COSTS

Round trip efficiency of the CES plant remains fairly constant over a wide range of power levels, storage times, and charge to discharge power ratios. The round trip efficiency is dependent on the parasitic power consumption during both charge and discharge cycle. Parasitic power consumption during the discharging is minimal; but during the charging mode, the parasitic power requirements (product compressor, oxygen compressor, helium compressor) may be substantial unless the process operating parameters are carefully optimized.

4.3. RCR Storage System Technical Assessment

This section presents the results of the technical assessment of the SO_2/SO_3 RCR storage system for the Solar Brayton power plant. The results are presented in six sections which include the topics of availability, life, operation and maintenance, safety, environment, and critical technical problems.

4.3.1 Availability and Cost of Storage Media

Sulfur trioxide is readily available because it constitutes an intermediate product in the production of sulfuric acid. 65,000,000,000 pounds of sulfuric acid were produced in 1974, which corresponds to 53,000,000,000 pounds of sulfur trioxide. Most of the sulfur trioxide is not isolated as such but reacted with water in the same process. A small fraction of sulfur trioxide is liquefied and used for the sulfonation of long-chain paraffins in the production of surfactants. There are two major sulfur trioxide manufacturers in the United States, du Pont and Stauffer. Sulfur trioxide currently sells for \$120/short ton in tank car quantities. The long-term forecast for availability of sulfur is excellent because large quantities of sulfur have to be removed from coal before this abundant resource can contribute to the U. S. energy economy. Diminishing supplies of sulfur come from natural gas purification, petroleum refining, and ore roasting. Elemental sulfur deposits are being mined by the Frasch process. Provided that a cheap energy source can be found, sulfur trioxide can also be recovered from gypsum, the

second largest resource of sulfur in the U.S.

Sulfur is currently available in large quantities, and it has been considered as an asphalt additive or as building insulation material in an effort to find additional outlets for surplus sulfur. Sulfur trioxide constitutes a cheap and readily available chemical for RCR systems.

As an alternate to loading the RCR plant with sulfur trioxide, sulfur dioxide and oxygen can be purchased separately. Sulfur dioxide sells for \$130/short ton and is a more common commodity in chemical trade than sulfur trioxide. Large quantities of sulfur dioxide are consumed by the paper industry.

Assuming that a vanadium catalyst can be developed which does not have the volatility problem of current catalysts, the supply of vanadium would not constitute a limitation to the SO_2/SO_3 CES. For sulfuric acid production, depending on the type of catalyst used and the feed gas composition, 117 to 160 kg catalysts are used per metric ton/day capacity. With a U.S. installed sulfuric acid capacity of 70 billion pounds/year, there must be approximately 1,100 metric tons of catalyst corresponding to 49 metric tons vanadium in use in the U.S. at this time. This constitutes only a small fraction of the 6,000 metric tons (1974) annual consumption of vanadium in the U.S. The addition of CES catalyst vanadium requirements would have no significant impact on the vanadium market.

4.3.2. Useful Life of Storage System

The useful life of the storage system is limited by the life of the catalyst and system components. Catalyst durability and useful life predictions is certainly the most critical concern as discussed above. Next to the uncertainty about catalyst life, moving parts in the dissociation product compressor and the sulfur oxide feed pumps must be considered as high maintenance items. Based on experience in paper mills where sulfur dioxide is pumped from tank cars to vaporizers and sulfite absorbers, liquid sulfur dioxide pumps used can operate in excess of 10 years without problems. Sulfur dioxide has been in household refrigerators for many years prior to the introduction of fluorocarbons, and many units have operated in excess of 10 years with virtually no maintenance.

Less data are available for long-term operation with sulfur trioxide.

Generally sulfur trioxide is more corrosive than sulfur dioxide because it forms sulfuric acid in moist air if a leak develops. Because the solar power plant RCR storage system will be located in a dry climate, corrosion from SO_3 leaks will be less severe than in a humid climate.

4.3.3 Operation and Maintenance Requirements of the RCR Storage System

The RCR storage system requires more operation supervision and will require more maintenance than the other thermal energy storage systems. Plant operation discussed in this section includes initial startup, operational startup, process controls, and shutdown.

For the initial startup, it is assumed that the system has been thoroughly cleaned and dried after assembling the components and loading the catalyst. This will be achieved by evacuating and backfilling with oxygen. If a supported catalyst is used, the catalyst should be dried prior to admitting sulfur trioxide by heating in vacuum or with a stream of oxygen flowing. The heat can be provided by hot helium flowing through the internal heat exchanger tubes. The oxygen stream can be recirculated and dried by operating the oxygen compressor at partial load and passing it through the molecular sieve filters. After drying the system and filling it with dry oxygen, the sulfur trioxide tanks will be loaded from tank cars. The system is then ready to operate in the endothermic mode as soon as excess hot helium is available beyond that required for operating the gas turbine. During initial trial runs, the endothermic reactor can also be operated without sharing the helium supply with the gas turbine.

After all sulfur trioxide has been decomposed, the system is ready to begin trial runs in the exothermic mode. It would be preferable to conduct the exothermic startup shortly after completing the endothermic test while the reactor is still hot. Depending on the catalyst used, the exothermic reaction becomes self-sustaining above 670°K (750°F). Lower ignition temperatures can be achieved with platinum catalysts. The necessity to start with a preheated reactor does not constitute a severe problem because the reactor will remain hot enough for several days after its last operation. An exothermic startup from a cold condition is very rarely required. If this requirement should ever arise, existing marginal isolation will produce

helium hot enough to preheat the reactor early in the morning or late in the afternoon.

The RCR storage plant will be thoroughly instrumented to monitor process conditions, to sense process upsets, and will be remotely controlled from a central control room. Similar fully automated chemical process plants operate with a minimum of personnel and usually do not require any personnel outside the control room.

If the RCR plant has to be shut down between charging and discharging cycles, the sulfur oxide feed will be shut off and a slow flow of oxygen will be maintained during the cooldown to maintain a positive pressure throughout the system. During standby, a positive pressure (20 psia) will be maintained to prevent leakage of ambient moisture into the system.

System components which require regular maintenance are pumps and compressors. These components will be continuously monitored for leaks by electronic leak detectors. The plant will have one set of operating and one set of standby pumps and compressors. In this way, the plant can continue to operate while the defective pump or compressor is repaired or replaced.

Another major maintenance job would be catalyst replacement. The temperature profile in the reactor units will be measured. If the catalyst should become deactivated, this will result in a different temperature distribution in the reactor. Diagnostic tests performed on catalyst samples removed from the reactor will determine if the catalyst bed needs replacement or not. This type of replacement applies to packed bed reactors or tube wall reactors only. Fluidized bed or molten catalyst reactors can be regenerated or replaced continuously.

Operation and maintenance costs for the RCR storage system have been included separately in the plant energy economics. These cost estimates are based on chemical process industry maintenance experience with similar sulfuric acid plants which indicates that annual maintenance materials cost is approximately 2% of capital investment.

4.3.4 Plant Safety Analysis

Sulfur dioxide and, in particular, sulfur trioxide are hazardous chemicals. However, these chemicals are routinely handled in large quantities in the industry, and sufficient experience has been accumulated to allow safe handling. In the RCR system, the chemicals would be hermetically sealed most of the time, and the chemicals have to be handled only during initial loading of the system and eventual repair work.

The inhalation, direct skin or eye contact with either SO_2 or SO_3 represents extreme personnel hazards. Safety and treatment procedures will have to be adopted and readily available throughout the plant.

In order to minimize the problems that can develop when liquid sulfur trioxide is spilled, every plant using or storing liquid sulfur trioxide should develop a predetermined plan to contain possible minor and major spills of liquid sulfur trioxide. Should a small leak or spill occur, the best procedure is to absorb the sulfur trioxide on dry sand or dirt, expanded clay, diatomaceous earth or another non-reactive absorbent material until repairs can be made. It can then be removed from the area and neutralized with water or a solution of soda ash, lime, or any caustic material. A large or uncontrolled spill of liquid sulfur trioxide will release tremendous volumes of "smoke". The "smoke" obscures the source of the liquid sulfur trioxide and makes it extremely difficult to determine the cause of the spill. "Smoke" from such a spill should be controlled with water or a mechanical foam system. Use of water fog or mechanical foam to control the "smoke" generates sulfuric acid mist that is formed by the reaction of the water with the liquid sulfur trioxide. Liquid sulfur trioxide confined within an open reservoir or sump can be sealed over with an inert immiscible fluorocarbon oil mixed with glass bubbles. The seal prevents reaction of the moisture vapor in the air with the sulfur trioxide with the resultant release of tremendous volumes of "smoke". All plants should be equipped with either an in-place slurry seal system, or with a manifold installed to dispense the slurry seal over the spilled liquid sulfur trioxide surface within the storage area.

4.3.5 Environmental Effects

The operation of an RCR system in a normal operating mode is not expected to result in any significant environmental effects. Any SO_2 and SO_3 which should escape through small leaks are readily absorbed by rain and soil. A

minimum sulfur (sulfate) content of soil has to be maintained if optimum crop yields are expected from agricultural land. Neither SO_2 or SO_3 are persistent contaminants such as polychlorinated biphenyl heat transfer fluids or other halocarbons. SO_2 and SO_3 are naturally occurring in volcano vents and fumaroles, and the SO_2/SO_3 content of the Earth's atmosphere was most likely much higher in early geological times of high volcanic activity.

4.3.6 Critical Technical Problems

As already mentioned in previous paragraphs, the SO_2/SO_3 CES system will draw on the experience gained with the production of sulfuric acid. However, current sulfur dioxide converters do not operate at temperatures near those required for the Solar Brayton Power plant. The other technology gap is the lack of sulfur trioxide dissociation reactors. While the production of sulfur trioxide is a common industrial process, the dissociation is not. The dissociation of sulfur trioxide occurs as a yield-limiting process in the oxidation of sulfur dioxide, and it is current practice to minimize the back reaction.

The following, more detailed discussion deals with the technology status of high temperature packed-bed reactors and materials. The critical technical problems identified in this section forms the basis of the Phase I program plan presented in Section 7.

High Temperature Packed-Bed Reactors

Packed-bed reactors with supported catalysts operate routinely at temperatures up to $1,255^\circ\text{K}$ ($1,800^\circ\text{F}$) and pressures up to 620 bar (9,000 psia). Examples for this type of reactor are the monopropellant hydrazine decomposition reactors which are used in gas generators and rocket thrusters. Operating time of these devices is currently limited by the life of the catalyst and is short in comparison to a 30-year operating requirements for the RCR storage.

