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Survey of High Temperature Thermal Energy Storage

T. T. Bramlette, R. M. Green, J. J. Bartel, D. K. Ottesen, C. T. Schafer, T. D. Brumleve

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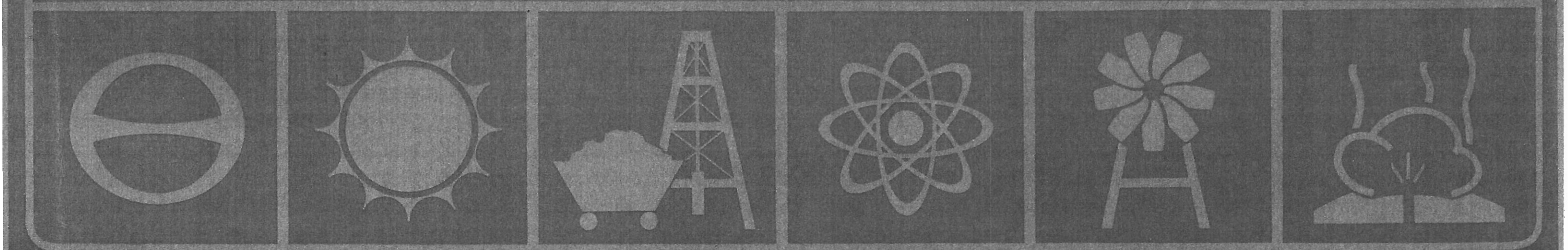

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ABSTRACT

This study represents a survey of current technology relating to high temperature thermal energy storage. The motivation for this study resulted from the need for energy storage in solar thermal applications; however, the results have much wider application. The generic classes of storage concepts considered are sensible heat, latent heat, and heat of reversible chemical reaction. The study includes a review of the basic thermodynamic aspects of thermal energy storage; a summary of storage concepts which have been conceptualized and/or built and tested, including comparisons of system characteristics within the generic classes; and, finally, specific technology surveys within the areas of materials problems, heat transfer and fluid mechanics problems and systems application. It is shown that the design and engineering of thermal storage systems have not progressed beyond the most simple concepts and that there has been only a limited effort in the design and construction of large scale systems. Current technology appears adequate to support the development of most sensible heat concepts and simple latent heat concepts while some degree of technology advancement will be required to develop advanced latent heat concepts and heat-of-reaction concepts. Specific recommendations for future research and development work are presented.

ACKNOWLEDGMENT

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SECTION 1. INTRODUCTION

This study assesses the state-of-the-art of high-temperature thermal energy storage and recommends future research and development. The prime motivation for the study is the existing need for storage for solar thermal conversion systems.* The study was restricted to methods which were applicable at temperatures greater than 200°C. The reasons for this restriction were two-fold. First, it avoided duplication of several recent and comprehensive reviews.[1.1, 1.2, 1.3, 1.4] Second, high-temperature storage is of interest for solar energy systems utilizing focused collectors, where the lack of a suitable high-temperature storage capability can lead to significant system penalties.

In this study, thermal energy storage implies a storage system where the energy is input and recovered as thermal energy. This definition allows the inclusion of some forms of chemical energy storage, while it does not include the broad class of storage systems which store chemical energy in the form of a fuel. Based upon this definition, three types of thermal energy storage systems are considered: (1) sensible heat systems, in which energy is stored by raising the temperature of the storage medium, which may be a liquid, a solid, or a combination of the two; (2) isothermal phase-transformation systems, in which energy is usually stored as the heat of fusion of the storage medium, although in some instances other transformations may be used (solid-solid, liquid-vapor, etc.); and (3) heat-of-reaction systems, in which energy is stored through the use of reversible chemical reactions.

In assessing these various storage methods, we have relied upon journal articles, conference and workshop proceedings, and personal contacts. Every attempt has been made to conduct a thorough survey. However, it is realized that this is a large field, and some sources of information may have been overlooked.

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*The results presented herein have much wider application, however. Several studies are being funded by ERDA which will identify both the necessary storage characteristics for, and the benefits which may be anticipated from, the integration of storage subsystems in such conventional energy conversion systems as electric power plants, heating, and cooling systems, etc.

Before reviewing the various storage systems which have been constructed or proposed, some general remarks are presented in Section 2 concerning the thermodynamic and heat transfer aspects of thermal energy storage systems.

Both operational and conceptual storage systems are discussed in Section 3. The purpose of this section is to present the general characteristics (physical configuration, storage material, storage capacity, input and output rates, costs, etc.) of the various storage systems which have been reviewed. These comparisons allow one to assess the advantages and disadvantages of one system relative to another in terms of such parameters as cost, maximum temperature, complexity of design, state-of-development, etc. These comparisons also dramatically illustrate the meager amount of research which has been conducted on high-temperature, high-input/output rate, thermal energy storage systems.

An assessment of the materials problems associated with sensible heat, heat of phase-transformation and heat-of-reaction storage systems is presented in Section 4. The known physical properties of potential storage media* are discussed, and required additional properties are identified. Basic material costs for selected storage media are presented. Possible limitations, such as chemical stability, corrosiveness, toxicity, flammability, etc., are discussed. Areas requiring additional research are identified.

The fluid mechanics and heat transfer problems associated with storage systems are discussed in Section 5. Theoretical analyses and experimental investigations of various storage systems are reviewed. The adequacy of available theoretical prediction techniques is assessed, and required additional research, both theoretical and experimental, is identified for each of the storage systems discussed in Section 3.

A systems analysis for a solar central receiver plant for electrical generation is given in Section 6. Pure solar and hybrid solar-fossil fuel plants are considered for both base and intermediate load demand profiles. After giving a brief description of the methodology employed, typical results are presented which illustrate the effects of the storage subsystem on the overall system performance and the need for detailed systems analysis.

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*In identifying potential storage materials for solar-thermal applications, it is necessary to satisfy certain economic constraints. For this reason, we have restricted attention to materials which are relatively inexpensive. For other applications, materials other than those considered herein might be appropriate.

Section 7 summarizes the major conclusions of the report and contains a set of recommended research tasks to lead to the systematic development of high-temperature thermal energy storage systems.

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SECTION 2. THERMODYNAMIC ASPECTS OF THERMAL ENERGY STORAGE

The purpose of this section is to discuss the basic thermodynamic and heat transfer characteristics of thermal energy storage systems. The general characteristics, such as storage capacity, are identified for the various thermal storage mechanisms (i.e., sensible heat, latent heat, and heat-of-reaction); this is followed by a discussion of heat transfer processes in terms of energy availability. The various definitions of storage efficiency are described and their impact on the performance of the total energy conversion system discussed.

2.1 General Characteristics of Thermal Energy Storage Systems

Thermal energy is considered a form of the internal energy of a system. The sensible heat content of a system, the most commonly discussed form of internal energy, is characterized by the system's temperature. The heat of phase transformation is not dependent upon the temperature, and generally occurs isothermally or over a small temperature increment. Within constraints, systems undergoing an exo- or endothermic chemical reaction can be very nearly isothermal.

The thermal storage systems discussed include concepts based on sensible heat, combined sensible and latent heat, and heat-of-reaction. Analysis of latent heat systems should include consideration of the sensible heat stored by the different phases, since isothermal operation at the phase change temperature can be difficult and the sensible heat contributions can be significant. On the other hand, the heats of reaction of typical materials can be as much as an order of magnitude greater than their sensible heat storage capacities; thus the sensible heat contribution can usually be neglected in discussions of heat-of-reaction systems.

The thermal energy content, $E(T)$, of a material at a temperature, T, which undergoes a phase change at some temperature, T_{PC} ($T_{PC} < T$), can be expressed as follows:

$$E(T) = M_s \left[\int_{T_0}^{T_{PC}} c_{s1}(T)dT + \Delta h_{PC} \int_{T_{PC}}^{T} c_{s2}(T)dt \right] \tag{2.1}$$

where

M_s = Mass of Storage Material

T_0 = Reference Temperature

c_{s1} = Specific Heat of Phase 1

c_{s2} = Specific Heat of Phase 2

Δh_{PC} = Latent Heat of Phase Transformation

As illustrated by the integral terms in Equation (2.1), the sensible heat capacity of a material depends on the temperature change (sometimes referred to as temperature swing) that can be tolerated. It is important to note that the allowable temperature swing may be limited by phase transitions, undesirable increases in vapor pressure, chemical reactions, and material instabilities. The fact that the storage of energy as sensible heat requires a temperature change in the storage material has an important thermodynamic implication. Whether this is a disadvantage depends upon the thermodynamic characteristics of the complete energy source/storage/conversion system.

In a phase change storage system, the storage capacity depends upon the temperature only to the extent of temperature swings of the sensible heat contributions to the total capacity. As the sensible heat contributions ("on either side" of the phase change) become small compared to the phase change contribution, the storage process becomes nearly isothermal.