Materials

Materials compatibility has to be ascertained for sulfur oxides both in the liquid and gaseous state. For storage of liquid sulfur dioxide or sulfur trioxide, sufficient experience exists in the chemical industry. Mild steel can be used as long as the reactants are kept dry.

Less information is available with regard to the compatibility of metals and ceramics with sulfur oxides at temperatures up to 1,144⁰K (1,600⁰F). The Stellite Division of Cabot Corporation and Huntington Alloys have been contacted and asked for compatibility of Haynes 188 and Inconel 617, respectively, with sulfur oxides at 1,500⁰F. However, no experimental data were available on either alloy. Limited compatibility data were available on Inconel 617 in flue gases that were rich in sulfur oxides. However, the presence of water (steam) results in a different corrosion mechanism. Corrosion in dry SO₂/SO₃ may be less severe than in the wet system.

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Section 5. SYSTEM ANALYSIS

Thermal energy storage system analysis and plant integration studies were undertaken in order to assess the impact of storage on plant performance and resultant energy costs. The ultimate objective of the system analysis effort is to establish a data base which will support the relative evaluation of the various TES alternatives. This section presents the results of the system analysis studies and includes a description of the solar plant operation the energy cost calculations, the solar plant/storage sizing for minimum energy cost, and the comparative economic of the various storage system alternatives in the Solar Brayton power plant.

Figure 5-1 illustrates the overall approach to the system analysis task. The solar power plant definition was established as a part of the ground rules to the study reported here. The storage system concept definition, plant integration, and optimization has been described in depth in Sections 2, 3, and 4. The solar plant, optimization and energy cost analysis are the primary subjects of Section 5. The results of this complete process must ultimately become input data to the utility grid integration and impact analysis which is the subject of further work beyond those results presented here.

5.1 PLANT INTEGRATION AND OPERATION

Plant schematics illustrating the approach used to integrate storage into the solar power plant thermodynamic loop is shown in Figure 5-2. The bold lines shown in the two schematics identify the helium flow lines that are active during the storage charge and discharge cycles. The thermodynamic state variables (pressure and temperature) at the design point conditions for the two modes of operation are shown in tables below each schematic. The state point data shown in Figure 5-2 are based on the phase charge storage device with a pinch point temperature limit of 84°C . State point data for the sensible heat and RCR storage devices are shown in Tables 5-1 and 5-2 respectively.

The operation of the plant, the plant control algorithm, and a representative daily operating cycle are described in the following paragraphs.

Figure 5-1. **System Analysis—Approach**

- OPERATIONAL FLEXIBILITY
- STORAGE ALTERNATIVES
- MINIMIZE ENERGY COST

Plant Operation

During periods of high insolation, energy in excess of that required to drive the turbine is used to charge storage in a fluid circuit that operates in parallel with the turbine as shown in Figure 5-2. The duration of charge cycle is limited by the energy capacity of the storage device. For the RCR device this limit is simply established by the amount of reactant constituents available in the storage device. For both thermal devices, the charge cycle limit is established by the rise in temperature of the storage discharge gas. This temperature rise occurs very rapidly as the storage device reaches its thermal energy capacity, establishing the "pinch point" cycle design point operating conditions presented in the tables accompanying Figure 5-2.

During periods of reduced or no insolation, thermal energy is withdrawn from storage to supplement or replace the receiver as a heat source. The discharge time is established by the amount of energy that has been put into storage during the charge cycle, and by the rate at which the device is discharged. Once again for the RCR device this limit is simply established by the amount of reactants that have been generated and are thus available for the reverse reaction. For both thermal devices this limit is established by the drop in temperature of the storage discharge gas. This temperature drop occurs very rapidly as the storage device reaches its original energy level, establishing the minimum turbine operating conditions presented in the tables that accompany Figure 5-2. A helium inventory system will be used in the power plant control loop under these reduced turbine inlet temperature conditions in order to maintain and control the plant output at the rated capacity.

Plant Control Algorithm

The following plant operation policy is the framework of the power plant control logic, that has been developed to support the analysis of the plant operation.

- o Generator output for demand load is always first priority.
- o Insolation energy in excess of generator demand is used to charge storage.
- o Demand load profile is flat with a specified start time

Figure 5-2. Storage/Plant Schematic

State Point	Temperature (°C)	Pressure (MN/m ²)
1	49	.95
2	152	1.75
3	581	1.70
4	816	1.70
5	609	.95
6	179	.95
7	816	1.65
8	699	1.60
9	732	1.70
10	663	1.70
11	816	1.70

Pinch Point
 $\Delta T = 84^\circ\text{C}$

State Point	Temperature (°C)	Pressure (MN/m ²)
1	49	2.0
2	143	3.5
3	435	3.5
4	598	3.4
5	454	2.1
6	165	2.0
7	598	3.4
8	435	3.5
9	435	3.5
10	--	--
11	--	--

Minimum turbine inlet temp. — inventor ratio=2.

Phase Change TES State Point Tables

Charge Cycle

State Point	Temperature (°C)	Pressure (MN/m ²)
1	49	.95
2	152	1.75
3	581	1.70
4	816	1.70
5	609	.95
6	179	.95
7	816	1.65
8	673	1.60
9	705	1.70
10	642	1.70
11	816	1.70

Discharge Cycle

State Point	Temperature (°C)	Pressure (MN/m ²)
1	49	2.0
2	143	3.5
3	435	3.5
4	598	3.4
5	454	2.1
6	165	2.0
7	598	3.4
8	435	3.5
9	435	3.5
10	--	--
11	--	--

Minimum turbine inlet temp. — inventory ratio=2.0

Pinch Point $\Delta T=111^{\circ}\text{C}$

Table 5-1 State Point Data (Sensible Heat TES)

Peak
Charge
rate =
102 MW_t

Charge Cycle

State Point	Temperature (°C)	Pressure (MN/m ²)
1	49	1.9
2	152	3.5
3	581	3.5
4	816	3.4
5	609	1.9
6	179	1.9
7	816	3.4
8	552	3.2
9	581	3.5
10	581	3.5
11	816	3.4

Discharge Cycle

State Point	Temperature (°C)	Pressure (MN/m ²)
1	49	1.3
2	152	2.4
3	581	2.4
4	816	2.3
5	609	1.3
6	179	1.3
7	816	2.3
8	581	2.4
9	581	2.4
10	--	--
11	--	--

Table 5-2, State Point Data (RCR Storage)

Plant Control Algorithm (Cont'd)

- o Early morning insolation prior to generator start-up is used to charge storage.
- o Insolation energy in excess of storage limit is rejected in the reflector field.
- o Storage is charged in a separate flow circuit (See Figure 5-2)
- o Storage is discharged in a series circuit with receiver (See Figure 5-2).
- o Power plant operates as a stand-alone system with the turbine providing all power requirements including grid demand and storage parasitic power.
- o Plant operation is based on a complete daily cycle; daily operation is complete when storage is fully depleted.
- o Plant begins daily operation with storage fully depleted.

The mathematical logic used in the computer program to implement this operation policy was developed with two key objectives in mind. First, to represent the functional interface among the plant subsystems in terms of the operating variables most likely to enter the real plant control system. Secondly, to provide a simple, flexible system which will eventually allow the investigation of alternate operation policies. Both objectives have been met. The resultant logic algorithm is shown in Figure 5-3.

The first level plant operating condition checks are shown in Figure 5-3 in conjunction with the five major plant operating modes which are shown in the shaded blocks. The operation of the power plant in each of the five modes is controlled by a separate subroutine in accordance with the plant operation schematics shown in Figure 5-2. During periods of high insolation with the utility grid demand active, energy input to the helium stream in excess of that required to drive the turbine is used to charge storage. The high temperature gas flow from the receiver is transported in part to the turbine to meet the plant demand output, and in part to a separate fluid circuit which includes the storage device and a high temperature pump. The pump provides the input energy required to circulate the helium and must be sized to meet the flow requirements encountered as the storage device reaches its fully charged condition. This particular mode is identified in Figure 5-3 as mode 5. Mode 2 is analogous to 5

Figure 5-3. Plant Control Algorithm

except there is no demand, and the corresponding control algorithms are simplified.

During periods of reduced or no insolation, thermal energy is withdrawn from storage to supplement the receiver input or to replace the receiver as a heat source in the absence of insolation. During periods of no insolation (control mode 3), the storage device is used directly as the heat source in the helium turbine cycle. In this mode, there is no helium flow into the receiver circuit and the high temperature pump is bypassed on the inlet side of the storage unit.

During periods of partial insolation (control mode 3), helium from the recuperator first passes through the receiver and then through the storage device. In this mode, the receiver and storage device act in series as the heat source for the helium turbine, with the receiver providing the low temperature heat increment and the storage providing the high temperature increment. This approach keeps the high temperature end of the storage unit nearest the turbine inlet and gives the highest conversion efficiency in the receiver.

In mode 4 the storage circuit is inactive. The turbine is the only heat consumer in the power plant loop, and the insolation input to the receiver is adjusted by this plant control algorithm to meet the turbine heat consumed for the demand load.

Representative Daily Operating Cycle

A representative daily plant operating power cycle is shown in Figure 5-4. The upper curve shows the receiver heat input as it comes from the collector field. The broken curve below it is the amount of heat absorbed in the helium circuit. This heat is divided into components (also indicated) for direct use in the turbine generator cycle and to charge storage. The particular mode of operation shown uses the first few hours insolation to charge storage with a limited amount of heat used in the turbine-generator to produce the power to run the storage mode (plant control mode 1).

The generator is put on-line to furnish 50 MW_e to the grid at 8 AM. The plant module runs uninterrupted in control mode 5 until shortly before 1300 hours (1 PM) when the 6-hour storage limit is achieved. At this time, until 1800 hours the amount of heat from the collector field is excessive and some heat must be rejected (shaded region). At 1800 hours, the storage system begins discharging as the

Figure 5-4. Plant Operation—Representative Daily Cycle
(Power Distribution)
(Phase Change TES System)

Representative Daily Operating Cycle (Cont'd)

receiver output drops off (control mode 3) until finally the plant is running only on heat from the phase change storage device (plant control mode 2). The daily cycle in summer is completed shortly after 2400 hours, the plant then having been operated for 16 hours.