The energy released (or absorbed) by a material undergoing a chemical reaction is nearly independent of temperature. However, the rate at which the reaction proceeds and the point at which equilibrium is reached are both highly temperature-dependent. Equilibrium and rate phenomena can have an important effect on the operation of a storage system and must be considered in its design. Thus, the capacity of a thermal storage system employing the heat of reaction of the storage medium will depend upon the extent to which the reaction goes to completion (i.e., the equilibrium state), in addition to the heat of reaction of the process.

The specific application for which a thermal storage system is being used will, in addition to requiring a specified storage capacity, require that the system be capable of accomplishing the energy input and output processes at prescribed rates. Each type of thermal storage system will have its own particular type of heat exchangers for energy input and output processes. Sensible heat storage systems can usually use the classical form of heat exchanger for liquids and gases and fixed and fluidized beds for solid/liquid or solid/gas heat exchangers. Phase transformation or heat-of-reaction systems may require a more refined heat transfer process. Specific comments on heat exchanger concepts are deferred until Section 5; analytical expressions for heat-of-fusion systems are presented in Appendix A.

One of the most important thermodynamic characteristics of thermal energy storage systems is the "quality" of the energy stored. In most thermal storage applications, the storage temperature is the typical measure of the energy quality. Factors that affect the quality of stored energy (such as energy losses to the environment and temperature drops in heat exchangers) must be thoroughly understood and taken into consideration when analyzing the operation of a thermal storage system.

A description of the energy transfer and storage processes in thermal energy systems that is based upon only the quantity of energy transferred could be somewhat misleading. For example, consider the situation where equal quantities of heat are transferred, without losses, from a reservoir at temperature T_R to two materials, A and B, whose temperatures are raised to T_A and T_B (where $T_R > T_A > T_B$) by the addition of the heat. Note that in both cases, since there were no losses, an energy accounting based on the First Law of Thermodynamics implies a "perfect" energy transfer. This "First Law" accounting, however, says nothing about the usefulness (or quality) of the energy. The usefulness of thermal energy is known as its "availability" or "available energy," which is a property of an energy system and is defined as the maximum fraction of the total energy which can be converted into useful work.

Expressions describing the availability of the various forms of thermal energy (sensible, latent, and combinations of the two) are formulated in Appendix A. These expressions are then used to develop the relationships describing the loss of availability due to heat transfer processes between the storage system and energy supply or conversion systems, as well as heat losses to the environment. Comparisons are performed to illustrate how different heat transfer processes can affect the availability of the energy transferred and to show the effects of energy losses.

2.2 Thermal Storage System Efficiency

In dealing with energy storage systems, it is sometimes convenient to be able to describe the performance of the system in terms of an efficiency. Conceptual system designs, system comparisons, and economic system analyses are examples of situations where the storage efficiency is a useful performance characteristic.

The net storage efficiency can be defined as the ratio of the energy extracted from storage to the energy initially input to storage. It is simply a measure of the energy losses resulting from the processes related to the storage of the energy.

$$\eta_{\text{net}} = \frac{\text{Thermal Energy Out}}{\text{Thermal Energy In}}$$

The usefulness of the net storage efficiency is limited by the fact that it contains no information about the availability change that the energy may undergo due to the storage system; it represents only a "First Law" energy accounting.

A storage efficiency defined in terms of the energy availability would overcome the "energy quality" limitation of the net storage efficiency. Since the availability describes the maximum amount of work obtainable from a quantity of thermal energy, the available energy storage efficiency compares the maximum work obtainable from the energy taken from storage to the maximum work obtainable from the energy originally supplied to storage. Specifically, the definition of available energy storage efficiency is the ratio of the availabilities of the energy discharged to the energy used to charge; i.e.,

$$\eta_{\text{avail}} = \frac{\text{Availability of Energy Extracted}}{\text{Availability of Energy Input}}$$

A further refinement in the definition of storage efficiency could be the inclusion of the actual efficiencies of the devices used to convert the thermal energy to work. An efficiency defined in this manner would, in addition to accounting for the energy quality changes in storage, also account for the energy conversion penalties which occur in real systems. This system efficiency can be expressed as follows:

$$\eta_{\text{actual}} = \frac{\text{Energy Out x } \eta_{\text{Output}}}{\text{Energy In x } \eta_{\text{Initial}}}$$

where

η_{initial} = the efficiency of the energy conversion device if storage is not used,

η_{output} = the efficiency of the energy conversion device if storage is used.