The heat rejected due to storage limits represents lost energy for the summer insolation condition. For the winter, spring and fall insolation conditions, the storage limit is not reached during the daily operating cycle; consequently there is no rejected or lost insolation. Approximately 5% of the yearly insolation is rejected for the 6 hour phase change TES device in the baseline 50 MW_e power plant. Heliostat field size and storage time both effect this loss and consequently effect the energy output of the plant. The relationship between storage time, heliostat field size is the primary subject of Section 5.4.

5.2 WEEKLY CYCLE FOR RCR STORAGE

Energy capacity in the RCR system is dependent only on the amount of reactant constituents in the storage system. Consequently, the RCR storage device tends to become economically attractive at very long storage times (20 - 30 hours). Storage times up to 15 hours can be achieved with the daily operating cycle described in Section 5.1 by increasing the collector area and/or reducing the power rating of the plant. This approach increases the charge to discharge power ratio of the storage device dramatically (see Figure 5-5), which increases the RCR system cost, offsetting the economic advantage of long storage times. Longer charge cycles must therefore be employed in order to fully exploit the long time storage device.

The weekly operating cycle, described in the following paragraphs, was evaluated as one approach to accomplishing this objective. The object of the weekly storage cycle, as shown schematically in Figure 5-6, is to store energy at zero plant output on the weekend and to then use this stored energy to extend the plant operating hours during the week. The two power distribution curves shown in Figure 5-7 are representative weekly plant operating cycle charts for the baseline solar power plant.

Figure 5-5. RCR Storage/Solar Brayton Plant Integration

Figure 5-6. **Weekly Cycle Analysis**

Figure 5-7. Plant Operation—Representative Weekly Cycle
(SO₂/SO₃ RCR Storage)

5.2 WEEKLY CYCLE FOR RCR STORAGE (Cont'd)

The operating chart at the top of the figure shows the weekend daily operating cycle with no electrical output to the utility grid. The plant operates throughout the weekend in control mode 1, simply dividing the input power into power to storage and power to the turbine generator to meet the storage charge cycle parasitic load.

The operating power chart at the bottom of Figure 5-7 shows the typical summer weekday power cycle with 50 MW_e electric output on a 24 hour a day basis.

This cycle is similar to the daily operations shown in Figure 5-4 with no storage limit encountered and continuous electrical output. During the summer season the storage time limit is encountered late Sunday afternoon and some insolation energy is rejected until late Monday afternoon. For the winter, spring and fall seasons the storage limit is generally not encountered. Heliostat field size and the storage time both effect the amount of rejected insolation and consequently effect the energy output of the plant. The relationship between storage time, heliostat field size, and energy cost for the weekly cycle is discussed in Section 5.4.

5.3 ENERGY ECONOMICS

Energy costs are developed to serve as a basis for overall economic comparison of the various solar power plant subsystem alternatives. The approach used is based on the levelized fixed charge rate method suggested in the Aerospace Mission Analysis report (reference 1). This particular approach provides a simplified method to relate plant capital investment and plant energy output to a common variable - busbar energy cost expressed in mills per kilowatt hour. The method of implementation of this approach in the work reported here is presented in the following paragraphs.

A summary of the energy cost methodology is shown in Figure 5-8. The busbar energy cost computed by this approach is the cost of energy at the busbar levelized over the operating life of the plant. This cost is composed of three parts:

Figure 5-8. **Energy Cost**

Generation cost

- Busbar energy cost = fixed charges + incr fuel cost + O&M

$$BBEC = \frac{CC \times FCR}{CF \times 8.76} + \frac{FUF \times HR \times FC}{10^3} + VO\&M + \frac{FO\&M \times 100}{CF \times 8.76}$$

Where CC	=	capital cost, \$/kW*
FCR	=	fixed charge rate, %/year
CF	=	capacity factor, %
FUF	=	fuel utilization factor, %
HR	=	heat rate, Btu/kWh
FC	=	levelized fuel cost, ¢ /million Btu
VO&M	=	variable operating and maintenance cost, mills/kWh
FO&M	=	fixed operating and maintenance cost, \$/kW/yr

Fixed charges

- Fixed charges = depreciation + cost of money + insurance + taxes = 15%
- Fixed charge rate is levelized average discount expressed as percent of capital investment at year of commercial operation

* Year of commercial operation

5.3 ENERGY ECONOMICS (Cont'd)

1) cost of the capital investment, 2) incremental fuel cost, and 3) the cost of operating and maintaining the power plant.

The cost of the capital investment is determined on the basis of a levelized annual discount rate which includes depreciation, cost of money, insurance, and taxes. This is a fixed annual charge, it is based on total capital investment at the time of initial commercial operation, and it is proportioned to the total yearly energy output of the plant.

The incremental fuel cost is simply determined by the levelized cost of fossil fuel, if any, consumed to generate each kilowatt hour of output. Levelized operation and maintenance costs consist of two parts: 1) variable operating and maintenance costs incurred in the generation of each kilowatt hour of output (e.g. fuel handling costs in fossil supplement), and 2) fixed operating and maintenance costs which are incurred independent of the energy output of the plant (e.g. heliostat cleaning) and must be proportioned to the energy output of the plant.

The plant capital cost (which is to be discounted by the fixed charge rate) is established for each plant /storage configuration by combining the cost of the alternative storage subsystems with the baseline cost accounts defined in the study ground rules. The resultant cost is expressed in dollars of capital investment at the time of initial commercial operation per kilowatt of rated plant capacity.

The yearly energy output of the plant (i.e. capacity factor) is determined by the plant operation analysis discussed in Section 5.1. The capacity factor is expressed as a percent of continuous operation at the plant rated capacity, and includes a 10% reduction for planned maintenance.

5.4 PLANT/STORAGE SIZING FOR MINIMUM ENERGY COST

This section presents the results of three trade studies which demonstrate the approach used to size the solar power plant and the thermal storage system for minimum energy cost. The studies include both advanced storage system concepts (phase change, and RCR) and the weekly cycle with RCR storage.

Collector area per plant module was varied from $.42\text{Km}^2$ to $.74\text{Km}^2$ and a single module plant was investigated with the weekly cycle operation. Storage times were varied from 4 hours to 15 hours for the daily cycle, and from 15 hours to 35 hours for the weekly cycle.

The baseline power plant characteristics were used throughout the trade studies except as noted in the following paragraphs.

5.4.1 Receiver Sizing and Cost Scaling

Ideally, the solar receiver is sized by the collector area and adjustments in many of the receiver design characteristics as well as the receiver cost and performance should accompany the collector area variations. The extent to which this has been accomplished is reported here.

The receiver configuration selected as the baseline concept during the RP377-1 study is shown in Figure 5-9. The aperture to admit reflected energy from the collector field is circular and is located at the bottom of the receiver facing downward. Aperture area is one of the key determinants of the receiver performance as described in Volume IV of this report. The aperture area is sized to assure that the maximum amount of available heat is collected by the receiver to be passed to the helium.

A plot of the heat flux distribution with radial position of the aperture is shown on Figure 5-10. The aperture radius is determined at the position when more heat would be lost by reradiation from the receiver than could be gained from the field by increased aperture size. Aperture size determined on this basis as a function of collector area is as follows:

Figure 5-9. Receiver Configuration

Figure 5-10. Heat Flux Distribution—Horizontal Circular Aperture

Table 5-3
RECEIVER APERTURE SIZES

Collector area (km ²)	Aperture radius (m)
1.36	11.20
1.16	10.25
1.00	9.60
0.84	9.35

Preliminary cost estimates for the RP 377-1 receiver were reviewed for the purpose of establishing an appropriate receiver cost scaling relationship. Virtually all of the receiver subsystems are directly related to the power capacity of the receiver which is directly related to the collector area for a fixed collector/tower/receiver optical configuration. Consequently, the receiver cost can be simply stated as a cost per square meter of collector area. The RP 377-1 receiver cost of 17\$/m² was used in the results presented here.

The tower, which is considered a part of the receiver subsystem, must also be changed with changes in collector area. In this case, the assumption of constant optical properties, dictates the change required in tower height and thus tower cost.

For a fixed optical configuration tower height varies directly with collector field width. The tower cost is approximately proportional to its height, and is therefore directly proportional to the collector field width. The RP 377-1 tower cost of 40\$/m (field width) was used in the results presented here.

5.4.2 Heliostat Field Performance and Cost

The heliostat field performance is given in the study ground rules for the base-line power plant. Field performance is given there in terms of overall field efficiency as a function of time of day and season of the year. For the purpose of the preliminary sizing studies presented here, these data were not changed with collector area. This approach is equivalent to the assumption of constant optical properties.

Collector field cost used in the results presented in the following section is 60\$/m² as stated in the study ground rules.

5.4.3 Storage System Costs

Parametric conceptual design data is presented in Sections 3 and 4 for the two advanced storage system concepts. Cost data taken from those studies and used in the results presented here are shown in Figure 5-11.

For the phase change device, storage system costs are based on a fully integrated 6 hours design. The data for other storage times as described in Section 3 are based on performance requirements consistent with the six hour data. This approach is valid for charge to discharge power ratios less than about 1.5 at which point the phase change heat exchanger will be sized by the charge condition rather than the discharge condition.

For the RCR storage system, the costs include integration studies at each collector area as indicated in Figure 5-11. Integration studies are required, as discussed in Section 4, since the RCR device cost and performance are strongly dependent on charge to discharge ratio.

5.4.4 Sizing Study Results

Results of the sizing study are shown in Figures 5-12, 5-13 and 5-14. Figures 5-12 and 5-13 show the sizing study data for the daily cycle with phase change storage and RCR storage respectively. Figure 5-14 shows the results of the weekly sizing study for RCR storage system. Each figure shows seasonally adjusted gross capacity factor and levelized busbar energy cost as a function of storage limit in hours and collector area in km^2 .

The data shows that a reasonably wide range of storage times and collector areas produce the same near minimum value of energy cost, even though the plant capital costs vary significantly over the same range of variables. The daily data also shows that the energy costs for the baseline plant (i.e. 6 hour/.5 km^2) are near these minimum values for the phase change system.

For the RCR daily cycle, the data indicates that storage time should be increased to approximately 9 hours. In the case of the weekly cycle, there is very little change in the minimum energy cost over the entire range of collector areas studies. Consequently, the design point selected for the weekly cycle was based on the capacity factor rather than the energy cost.

FIGURE 5-11. ADVANCED TES COSTS

Figure 5-12, Solar Power Plant Sizing - Daily Cycle

- Phase Change Storage
- 50 MWe Capacity
- Inyokern, Ca.

5-23

Figure 5-13. Solar Power Plant Sizing – Daily Cycle

- SO_2/SO_3 RCR Storage
- 50 MWe Capacity
- Inyokern, Ca.