This particular expression for efficiency requires real performance characteristics for its evaluation. Thus, the energy supply, storage, and conversion systems must be designed and analyzed in order to obtain the needed characteristics, making it somewhat less attractive for making "quick and simple" comparisons of storage system applications.

SECTION 3. REVIEW OF OPERATIONAL AND CONCEPTUAL THERMAL ENERGY STORAGE SYSTEMS

The previous section discussed in general terms the factors to be considered in the selection and design of a thermal energy storage system. The present section reviews the various sensible heat, phase transformation,* and heat-of-reaction storage systems which have been constructed or proposed. The discussion is limited to a description of the systems, the applications for which they have been utilized or proposed, their current status, their physical characteristics, and their projected costs. Comparisons of the various systems are given and the advantages and disadvantages of each system are discussed. A discussion of the technical problems associated with these systems is given in Sections 4 and 5.

3.1 Sensible Heat Storage Systems

Table III.1 is a compilation of operational and conceptual systems for storing energy in the form of sensible heat. As discussed earlier, the amount of energy stored depends on the temperature swing of the storage material. The temperature difference indicated in Table III.1 are those proposed in the original references. Thus, care must be exercised when comparing characteristics such as kw_t-hr/(kg, m^3, or \$). It was decided to quote the original temperature differences rather than convert them to a uniform temperature difference, since for some of the methods, such a change in temperature limits would not be compatible with the original system for which the storage was proposed. However, such a conversion may be readily accomplished if desired.

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*These systems may involve more than one transition, and in general, utilize the sensible heat content of the storage material on either side of the transition(s).

TABLE III. 1
OPERATIONAL AND CONCEPTUAL SENSIBLE HEAT STORAGE SYSTEMS

Storage Configuration	Storage Medium	Applications	Status	Temperature (°C)			Capacity		Input Rate	Output Rate	Cost	Heat Exchanger	Comments	Ref
				T_{MAX}	$T_{MAX}-T_{MIN}$	MW_t-hr	$\frac{kW_t\text{-hr}}{m^3}$	$\frac{kW_t\text{-hr}}{kg}$	kW_t	kW_t	$\$/kW_t$-hr			
Above Ground Tank H-10m, R=0.5m	Water	Solar Central Receiver	Engineering Design	210 300	87 87	4.1 4.1	86	0.086		42,500 to 5640	8.0 22.0	Conventional-External to Tank	Capacity figures based upon modules of seven tanks	3.1
Above Ground Tank H=3.15m, R=0.89m	Water, Therminol	Solar Total Energy System	Preliminary Testing	232 343	56 56	.41	64.6	0.064	100-120	25-50	–	Conventional-External to Tank	Instrumented with thermocouples	
Steam Accumulator H=14.6m, R=1.83	Water	Solar Central Receiver	Engineering Design	200 300		14 37	99.3 262.4	0.11 0.29		33,300 41,800	3.0 6.0		Indicated output is peak value	3.1
Underground Tank H=30m, R=13m Depth=60m	Water	Storage for Nuclear Plant	Preliminary Design	217	141	4370	146	0.146		624	0.4	Conventional	Pressurized cavern eliminates need for thick-walled vessels. Storage used for feedwater heating	3.4, 3.5
Acquifers	Water and Sand	Waste Heat Storage	Conceptual	170	110	42,000	31.5		19,400	19,400	0.003	Conventional	Simple performance calculations discussed	3.7, 3.8
Above Ground Tanks (Other Fluids)	Therminol-55 Therminol-66 Caloria-HT-43 HITEC	Solar Central Receiver	Engineering Design	315 315 302 500	55 55 83 300	226 226	24.4 24.4 47.2 220	0.032 0.032 0.068 0.12		452,000 452,000	62 27 11 4			3.9 3.9 3.10 3.11
Solid Storage Materials	- Cast Iron	Industrial Space Heating Paint Manufacture	 Operational Operational	 750 700	 480 430	 0.75 0.64	 60	 0.17 0.1	 96 80	 ~50 180	 ? ?	Core to Air	Electrical resistance heaters used for input	3.12 3.13
Packed Beds H=17.3m, R=9.7m	Granite Caloria-HT-43	Solar Central Receiver	Preliminary Design	302	84	195	60	0.027	42,200	30,400	5.13	Direct Contact	Some small scale experiments complete	3.10
Fluidized Bed	Sand Fly Ash	Storage for Power Plant	Conceptual	800	400	4000	64	0.04	500,000	500,000	?	Fluidized Bed Heat Exchanger		3.15
Underground	Soil	Sink for Waste Heat for Underground Power Sources	Preliminary Design	100	85	500	52		1000		0.4-0.8	Grid of Pipes	Excellent review of soil properties, detailed modeling	3.17, 3.18
	Limestone or Granite	Solar Central Receiver	Conceptual	500	400	500,000				625,000	?	9000 Vertical Holes		3.19