Figure 5-14. **Solar Power Plant Sizing – Weekly Cycle**

- SO_2/SO_3 RCR Storage
- 100 MWe Capacity
- Inyokern, Ca.

In all three cases the data shows that capacity factor can be increased significantly at very little increase in the busbar energy cost. This implies that utility margin requirements and the associated backup capacity requirements, which are affected by the solar plant capacity factor, will ultimately become a direct determinant in the sizing of the solar power plant.

5.5 COMPARATIVE ECONOMICS

This section presents the results of the comparative economics study that was undertaken to establish a final figure of merit for each of the storage system alternatives. Two conventional storage concepts were introduced on the basis of the survey work carried out by Public Service Gas and Electric of New Jersey (Reference 2) for comparison with the thermal systems.

In contrast to the thermal storage devices, the conventional storage devices operate on the basis of electric energy input as shown schematically in Figure 5-15. Consequently, a short term thermal storage device is also required in the plant thermodynamic loop to satisfy the buffering requirement. Each of the conventional storage devices discharge through a conventional power plant. The cost range for these devices presented in Reference include all the elements of the associated power plants and these costs are included in the results presented here.

Figure 5-16 presents all the pertinent economic parameters for each of the seven Solar Brayton Power Plant configuration alternatives. All data for the compressed air and underground pumped hydro storage systems are based on the data presented in Reference 2. Data for the hybrid concept are taken from the RP 377-1 study results and the data for all TES systems are as previously presented.

Itemized cost accounts for each of the seven plant configurations are shown in Tables 5-4 through 5-10. Final comparative performance, cost, and levelized busbar energy cost estimates are presented in Figure 5-17. The hybrid system as expected gives the lowest busbar energy cost. A capacity factor of 62% was used in the hybrid concept to put it on a comparative basis with the other plant alternatives. A higher capacity factor for the hybrid concept will decrease the resultant busbar energy cost further increasing the advantage of the hybrid concept.

Figure 5-15. **Storage Alternatives**

Alternative	(1)	(2)
Compressed air		
Underground pumped hydro		
TES		
Hybrid		

Figure 5-16. **Storage System Economic Parameters**

Storage system	Storage capital cost		Operation and maintenance cost		Heat rate	Fuel cost	Charge to discharge rate
	\$/kW	\$/kWh	\$/kW/yr	mills/kWh	Btu/kWh	¢ /MBtu	
Fossil fired hybrid	—	—	—	8.0	11,000	250	—
Phase change	50	15.2	—	6.0	—	—	0.65
Sensible heat	42	52.1	—	6.0	—	—	0.74
Reversible chemical reaction (9 hr)	217	7.6	5.3*	6.0	—	—	0.90
Compressed air	135	6.5	—	11.3	4,850	250	1.00
Underground pumped hydro	118	6.0	1.6	6.0	—	—	1.00
Reversible chemical reaction (30 hr)	340	7.6	11.4*	6.0	—	—	1.54

* 2% RCR system cost per year

Table 5-4
100MW_e BASELINE COST ACCOUNTS (HYBRID)

Collector area (km ²) - 1 module	.5
Storage time (hour)	.5
Account	
Land	1
Structures and facilities	51
Heliostats	300
Central receiver/tower heat exch	105
Storage/tanks	68
Boiler plant	73
Turbine plant equipment	105
Electric plant equipment	20
Misc plant equipment	16
Allowance for cooling towers	15
Total direct cost	754
Contingency and Spare parts allowance (5%)	38
Indirect costs (10%)	75
Total capital investment (1975)	867
Interest during construction (15%)	130
Total cost at year of commercial oper.	997

42 \$/kW
52.1 \$/kWh

Table 5-5

100MW_e BASELINE COST ACCOUNTS (PHASE CHANGE TES)

Collector area (km ²) - 2 modules	1.0	
Storage time (hour)	6	
Account		
Land	2	
Structures and facilities	44	
Heliostats	600	
Central receiver/tower heat exch	209	50 \$/ kW
Storage/tanks	141	15.2 \$/ kWh
Boiler plant	---	
Turbine plant equipment	119	
Electric plant equipment	20	
Misc plant equipment	28	
Allowance for cooling towers	15	
Total direct cost	1178	
Contingency and Spare parts allowance (5%)	59	
Indirect costs (10%)	118	
Total capital investment (1975)	1355	
Interest during construction (15%)	203	
Total cost at year of commercial oper.	1558	

Table 5-6
100MW_e BASELINE COST ACCOUNTS (SENSIBLE HEAT TES)

Collector area (km ²) - 2 modules	1.0	
Storage time (hour)	6	
Account		
Land	2	
Structures and facilities	44	
Heliostats	600	
Central receiver/tower/heat exch	209	42 \$/ kW
Storage/tanks	355	52.1 \$/ kWh
Boiler plant	--	
Turbine plant equipment	119	
Electric plant equipment	20	
Misc plant equipment	28	
Allowance for cooling towers	15	
Total direct cost	1392	
Contingency and Spare parts allowance (5%)	70	
Indirect costs (10%)	139	
Total capital investment (1975)	1601	
Interest during construction (15%)	240	
Total cost at year of commercial oper.	1841	

Table 5-7
100MW_e BASELINE COST ACCOUNTS (RCR STORAGE)

Collector area (km ²) - 2 modules	1.0	
Storage time (hour)	9	
Account		
Land	2	
Structures and facilities	44	
Heliostats	600	
Central receiver/tower/heat exch	209	217 \$/kW
Storage/tanks	287	7.75 \$/kWh
Boiler plant	--	
Turbine plant equipment	119	
Electric plant equipment	20	
Misc plant equipment	28	
Allowance for cooling towers	15	
Total direct cost	1324	
Contingency and Spare parts allowance (5%)	66	
Indirect costs (10%)	133	
Total capital investment (1975)	1523	
Interest during construction (15%)	228	
Total cost at year of commercial oper.	1751	

Table 5-8
10MW_e BASELINE COST ACCOUNTS(CAES)

Collector area (km ²) - 2 modules	1.0	
Storage time (thermal hours)	.5	
Storage time (hour)	6.0	
Account		
Land	2	
Structures and facilities	44	
Heliostats	600	
Central receiver/tower/heat exch***	209	42 \$/kW
Storage thermal (2-100 MW _e)	136	52.1 \$/kWh
Storage system (1-100MW _e)	174	135 \$/kW
Boiler plant	---	6.5 \$/kWh
Turbine plant equipment (2-100 MW _e)	210	
Electric plant equipment (2-100 MW _e)	40	
Misc plant equipment	28	
Allowance for cooling towers (2-100 MW _e)	30	
Total direct cost	1473	
Contingency and Spare parts allowance (5%)	74	
Indirect costs (10%)	147	
Total capital investment (1975)	1694	
Interest during construction (15%)	254	
Total cost at year of commercial oper.	1948	

Table 5-9

100 MW_e BASELINE COST ACCOUNTS (UGPH STORAGE)

Collector area (km ²) - 2 modules	1.0	
Storage time (thermal hours)	.5	
Storage time (hour)	6	
Account		
Land	2	
Structures and facilities	44	
Heliostats	600	42 \$/kW
Central receiver/tower/heat exch	209	52.1 \$/kWh
Storage thermal (2-100MW _e)	136	118 \$/kW
Storage/system (1-100MW _e)	154	6.0 \$/kWh
Boiler plant	---	
Turbine plant equipment (2-100MW _e)	210	
Electric plant equipment (2-100MW _e)	40	
Misc plant equipment	28	
Allowance for cooling towers (2-100MW _e)	30	
Total direct cost	1453	
Contingency and Spare parts allowance (5%)	73	
Indirect costs (10%)	145	
Total capital investment (1975)	1671	
Interest during construction (15%)	251	
Total cost at year of commercial oper.	1922	

Table 5-10
100 MW_e BASELINE COST ACCOUNTS (RCR WEEKLY CYCLE)

Collector area (km ²) - 2 modules	1.0	
Storage time (hour)	30	
Account		
Land	2	
Structures and facilities	44	
Heliostats	600	
Central receiver/tower/heat exch***	209	340 \$/kW
Storage/tanks	568	7.6 \$/kWh
Boiler plant	---	
Turbine plant equipment	119	
Electric plant equipment	20	
Misc plant equipment	28	
Allowance for cooling towers	15	
Total direct cost	1605	
Contingency and Spare parts allowance (5%)	80	
Indirect costs (10%)	161	
Total capital investment (1975)	1856	
Interest during construction (15%)	278	
Total cost at year of commercial oper.	2134	

Figure 5-17. **100 MWe Solar Power Plant Concept Comparisons**

Storage system	Storage round trip efficiency (%)	Plant capital cost (\$/kW)	Seasonally adjusted capacity factor	Busbar energy cost (mills/kWh)
Fossil-fired hybrid plant (½ hr)	NA	997	62%(37%)***	48.8
Phase change (6 hr)	64.8	1,558	61.3%	54.0
Sensible heat (6 hr)	77.0	1,841	61.3%	63.0
Reversible chemical reaction (9 hr)	68.5	1,751	64.1%	59.1
Compressed air (6 hr)	66.0	1,948	62.4%(35%)***	74.9
Underground pumped hydro (6 hr)	72.0	1,922	63.0%	64.3
Reversible chemical reaction (30 hr)*	65.0	2,134	58.4%**	78.0

* Weekly operating cycle

** Seasonally adjusted weekday capacity factor = 81.8%

*** Fossil fuel utilization factor

The phase change and RCR daily cycle concept gives the lowest busbar energy costs excluding the hybrid concept and neither conventional storage concept is competitive. The 30 hour RCR weekly cycle concept is not competitive on a busbar energy cost basis; however, the weekday capacity factor of nearly 82% can be equated to a smaller backup capacity in the utility grid which at this time has not been included in the busbar energy cost estimates.

A clear selection of the preferred advanced storage concept cannot be made on the basis of the data presented here. The phase change concept which has less technical problems appears to be the most economical. However, the RCR system has the flexibility of expansion in storage time for very little cost increase, which may be attractive to the utility integrator. Utility impact studies are required, continued economic evaluation is essential to design decisions, and the technical feasibility of both advanced concepts must be established by research experiments and detailed conceptual design.

5.6 REFERENCES FOR SECTION 5

1. The Aerospace Corporation, "Solar Thermal Conversion Mission Analysis," NSF-C797, November 15, 1974.
2. Public Service Electric and Gas Company, Newark, New Jersey: An Assessment of Energy Storage Systems Suitable for Use by Electric Utilities, EPRI EM-264, EPRI Project 225, ERDA E(11-1)-2501 (July 1976)

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Section 6

MATH MODELS

Analytical models and computer programs which mechanize these models have been developed to support the sizing and performance analysis of the sensible heat, phase change, and chemical energy storage systems. Each of the three major models presented in this section has been programmed in Fortran for the IBM 360. Separate supporting documentation is presented in Volumes II, III, and IV of this report.

The math model for sizing the sensible heat and phase change storage system (Section 6.1) performs the basic function of initial thermal sizing, conceptual configuration sizing, and preliminary cost estimating. The math model for the sizing of the CES system (Section 6.2) includes the chemical analysis, initial thermal sizing for the reactor and fractionating column, preliminary cost estimating, and overall configuration synthesis. The plant operation math model described in Section 6.3 is the result of a major modification to a similar program developed during the EPRI Solar Receiver Program RP377-1. This particular computer program is an integrated operational analysis program for the high temperature Brayton cycle solar thermal conversion power plant.

A summary of each of these three computer programs is presented in the following text. The analytical basis, input, output, operating instructions, and Fortran listings for each of the three Fortran programs are included in the supporting documentation in Volumes II, III, and IV of this report.

6.1 TES SYSTEM SIZING

The purpose of the TES System Sizing math model is to physically size a sensible heat or a phase change thermal energy storage device given a set of performance requirements and operating conditions. Cost estimates of system components are made on the basis of the sizing results. The actual computations are carried out in a computer program, the details of which are presented in Volume II of this report.

The inputs to the analysis include TES system performance requirements and operating conditions, storage media and working fluid material properties, and storage vessel wall and heat exchanger tubing mechanical restrictions. The performance requirements and operating conditions are obtained from the plant operation math model and include the storage time, discharge rate, heat exchanger NTU value, TES system temperatures, temperature swing of the media, mass flow rates, turbine efficiencies, system pressure and pressure drop criterion. Helium is used as the working fluid, and its thermophysical properties of interest for this analysis include thermal conductivity, density, viscosity, heat capacity and specific heat ratio. The required material properties of the storage media include thermal conductivity, density, solid and liquid heat capacity, heat of fusion, and melt temperature. The key physical parameter input into the analysis is a characteristic vessel dimension. For a vessel with a square cross-section the dimension is the inside width; for a circular cross-section, the dimension is the inside diameter.

The outputs of the analysis include geometrical data (tubing diameter, tubing thickness, intertube spacing, vessel height, vessel wall thickness, etc.), required quantities of TES media, tubing, and container vessel materials, required size of helium pump circulation system, and cost estimates of the components.

The structure of the math model is shown in Figure 6-1. The major steps of the analysis are represented by the subroutine blocks shown in the figure with accompanying notes to describe the function of each block. A group of nested iterations are used to define a single design which meets the heat rate, energy storage, and pressure loss requirements stated in the program input.

6.2 CES SIZING

The conceptual design study results for the CES system reported in Section 4.0 have provided the baseline for more detailed design and trade studies. However, the systematic variation of the design parameters in an effort to determine their effect on storage efficiency and cost sensitivity would require an extensive effort because of the complexity of the CES system. At the conclusion of the RP377-1 study, it was, therefore, proposed to develop a computer model with which

Figure 6-1. Thermal Energy Storage Sizing Computer Program Structure

these calculations could be performed. The primary objective of the chemical energy storage (CESTOR) computer program was to develop a design tool for the sizing of the various components as a function of output power and storage time and then to determine the efficiency, weight, and cost of the overall CES system.

The block diagram of the CESTOR program is shown in Figure 6-2. A detailed description of the program is contained in Volume III of this report.

The program contains several subroutines which can also be operated as separate entities if one CES system component is to be studied by itself. The subroutines are called RCTSIZ (reactor sizing), VAPCON (vaporizer-condenser), SEPCOL (separation column), and CMPRSR (compressor). The CHMEOL (chemical equilibrium) subroutine has been integrated into the reactor sizing subroutine. Each subroutine is called upon repeatedly as the program goes through the sizing in the endothermic and exothermic modes. The endothermic mode is sized first because it is expected that, because of the lower operating pressure in this mode, most components will be larger than in the high-pressure exothermic mode. After the sizing of all components in the endothermic mode is complete, the program calculates an independent set of exothermic energy output required. Presently, the program results in two sets of output data, one for the endothermic and one for the exothermic mode of operation.

Because several components of the system are used in either mode, it is not possible to obtain total system weight and cost by simply adding weights and costs for all components shown in both printouts. Instead, weights and costs of the larger component must be chosen for the summation to make sure that the component can handle both flow rates.

Ultimately, after further refinement of the model during an ERDA part of the study, the dimensions of the reactor, external heat exchanger, distillation column, and vaporizer/condenser, as calculated for the endothermic mode can be frozen and the performance of the exothermic mode can be calculated using components sized for the endothermic mode. For most practical charge-to-discharge power ratios, the endothermic

Figure 6-2. Chemical Energy Storage (CESTOR) Math Model Structure

system will result in larger components than the exothermic mode. During further evolution of the computer model, a diagnostic message will be included which indicates that this assumption is no longer true if the charge-to-discharge ratio is decreased below a certain limit.

Another refinement which will be required will be to calculate wall thicknesses, weights, and costs of the (oversized) endothermic components for the higher exothermic operating pressure. This is necessary because the dimensions are dictated by the endothermic mode and the maximum operating pressure is dictated by the exothermic mode. Currently, the two systems are sized independently and the higher of the two numbers has to be chosen manually for a weight and cost summation.

6.3 PLANT OPERATION MATH MODEL

The operation and control of the STC power plant operation was developed as a part of the earlier EPRI Advanced Thermal Energy Storage study to support the plant design and performance analysis. This model predicts the plant performance on an hour-by-hour daily cycle basis as well as a weekly cycle for chemical storage systems. Included are the effects on performance of all of the major plant subsystems. It has been extensively modified and expanded as a part of the study being reported here.

A technical summary of the math model is included in this section. The principal objective of this work was to create a capability to relate storage system design requirements to the daily insolation cycle and the basis operating requirements of the power plant. Consequently, it is appropriate to simplify the demand profile and plant operating policy, recognizing that the resultant plant performance estimates are limited by these simplifications. The work reported here is based on a flat demand profile, and the plant operating policy simply provides energy for storage on an as-available basis with first priority to direct generation.

A simplified schematic of the plant operation math model is shown in Figure 6-3. Each of the major subsystems in the power plant is characterized in a separate program module. The effects of the major

- Insolation and field modeled as hour by hour solar heat into the receiver aperture

- Receiver modeled by efficiency

$$\eta_R = \frac{\text{Heat to helium circuit}}{\text{Solar heat into receiver}}$$

- Turbine generator cycle efficiency, mass flow, and He temperature distribution all modeled
- Energy storage — includes parasitic losses, thermal losses and He temperature distribution
- Fixed level power output — model determines capacity in hours
- Energy economics based on capital cost per unit energy output

Figure 6-3. Plant Operation Computer Program Schematic

parameters for each subsystem are included in these program modules.

The control logic for the program provides the framework for the simulation of the plant as a function of time. At each time step the current thermodynamic state data are combined with the solar heat input to the receiver and heat rates throughout the plant are determined. These rates are integrated to establish new thermodynamic state data. Input data to the program includes hourly insolation data, reflector field conversion efficiency data, component design parameter data such as storage media thermal properties, component performance characteristics such as turbine performance data, plant operation data such as storage limits, and energy economics parameters such as itemized cost account numbers. The results of each complete cycle are analyzed to determine component efficiency, overall plant efficiencies, component energy consumption, and component energy output. Printed results include thermodynamic state data at each time point, daily analysis results, and the overall results with energy economics of all four seasons analyzed as a yearly operation.

Section 7

PHASE I PROGRAM PLAN

A Phase I conceptual design program plan has been developed on the basis of the work reported above. This section presents the resultant plan as a statement of work.

The objectives of the planned work are to: 1) formalize the conceptual design of the candidate storage concepts, and 2) carry out those exploratory research experiments required to verify the analysis and simulation results and to provide data and concept verification for further storage system design activity. Results of the planning activity are presented in two sections - Section 7.1 describes the program plan for the phase change storage device and Section 7.2 describes the work planned for the reversible chemical reaction (RCR) storage system.

7.1 PHASE I - PHASE CHANGE TES

The continuing conceptual design program for the high temperature phase change TES device in the Solar Brayton power plant is planned in three tasks: Task I is the system analysis effort, Task II is the device design effort, and Task III is the research experiments. Figure 7-1 shows a summary schedule of the twelve month program and the three tasks. The major program milestones, study review dates, and material and manpower requirements by task are shown in the schedule. The following sections describe the work to be accomplished in each of the three tasks.

7.1.1 Task I - System Analysis - Phase Change TES

System Requirements

The TES system requirements data book developed as a part of the E(04-3)-1300 study will be updated as required and submitted for ERDA approval at the end of the first month of the Phase I study. The system requirements to be included in the data book are:

1. Storage device operating requirements and design standards,
2. Solar power plant interface requirements, and
3. Power plant/storage economic analysis standards.

Figure 7-1. **Phase I Program Plan**
(Phase Change)

System Requirements (Cont'd)

This data book will serve as the control point for the definition of all requirements used in the conceptual design work. In addition to system requirements definition, the System Analysis task will include five supporting system level studies. The scope and objectives of each of these tasks are presented in the following paragraphs.

Plant Operation Math Model

During the Phase 0 study, a solar power plant operation analysis computer program was developed to support the plant/storage interface studies. Two major modifications will be made to this computer program during the Phase I study.

Power plant/storage sizing and interface sensitivity studies require the iterative operation of two computer programs - the plant operation model, and the thermal storage sizing and cost analysis model. As a part of the Phase I System Analysis task these two programs will be combined in an effort to simplify the iterative sizing and interface sensitivity studies.

Modifications will also be made in the solar receiver model and in the cost models for the solar components of the power plant. These modifications are intended as a general upgrading of the plant operation program and will provide the capability to more accurately reflect storage interface sensitivities. Effects of inventory ratio and solar multiple on the solar power plant characteristics and cost are of particular interest.

Alternative Melts

During the E(04-3)-1300 study a preferred fluoride melt $7\text{CaF}/54\text{KF}/39\text{NaF}$ was selected for the 816°C Solar Brayton TES application. A number of alternative fluoride melts are available in the melt temperature range of interest (i.e. $600 - 750^{\circ}\text{C}$). An alternative melt study will be undertaken as a part of the Phase I System Analysis effort.