3.1.1 Water Systems

The first entry in Table III.1 is an above-ground tank for storing hot water.[3.1] It was chosen as a representative design for thermally stratified tanks because of the application, which was solar thermal electrical power generation, its large capacity and discharge rate (4.1 MW_t-hr, and 42.5 to 5.64 MW_t*), and because a detailed cost analysis was performed. The characteristics indicated are representative of other designs (Ref. 3.2, for example). The problem of high pressure containment at elevated temperatures is reflected quite clearly in the cost column; an increase in storage temperature of 90°C results in a factor of 2.75 increase in cost.

The second entry in Table III.1 is an experimental storage subsystem which is being integrated into the Sandia Laboratories Total Energy System. Although its capacity and input/output rates are less than those of Ref. 3.2, they are large enough to provide operating experience when coupled with a complete solar system. The system is instrumented to provide information regarding thermal stratification and has a multi-fluid capability. Some preliminary testing with a simulated solar input has been completed. Because the system is designed to test a variety of storage fluids, which requires components with both high temperature and high pressure capability, cost figures are not particularly meaningful.

The steam accumulator configuration[3.1] described in Table III.1 is representative of the capacities (14-37 MW_t-hr) and peak discharge rate (33-42 MW_t) which can be achieved with these systems. The accumulator, an example of which is shown in Figure 3.1, is similar to a hot water tank in that the energy is stored as the sensible heat of water. It differs, however, in that both the input and output are steam. During charging, steam is passed through the water, where it condenses and raises the temperature and vapor pressure. Discharging is accomplished by decreasing the pressure slightly, which allows the water to boil, and if discharge is not too rapid, the system will delivery dry saturated steam. The state-of-the-art of accumulators is quite advanced;[3.3] they find wide spread application in Europe where they are used primarily to meet fluctuating steam demands for industrial purposes. As with hot water storage systems, the problem of high pressure containment results in increased cost at high temperatures.

The above examples illustrate the limitations of above-ground storage systems utilizing high-temperature water. It has been proposed[3.4, 3.5]

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*The decreasing output results from the discharge strategy which was adopted for each tank; this is not a general characteristic of hot water storage systems.

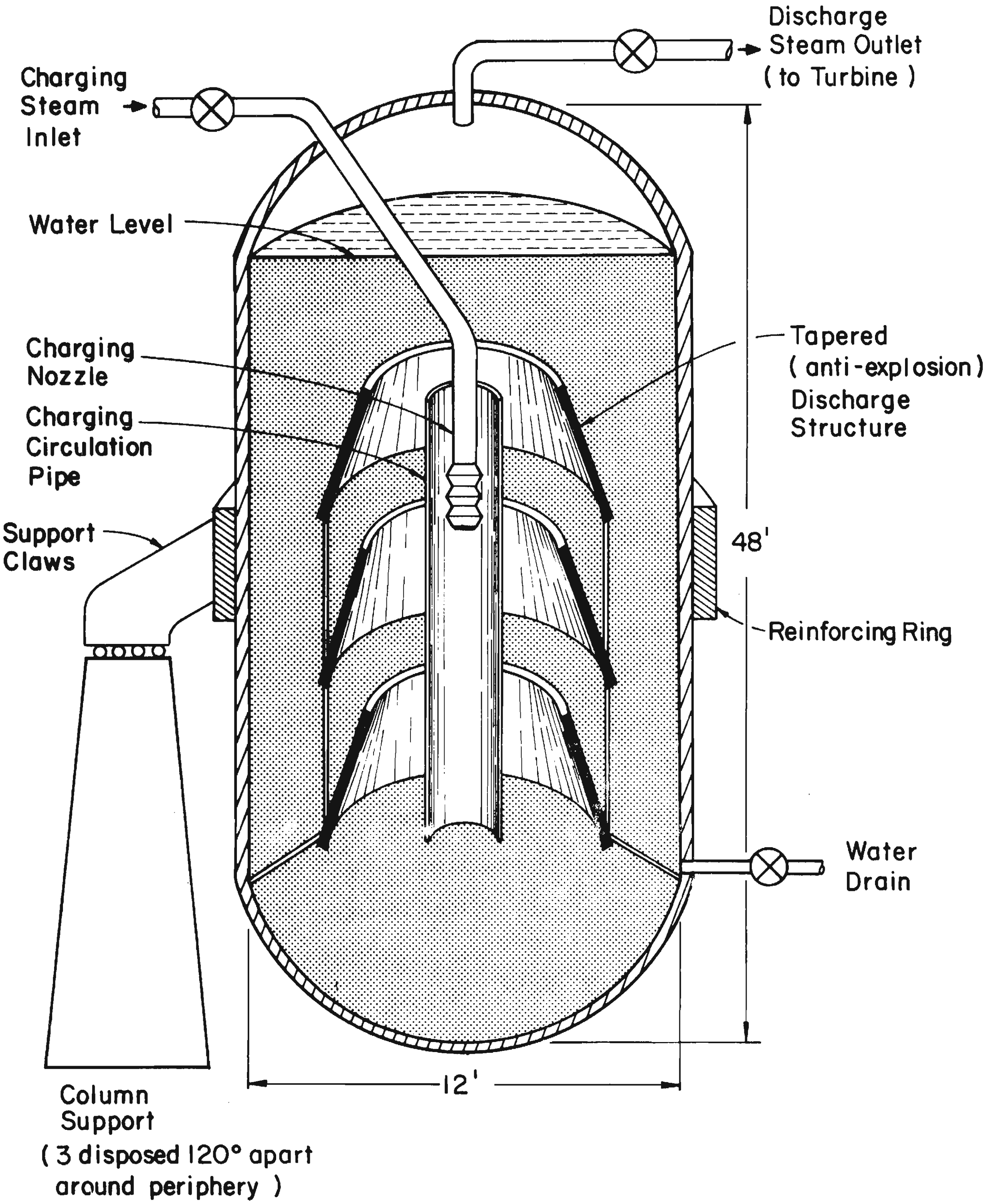

Figure 3.1 Cut-Away View of Vertically Mounted Steam Accumulator Thermal Storage Tank (Ref. 3.1, reproduced with permission)

that these limitations could be reduced by taking advantage of the lithostatic pressure field of the earth. Figure 3.2 is an example in which a large tank ($h = 30$ m, $r = 13$ m) is located in an excavated cavern at a depth of approximately 60 m. By pressurizing the cavern, thin-walled vessels may be utilized and the cost of storage is reduced significantly (see Table III. 1). In spite of the fact that this idea was patented in 1958, it does not appear to have been put into practice.

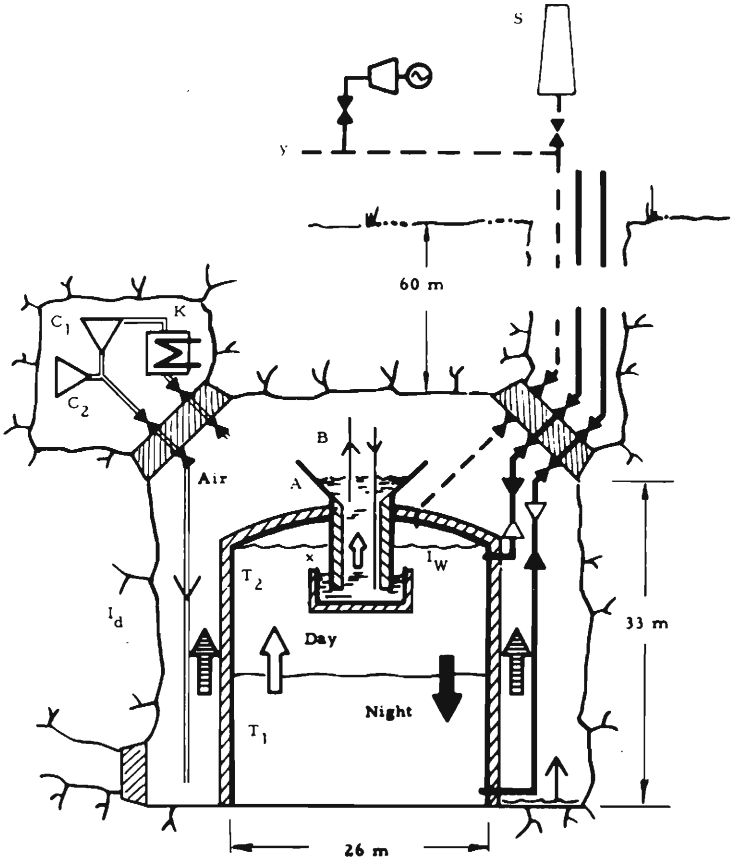

Figure 3.2 Underground Storage Tank With Dry Insulation and Internal Steam Expansion Volume (Ref. 3.4, reproduced with permission)