Alternative Melts (Cont'd)

Five alternate melts will be identified and carried through the complete TES conceptual design cycle. In each case trade studies will be performed to define the "optimum" TES device configuration. These trade studies will include the following factors:

- 1) Constituent fluoride salt cost,
- 2) Melt thermophysical properties
- 3) Charge and discharge temperature extremes,
- 4) Heat exchanger capacity,
- 5) Phase change media mass, and
- 6) Device configuration (i.e. characteristic dimension)

Module Sizing

A single module TES device configuration was used throughout the Phase 0 study. During the Phase I System Analysis effort multiple module configurations will be investigated. These studies will include different melt compositions in each module and will be undertaken on a complete conceptual design cycle basis. Each configuration study will include those trades required to define a "optimum" device configuration as described in the preceding paragraph. A separate study will be undertaken to evaluate the operation and the maintenance flexibility afforded by the multi-module configuration.

Comparative Economics

Solar power plant energy economic studies are required to support subsystem parameter decisions. These studies were carried out during the early Phase 0 work and will be carried out on a continuing basis to support the Phase I System Analysis activities.

The specific plant economic studies to be performed as a part of this subtask are:

- 1) Solar plant sizing for minimum energy cost, including variations in heliostat field size and storage time limit; and
- 2) A continuing evaluation of alternative storage concepts including the sensible heat concept, the RCR concept, the hybrid fossil fuel supplement, compressed air, and underground pumped hydro.

Comparative Economics

These supporting studies will be carried out throughout the Phase I effort to insure that all design requirements decisions are made on a consistent basis.

Interface Sensitivities

An initial set of interface sensitivity studies were carried out during the Phase 0 conceptual design work. These sensitivity studies will be repeated and expanded as a part of the Phase I System Analysis work. Sensitivity data to be developed for the phase change TES device include:

- 1) Sensitivity to Brayton cycle working fluid pressure drop.
- 2) Sensitivity to heat loss rate through the walls of the TES device, and
- 3) Sensitivity to the gas inventory ratio capability of the Solar Brayton turbomachinery.

7.1.2 Task II - Device Conceptual Design

Conceptual Design Support

As a part of the Phase 0 TES conceptual design activity, a computer program was developed to support the TES device design synthesis and cost analysis work. This computer program will serve as the focal point of the Phase I Conceptual Design Task. The program will be updated during Task II, as required, and the multi-module capability will be added to the program.

All of the parametric conceptual design and TES system configuration work will be carried out by the TES design program. This work includes the conceptual design of the manifold and heat exchanger system, the container, and support systems such as the working fluid circulation pump.

Thermal Analysis

The transient thermal performance of the phase change TES device heat exchanger is one of the key concerns in the device design work. During the E(04-3)-1300 study a finite element transient thermal model was developed for the phase change device.

Thermal Analysis (Cont'd)

During Phase I this model will be upgraded and an in depth transient analysis of the basic phase change TES device heat exchange will be undertaken. New thermophysical property data developed as a part of Task III will be used as input to this analysis task. The resultant model will be used to support the design of the device demonstration hardware, and to predict the thermal performance of the device for comparison with the device demonstration experimental data. The same transient thermal analysis will be used to support the Bench model design and test program planning described in the following paragraph.

Bench Model Conceptual Design

A Phase II program plan will be developed as a part of the Phase I Conceptual Design work. A conceptual design of the bench model phase change TES device will be generated, preliminary test requirements will be established, a test plan will be generated, and test facility and facility options will be defined.

The bench model conceptual design will include initial material specs and conceptual design drawings. The test plan will include a schedule of the major test events, the objective of each test phase, the expected results, and will identify special instrumentation and test facility requirements.

Alternative test beds for the high temperature phase change TES device will be identified and a cost/schedule impact statement will be prepared for each alternative.

7.1.3 Task III - Research Experiments

A summary of the research experiments planned in support of the Phase I conceptual design work is presented in Figure 7-2. Each of the three major experiments are described in terms of the objective, scope and expected results. The following paragraphs describe the approach and facilities required to support each of the research experiments.

Figure 7-2. **Research Experiments (Phase Change)**

Experiment	Objective	Scope	Results
Salt thermophysical properties	Provide thermo-physical property data for selected salt mixtures	Eight major physical characteristics of five salt mixtures	Consistent thermo-physical property data for device design and performance analysis
Material compatibility	Determine compatibility of selected salts with heat exchanger and container materials	Three alloys with two selected salts under simulated service conditions	Initial verification data to confirm material selection
Device demonstration	Demonstrate single tube device thermal performance	Single tube of selected alloy in selected salt under simulated service conditions	Performance verification data to support device design and performance analysis

Thermophysical Properties

The objective of the Thermophysical Properties Program is to determine those physical and chemical properties of the selected fluoride salts that are necessary for design of the TES system.

The following properties of five salt mixtures will be determined:

Density	Heat Capacity (liquid & solid)
Vapor Pressure	Heat of Fusion
Viscosity	Thermal Conductivity (liquid & solid)
Phase Diagrams	Infrared Analysis

Analytical equipment for all determinations except viscosity and thermal conductivity is available in the Boeing Materials Laboratory. Viscosity and conductivity measurements will be conducted in outside laboratories. Infrared analysis will provide a unique chemical "footprint" for each salt mixture. This data will permit a rapid comparison of salt mixture chemistry of future lots of the same nominal composition.

Material Compatibility

The objective of the Material Compatibility Program is to determine the compatibility, under service conditions, of two selected fluoride salt mixtures with three structural alloy candidates for the TES system.

This program includes an analysis of the salt mixtures before and after contact with the metal specimens at service temperature. Where a salt/metal reaction is indicated aluminum will be added to the salt for a second run to determine its effect as a corrosion inhibitor. Commercial grade fluoride salts are known to contain impurities which have been identified as responsible for the salt/metal interaction. A very small quantity of aluminum effectively neutralizes these impurities and does not adversely effect the physical properties of the salt.

Metal specimens will be prepared from welded tubing to permit evaluation of the weld zone as well as the base metal. Metallurgical characterization of the specimens, both before and after exposure, will include microstructural analysis of interior and surface zones, micro hardness surveys and a microprobe analysis

Material Compatibility (Cont'd)

of the salt/metal contact zone. Photomicrographs will be provided as a record for all analytical work.

Device Demonstration

The purpose of the device demonstration is to establish the design feasibility of a fluoride salt TES system that is adaptable to the solar Brayton power plant.

This task includes the design, fabrication and operation of a single tube heat exchanger unit. Helium gas in this "closed" system will be heated to a temperature of $820^{\circ}\text{C} \pm 10^{\circ}\text{C}$ ($1508^{\circ}\text{F} \pm 18^{\circ}\text{F}$) using radiant heat lamps, and pumped around a closed loop. One section of the loop will pass through a storage container partially filled with a commercial fluoride salt mixture. The salt used will contain an aluminum addition if compatibility testing indicates the need.

The device will be operated for a period of not less than thirty days. Operation shall consist of one cycle per day from room to service temperature and held at service temperature (820°C) for a continuous period of 6 hours. Temperature measurements will be recorded at significant locations around the closed loop and in the salt container.

In addition to analysis of the thermal data critical portions of the system hardware will be removed, sectioned and examined for evidence of metallurgical degradation.

7.2 PHASE I - REVERSIBLE CHEMICAL REACTION (RCR) TES

The continuing conceptual design program for the high temperature RCR TES device in the Solar Brayton power plant is planned in three tasks: Task I is the system analysis effort, Task II is the process optimization/design effort, and Task III is the research experiments. Figure 7-3 shows a summary schedule of the twelve month program and the three tasks. The major program milestones, study review dates, and material and manpower requirements by task are shown in the schedule. The following sections describe the work to be accomplished in each of the three tasks.

7.2.1 Task I - System Analysis - Phase Change TES

System Requirements

The TES system requirements data book developed as a part of the E(04-3)-1300 study will be updated as required and submitted for ERDA approval at the end of the first month of the Phase I study. The system requirements to be included in the data book are:

1. Storage device operating requirements and design standards,
2. Solar power plant interface requirements, and
3. Power plant/storage economic analysis standards

This data book will serve as the control point for the definition of all requirements used in the conceptual design work. In addition to system requirements definition, the System Analysis task will include three supporting system level studies. The scope and objectives of each of these tasks are presented in the following paragraphs.

Plant Operation Math Model

During the Phase 0 study, a solar power plant operation analysis computer program was developed to support the plant/storage interface studies. Two major modifications will be made to this computer program during the Phase I study.

Power plant/storage sizing and interface sensitivity studies require the iterative operation of two computer programs - the plant operation model, and the chemical

Figure 7-3. **Phase I Program Plan**
Reversible Chemical Reactions

* Does not include accelerated life— cycle test

Plant Operation Math Model (Cont'd)

energy storage (CESTOR) sizing and cost analysis model. As a part of the Phase I System Analysis task these two programs will be combined in an effort to simplify the iterative sizing and interface sensitivity studies.

Modifications will also be made in the solar receiver model and in the cost models for the solar components of the power plant. These modifications are intended as a general upgrading of the plant operation program and will provide the capability to more accurately reflect storage interface sensitivities. Effects of inventory ratio and solar multiple on the solar power plant characteristics and cost are of particular interest.

Comparative Economics

Solar power plant energy economic studies are required to support subsystem design parameter decisions. These studies were carried out during the Phase 0 work and are required on a continuing basis to support the Phase I system analysis activities.

The specific plant economic studies to be performed as a part of this subtask are:

- 1) Solar plant sizing for minimum energy cost, including variations in heliostat field size and storage time limit;
- 2) A continuing evaluation of alternative storage concepts including the sensible heat concept, the RCR concept, the hybrid fossil fuel supplement, compressed air, and underground pumped hydro; and
- 3) An evaluation of long term RCR storage (up to 40 hours) including an initial assessment of the utility impact and the associated back up capacity (i.e. margin) requirements.

These supporting studies will be carried out throughout the Phase I effort to insure that all design requirements decisions are made on a consistent basis.

Interface Sensitivities

An initial set of interface sensitivity studies were carried out during the Phase 0 conceptual design work. These sensitivity studies will be repeated and expanded

Interface Sensitivities (Cont'd)

as a part of the Phase I system analysis work. Sensitivity data to be developed for the RCR TES device include:

- 1) Sensitivity to Brayton cycle working fluid pressure drop in the reactor heat exchanger.
- 2) Sensitivity to heat loss rate through the walls of the reactor, and
- 3) Sensitivity to the gas inventory ratio capability of the Solar Brayton turbomachinery (i.e. reactor discharge temperature).