A second concept[3.6, 3.7, 3.8] which takes advantage of the earth's pressure field involves hot water storage in acquifers. This concept, illustrated[3.7, 3.8] in Figure 3.3, involves injecting hot water into an acquifer which is roughly 150 m deep, and confined from above and below. Proposed injection and withdrawal rates and total capacity are quite large, 19.4 MW_t and 4370 MW_t-hr respectively, while the projected cost for storing water at 170°C is quite low (0.003/kW_t-hr). The illustration shows a single well which is used for injection and withdrawal. In some cases multiple wells may be required, e.g., if there is appreciable flow of the ground-water in the acquifer. This concept is still in an early stage of development. Some preliminary modeling has been completed, but no experimental work has been done. Initial applications will be at a relatively low temperature (170°C).

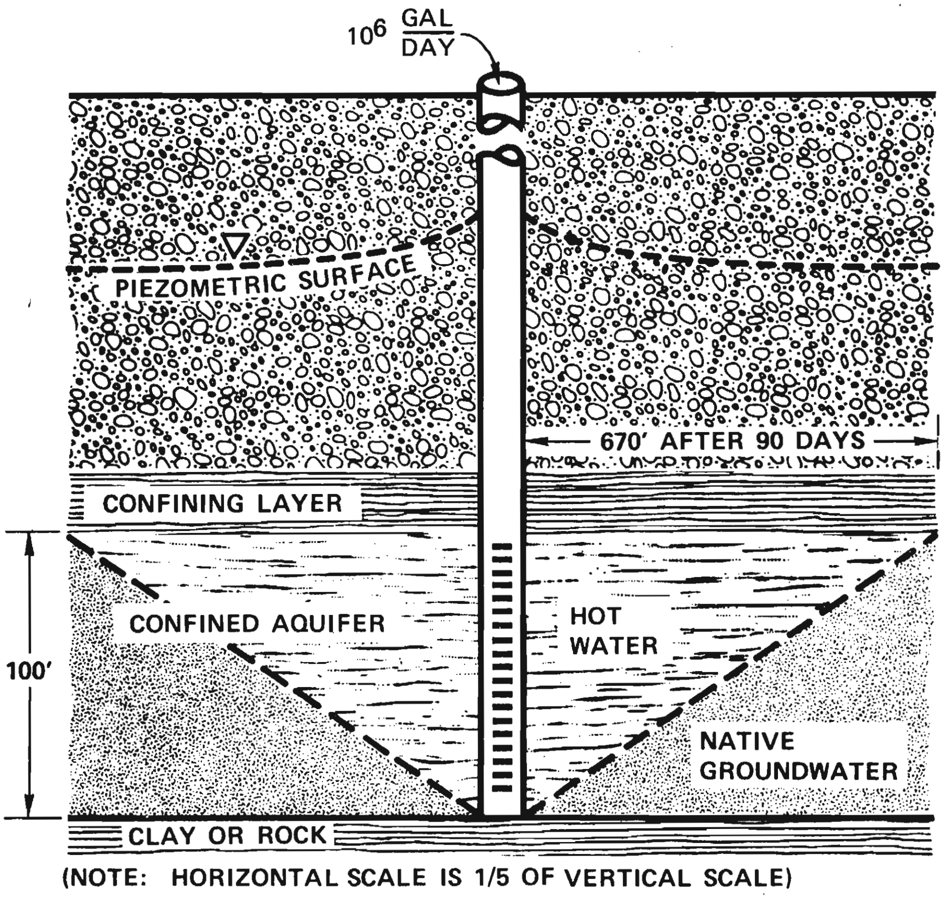

Figure 3.3 Heat Storage in a Confined Acquifer (Ref. 3.7, reproduced with permission)

3.1.2 Other Liquid Systems

All of the above examples have utilized water as the storage material for the obvious reasons that it is cheap, readily available, environmentally neutral, and has a large specific heat. Its disadvantage, of course, is its high vapor pressure at elevated temperatures. One solution to this problem is to utilize liquids[3.9, 3.10, 3.11] with low or negligible vapor pressures over the temperature range of interest. The most commonly proposed substitutes are petroleum-based heat transfer oils and molten salts. Some typical examples are presented in Table III.1 (additional candidates are discussed in Section 4). In general, the heat capacities are 25 to 40 percent of that of water. The petroleum-based oils are generally limited to temperatures less than 350°C, and can be prohibitively expensive. The one molten salt shown is HITEC, which is a mixture of $NaNO_2$, $NaNO_3$, and KNO_3. If the full temperature range of HITEC can be accommodated, it appears attractive when compared with heat transfer oil.