7.2.2 Task II - Process Optimization/Design

As a part of the Phase 0 TES conceptual design activity, a computer program was developed to support the RCR storage system synthesis and cost analysis work. This computer program (CESTOR) will serve as the focal point of the Phase I Process Optimization/Design Task. The program will be updated as a part of the Task II work, to reflect changes in the process system design philosophy and to reflect promising subsystem alternatives.

All of the parametric conceptual design and RCR system configuration work will be carried out by the CESTOR program. This work includes the process system synthesis and conceptual design, the conceptual design of the reactor and the heat exchangers, the conceptual design of support systems such as the working fluid circulation pump, and cost estimates for the entire RCR storage system.

Process Optimization

The optimization of the RCR process system is a key concern in the cost effectiveness of the RCR storage system. Initial process optimization studies were included in the Phase 0 work. These studies will be continued and expanded in support of the RCR storage system conceptual design task.

The process variables to be included in the optimization task are as follows:

- 1) Separation column operating conditions,
- 2) Endothermic and exothermic reactor operation conditions,
- 3) Reactant constituent storage conditions, and
- 4) Vaporizer/condenser operating conditions.

Process Optimization (Cont'd)

In each case operating conditions include temperature and pressure in the reactant product stream.

Process System Alternatives

The major components in the RCR system have been evaluated on a cursory basis to insure that the most cost effective approach is being used to accomplish the component function. This study will be repeated in depth for several promising component alternatives.

The process system alternatives study will include the following RCR components:

- 1) The separation column,
- 2) The vaporizer/condenser system, and
- 3) Compressed gas oxygen storage versus open cycle air operation

The open cycle air option will be included in the CESTOR program to allow an extensive evaluation of this particular option. Other process alternatives will be investigated during the study and modifications will be made to the CESTOR computer as required to support the evaluation of these alternatives.

Bench Model Conceptual Design

A Phase II program plan will be developed as a part of the Phase I Conceptual Design work. A conceptual design of the bench model RCR storage device will be generated, preliminary test requirements will be established, a test plan will be generated, and test facility and facility options will be defined.

The bench model conceptual design will include initial material specs and conceptual design drawings. The test plan will include a schedule of the major test events, the objective of each test phase, the expected results, and will identify special instrumentation and test facility requirements.

7.2.3 Task III - Research Experiments

A summary of the research experiments planned in support of the Phase I Conceptual Design work is presented in Figure 7-4. Each of the four major experiments

Figure 7-4. **Research Experiments**
(Reversible Chemical Reactions)

Experiment	Objective	Scope	Results
Catalyst development	Develop an inexpensive, durable high temperature resistant catalyst for SO_2/SO_3 reaction	Up to 12 current catalysts, 15-20 new catalyst formulations	Selected catalyst with backup data to support reactor design and accelerated life-cycle testing
Open loop reactor	Obtain reactor kinetics data and determine compatibility of heat exchanger and container materials with reaction constituents	One working and one backup subscale reactor, five metal coupon samples with four ceramic coatings	Reactor material selection with backup data and reactor performance data to support reactor design
SO_2/SO_3 phase diagrams	Develop SO_2/SO_3 physical data	Liquid vapor phase diagram, solid/liquid melting-point phase diagram	Binary phase diagrams to support separation and storage system design
Fractionation column	Verify separation system efficiency	One subscale fractionating column with selected packing materials, heat transfer verification, variable operating conditions	Fractionation column performance verification data to support separation system design

7.2.3 Task III - Research Experiments (Cont'd)

are described in terms of the objective, scope and expected results. The following paragraphs describe the approach and facilities required to support each of the research experiments.

Catalyst Development

The goal of the catalyst development program is to develop an inexpensive, durable, high-temperature resistant catalyst for the SO_2/SO_3 reaction. The catalyst should equally satisfy requirements for the endothermic and exothermic mode of operation.

The technical approach toward the development of a long-life/high temperature catalyst for the SO_2/SO_3 energy storage system is subdivided into three major tasks: evaluation of current technology, development and short-term testing of new catalysts, and an economic evaluation. These three tasks will be conducted during the proposed 12-month technical effort shown in Figure 7-3.

During Task 1, up to 12 catalyst samples will be solicited from commercial producers. This activity is already in progress, and 8 catalyst samples have been received and are awaiting testing. The fresh catalyst samples will be exposed to incrementally increased temperatures, and the effect of treatment temperature on remaining catalyst activity will be studied. In addition to work with fresh catalyst, spent catalyst samples will be solicited from users. Degradation mechanism will be identified by diagnostic techniques which are routinely used in catalyst development and investigations of catalyst degradation. The conclusions drawn from these tests will help to formulate the necessary changes to develop a more durable and more resistant catalyst.

The primary effort to be undertaken in the catalyst development task is the development of new and improved sulfur oxide conversion catalysts. All three catalyst types (i.e. packed bed, fluidized bed, and pumped molten) evaluated as a part of the Phase 0 conceptual design technical assessment work will be included in advanced catalyst development task. cursory screening tests will be carried out on one or more formulations of each catalyst type. The results of these tests will form the basis of the catalyst concept selection.

Catalyst Development (Cont'd)

Up to 20 formulations of the selected catalyst concept will be prepared and tested in the laboratory. The more promising catalysts will be tested for temperature limitations, temperature effects on performance, and short-term durability. The maximum bed loading (gaseous hourly space velocity) will be determined for different catalyst arrangements, and scaling criteria will be derived from experimental data which will allow the design of pilot plant or full-scale reactors based on the laboratory data.

A preliminary economic evaluation will be carried out as a part of the Catalyst Development Task. Cost estimates for large-scale production of the new catalyst will be prepared, energy and cost savings which can be realized by using the new catalyst in place of existing catalysts will be estimated, and other possible nonenergy-related commercial uses for the new catalyst will be identified.

Open Loop Reactor

The objective of the open-loop reactor tests is to obtain initial material compatibility data and kinetic rate data for SO_2 oxidation, and SO_3 dissociation to support reactor design studies for the reversible reaction system. The effect of temperature, pressure, feed mixture ratio, catalyst distribution, and catalyst age on the maximum space velocity which can be maintained with satisfactory conversion will be evaluated. Electronic sensors will be procured or developed which continuously measure the oxygen or sulfur dioxide concentrations in the feed and product gases. The electric output of these sensors will be recorded on strip chart recorders as an immediate indication of conversion. The sensor output will be calibrated with gas mixtures of known composition.

The majority of work conducted during this task will use steel and superalloy hardware designed to operate at pressures up to 1.4 MN/m^2 (200 psia). Material selection for this hardware has to be based on scarce compatibility information, and reactor failures at high pressure must be anticipated. This is the primary reason for test set up in remotely controlled test bays. Coupons of materials (e.g. dogbone-shaped tensile test specimen) to be evaluated in a metallurgical laboratory will be exposed to the reactor sulfur oxide environment in a "piggy-back" mode without interfering with the catalyst and space velocity tests. Ultimately,

Open Loop Reactor (Cont'd)

a more detailed materials compatibility test program will have to be conducted where samples are exposed to carefully controlled stationary or cyclic SO_x concentrations. Stressed and unstressed specimens of five alloys with welds and four ceramic coatings will be included in the coupon inventory. A complete before and after metallurgical characterization of the metals will be made and a corrosion product analysis will be carried out.

Depending on the type of catalyst used, reactors for the open-loop bench-scale tests would not exceed 0.10 (4 inches) in diameter or 0.3 m (1 foot) in length. One working reactor and one backup reactor will be constructed. Sufficient instrumentation (pressure gauges, thermocouples) will be attached to obtain reactor pressure, pressure drop, and a temperature profile through the reactor.

Catalysts which have been exposed to reactor operating environments during this program will be collected and subjected to diagnostic tests to measure remaining activity.

SO_2/SO_3 Phase Studies

A thorough review of the literature has not revealed sufficient physical data of the SO_2/SO_3 system to allow evaluation of appropriate separation techniques and identify alternate methods for safe storage of SO_3 .

It is, therefore, proposed to determine the liquid/vapor phase diagram of the binary SO_2/SO_3 system. This will be achieved by mixing known amounts of SO_2 and SO_3 and introducing them into an evacuated system, resulting in partial evaporation of the sample. After the system has reached equilibrium at a constant temperature, total pressure readings are taken and the vapor and the liquid phase will be analyzed. The test will then be repeated at a new temperature and with different compositions. If SO_2 and SO_3 should form an azeotrope (which is very unlikely), its location would become apparent in the vapor phase diagram. In addition to the binary system SO_2/SO_3 , some data are needed on the ternary system $\text{SO}_2/\text{SO}_3/\text{H}_2\text{SO}_4$ in order to see if sulfuric acid can be used as a solvent in an absorptive/extractive separation process for SO_2 and SO_3 .

SO₂/SO₃ Phase Studies

In addition to the vapor/liquid equilibria in the system SO₂/SO₃, the solid/liquid melting point phase diagram must also be known to evaluate the usefulness of SO₂ as an antifreeze in SO₃, and to evaluate the feasibility of separating SO₂ and SO₃ by crystallization/freezing. In this test, known amounts of SO₂ and SO₃ will be mixed in a glass vial, and a thermocouple will be inserted into the mixture prior to sealing it. The glass vial will then be cooled slowly and the temperature recorded. If the mixture begins to freeze, this will result in a temporary step in the temperature curve. The mixture will then be allowed to freeze completely, and the temperature will be recorded while thawing the sample. At the melting point, the temperature rise will again be delayed because all heat absorbed by the vial goes into latent heat. The freezing and melting point should agree closely, but this is not always the case for multi-component mixtures.

In a separate test, the precipitate of a partially solidified or a partially melted sample will be filtered and analyzed. Some oxides form well defined adducts, but it is doubtful that the mixed oxide SO₃ · 2SO₂ claimed by Rose in 1844 is a true addition compound (Reference 1). The date of this publication is also indicative of the time when the system SO₂/SO₃ was last studied.

The rate of phase transformation of alpha to the asbestos-like gamma modification of SO₃ will be measured in different container materials. The effect of moisture and/or SO₂ on the conversion rate will be evaluated.

Fractionation Column

Fractionating distillation is currently the prime choice separation technique for SO₂/SO₃/O₂ mixtures in the RCR storage plant. A small-scale design study for this key component will be conducted. The objective of this effort is to verify separation efficiency predicted by textbook-type analytical studies during the Phase 0 program. In particular, data are needed for fractionation coefficients at high column pressures. No such data exist in the literature. The data are needed for scaling up and designing large distillation columns. The design of the column and the selection of proper operating conditions will influence the purity of the product streams (distillate and bottoms) and the parasitic power requirements in the RCR charging mode.

Fractionation Column (Cont'd)

The experimental program will also verify the optimum feed storage selection, and different condenser arrangements will be tested.

It would be preferable to conduct the fractionation by distillation tests in glass hardware. However, the anticipated operating pressures (1.3 MM/m^2) = 200 psia) are in excess of a safe pressure for glassware. The fractionating column and condenser will, therefore, be made from stainless steel. A packing material survey will be made to establish the packing material and shape to be used in the sub-scale column. The packing material could be ceramic, glass, teflon, or steel. Raschig rings, Berl saddles, or other shapes offered by the chemical process industry can be used as column filling.

A single column will be constructed with one packing material. The condenser/vaporizer components and feed gas components will be constructed on a building block basis to provide the capability to evaluate various geometric arrangements.

In addition to fractionation column performance verification, heat transfer data to and from liquid and gaseous sulfur oxides will have to be determined experimentally in order to be able to size larger vaporizer/condenser components. Very little data of this type is available, however, a thorough literature search will be undertaken prior to commencing this test activity.

7.3 REFERENCES FOR SECTION 7

1. Casazza, J. A.; Schneider, T. R., and Sultzberger, V. T.: Energy Storage, in: Proceedings on Energy Technology III, March 29-31, 1976, Richard F. Hill (Ed.), Published by Government Institutes Inc., Washington, D.C., LC 76-12198.

Section 8

CONCLUSIONS AND RECOMMENDATIONS

This final technical report presents the results of work carried out as an EPRI/ERDA Program Coordination. The work is an extension to the storage subsystem studies included in the EPRI sponsored high temperature central receiver contract. The work performed here included development of three major analytical tools, system level trade studies and comparative economic assessment, in-depth technical assessment of baseline conceptual designs, and development of test plans for experimental verification.

Preliminary results show that direct storage of high temperature thermal energy for the gas cooled solar power plant is technically feasible with near term sensible heat TES technology. The two advanced TES concepts investigated for this application also show promise. Similar work has been carried out in several areas closely related to the advanced TES concepts. The Oak Ridge molten salt reactor work and the sulfur cycle water decomposition hydrogen production system are key examples. The experience in both cases indicates that an aggressive research and development program is required to realize the potential of the two advanced TES systems studies here. With the completion of the analytical systems level work, the next major step recommended by BEC is to carry out demonstrations of the technical feasibility of the proposed systems by basic research and subscale system experiments.

Specific interim conclusions and recommendations are included in each section of the preceding technical report. For convenience, these conclusions and recommendations have been collected and summarized in this section.

8.1 INTERIM CONCLUSIONS

Sensible Heat Concept

The magnesia firebrick checkerwork device shows promise as a near term technology solution to the high temperature solar power plant storage requirement. Magnesia is selected as the preferred media because of its thermophysical properties and its high temperature structural characteristics. No acceptable all liquid sensible heat storage media has been identified to date.

Phase Change Concept

The phase change concept offers the most economic incentive as an advanced technology system primarily as a result of its simplicity and its very high energy storage density. A passive tube in bath heat exchanger is the most likely near term heat exchange concept. Fluoride salts are the most promising class of salts for this particular temperature range because of their high heat of fusion, high thermal conductivity and relatively benign corrosion characteristics. An underground insulated concrete containment vessel appears to be the most economic, safe, and environment compatible approach. Finally, an aggressive development and test program is required, particularly in the area of materials compatibility and heat exchange device performance and life cycle tests.

Perhaps the most critical decision to be made in the design of the phase change device is the selection of the phase change media (PCM). There are thousands of known materials that melt at temperatures in the range of interest and an in-depth technical assessment of many of these materials is required. Economics must be evaluated on a total system basis and PCM costs must be based on bulk quantities with defined purity standards. Corrosion and material compatibility is a key concern and experimental verification is required for the working temperatures of this investigation. More than 100 M\$ has been spent in R&D of the molten salt reactor which is based on fluoride salts as the carrier at temperatures somewhat below the range of interest in the high temperature solar power plant. Fifteen years of research with fluoride salts at these temperatures has been carried by Philips Labs in Europe. Consequently, fluorides are the best defined salts and have been selected as the preferred media, even though bulk fluoride salt costs may be significantly higher than the next best contenders - chlorides and carbonates.

Thermochemical Concept

The thermochemical TES concept is particularly attractive because it is an active storage device that can control the temperature of the working fluid. An all liquid constituent reaction has not been found for the temperature range of interest. The SO_2/SO_3 reaction is the best compromise and does involve one gaseous constituent - oxygen. This is a catalyzed reaction that is controllable over a wide range of temperatures and pressures. Decomposition catalysts operating at the very high temperatures of interest have been reported in other research work. However, an aggressive practical catalyst development program will be required for the dual purpose CES reactor.

The subsystem technology is all near-term, because of the extensive working background with these chemicals in the sulfuric acid industry. The operation and integration of these subsystems into a working closed loop TES system has never been attempted even at the laboratory level. And, there is no commercial background related to the SO_3 dissociation reaction. An aggressive research and development program is required with particular emphasis on material life cycle and compatibility tests.

8.2 INTERIM RECOMMENDATIONS

The system level gaming models developed and exercised in this study provide significant insight into the comparative economics and design requirements for the TES device alternatives. These kinds of mathematical tools should be included as an initial step in any technical economic assessment study of energy storage systems. Specifically, the plant operation model developed here should be expanded to include:

1. A model of the closed cycle gas turbine and its control system,
2. A mathematical representation of the sizing of the gas cooled solar receiver,
3. An expanded and embellished version of the performance of the TES systems, and
4. A realistic load and environment simulation based on real operating scenarios and year-long insolation profiles.

The passive tube in bath heat exchanger as described above is the most likely concept for the phase change system because of its simplicity. An in-depth device development program is recommended. That program should include the continued development of a complete thermal model on the level of that initiated in this study with careful attention to all the heat transfer mechanisms, and subscale device model tests to verify the analytical performance predictions.

Several alternate heat exchange concepts for the phase change system are being pursued by other researchers. The potential of these should be evaluated and compared with the tube-in bath concept. Further heat exchanger technical assessment is recommended.

The operational flexibility afforded by the thermochemical system is very attractive. In view of the implication of this approach, a laboratory level closed cycle SO_2/SO_3 system operation test is recommended as an early program commitment. This recommendation is analogous to the sub-scale phase change device model thermal test recommendation.

Basic materials research and experimental work is required for both of the advanced TES devices. Life cycle tests must become an early program commitment and should include:

1. Practical low cost catalysts development for the SO_2/SO_3 reaction,
2. High temperature SO_2 , O_2 , SO_3 super alloy compatibility tests and,
3. High temperature fluoride salt compatibility tests.

All of the storage materials recommended for the advanced system are hazardous materials. Codes need to be developed for the handling, transportation, and assembly of devices using these materials.

Appendix I
CAST IRON SENSIBLE HEAT TES CONCEPT

An initial meeting with Siempelkamp Giesserei K.G. of West Germany was held in October, 1976 to discuss the design of a cast iron sensible heat TES system. In response to that initial discussion, design requirements and operating conditions characteristic of the baseline magnesia brick sensible heat TES conceptual design were sent. Siempelkamp responded by producing conceptual designs of sensible heat TES systems using both cast iron and magnesia bricks contained in welded steel and prestressed cast iron vessels. The performance requirements, operating conditions, and storage media properties assumed by Siempelkamp are listed in Table I-1. The heat capacity values used in the trade study presented earlier in Table 2-3 of Section 2.2 were $1130 \text{ J/kg-}^{\circ}\text{C}$ for magnesia and $837 \text{ J/kg-}^{\circ}\text{C}$ for cast iron. The cast iron heat capacity value given in Table 2-3 was obtained from Reference 1. The specific costs for magnesia and cast iron shown in Table I-1 correspond well to the specific costs used in Table 2-3 ($0.32 \text{ \$/kg}$ - magnesia and $0.66 \text{ \$/kg}$ - cast iron). Conceptual design data and system cost estimates derived by Siempelkamp are listed in Table I-2. The specific cost for the cast iron vessel of $1.19 \text{ \$/kg}$ corresponds to the $6.30 \text{ \$/kg}$ estimate for welded steel vessels derived from estimates from American pressure vessel manufacturers.

REFERENCE

1. "Thermophysical Properties of High Temperature Solid Materials, Vol.1: Elements," MacMillan Co, New York, N.Y., 1967, p.583.

Table I-1
BASIC DATA

Operational pressure (bar)	35	
Design pressure (bar)	37	
Discharge power (MWe)	50	
Average plant efficiency	0.383	
Discharge thermal power (MW)	130.5	
Discharge time (hours)	6	
Stored thermal energy (MWh)	783	
Upper fluid temperature ($^{\circ}\text{C}$)	816	
Average upper storage temperature ($^{\circ}\text{C}$)	777	
Average lower storage temperature ($^{\circ}\text{C}$)	513	
Nominal temperature swing ($^{\circ}\text{C}$)	264	
	<u>Magnesia</u>	<u>Cast Iron</u>
Storage media heat capacity ($\text{J/kg}^{\circ}\text{C}$)	1130	1350
Density (kg/m^3)	3000	7300
Porosity	0.9	0.9
Mass required (Mkg)	9.45	7.91
Storage volume required (m^3)	3150	1084
Specific costs (\$/kg)	0.26	0.60

Table I-2
CONCEPTUAL DESIGN SUMMARY

<u>Cast iron vessel</u>	<u>Magnesia</u>	<u>Cast Iron</u>
Inside diameter (m)	9.3	6.5
Height (m)	52	36.2
Wall thickness (m)	0.25	0.15
Weight (Mkg)	4.6	1.6
Specific cost (\$/kg)	1.09	1.19
<u>Cost comparison</u>		
Storage media cost (M\$)	2.46	4.75
Steel vessel cost (M\$)	11.00	3.75
Cast iron vessel cost (M\$)	5.00	1.90
Total cost with steel vessel (M\$)	13.46	8.50
Total cost with cast iron vessel (M\$)	7.46	6.65