3.1.3 Solid and Solid/Liquid Systems

An alternate solution to the vapor pressure problem of liquids is to utilize the heat capacity of solids. Storage units based upon this concept are in wide spread use in Europe, most frequently for space heating. The two examples[3.12, 3.13] selected in Table III.1 are representative of larger versions of this system and use "bricks" which are stacked in such a way as to provide channels. The system is charged with electrical resistance heaters and discharged by passing air through the channels in the storage core. Note that the operating temperatures are much higher (700 and 750°C) than those attained with liquid systems. In spite of the high peak temperature, the operation of these systems is such that the bulk temperature of the storage medium continually drops during discharge; i.e., the system is like a mixed liquid system. Although no cost figures were found, the low cost of the storage materials and simplicity of the system design suggest low system cost. The characteristics of a number of smaller systems are given in Refs 3.13 and 3.14. A packed bed of solid particles could also be used as a solid storage system. The large surface area of the solids results in excellent heat transfer with the working fluid, which may be either a gas or a liquid. A storage system*[3.10] based upon this concept is listed in the table and illustrated in Figure 3.4. The solid material is granite, and the heat transfer fluid is Caloria HT-43 (the heat capacity of the Caloria provides a significant portion of the total system capacity). Heat transfer characteristics are such that energy input and withdrawal occurs within a narrow thermal stratification zone. Utilization of granite results in a significant reduction in cost (approximately a factor of 3.5) compared to a system comprised solely of a petroleum-based oil. This system is a preliminary design for the Solar Central Receiver Program; small-scale testing is in progress.

A second system[3.15] utilizing solid particles for storage is illustrated in Figure 3.5. In this case, the hot and cold particles are stored in separate bins with energy input and output accomplished by fluidizing the particles and flowing them past a heat exchanger. This concept is attractive because of the high heat transfer rates associated with fluidized solids. The figures in Table III-1 are based upon representative heat capacities and temperature differences. The system is still in the conceptual stage; however, preliminary cost estimates[3.16] are encouraging.

The final two storage concepts listed in Table III.1 utilize the heat capacity of the earth. Strictly speaking, the first[3.17, 3.18] is not applicable to the present study because of the low temperature (100°C) and the application, which is to dissipate waste heat from an underground power

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*A patent application for this system has been filed by the McDonnell Douglas Astronautics Company and the Rocketdyne Division of Rockwell International.

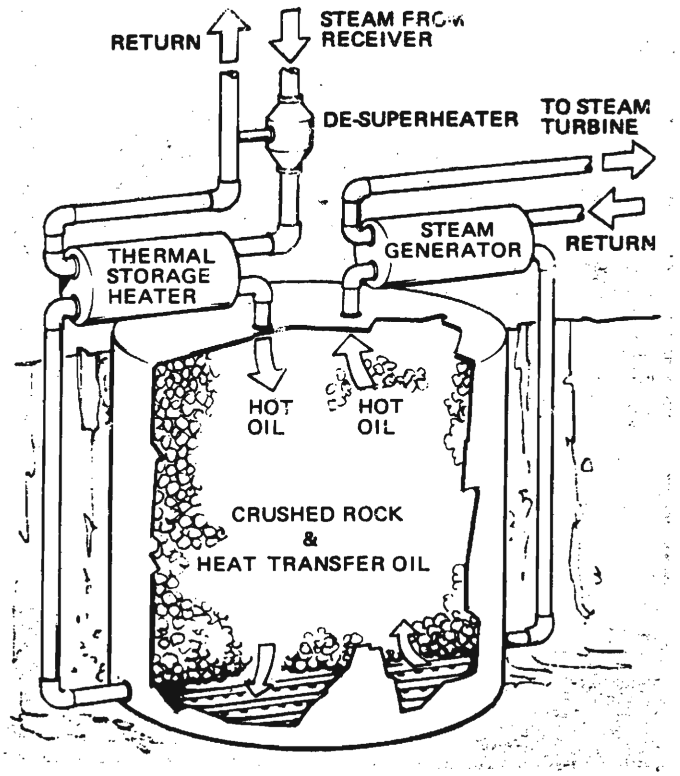

Figure 3.4 Packed Bed Sensible Heat Storage System
(Ref. 3.10, reproduced with permission)

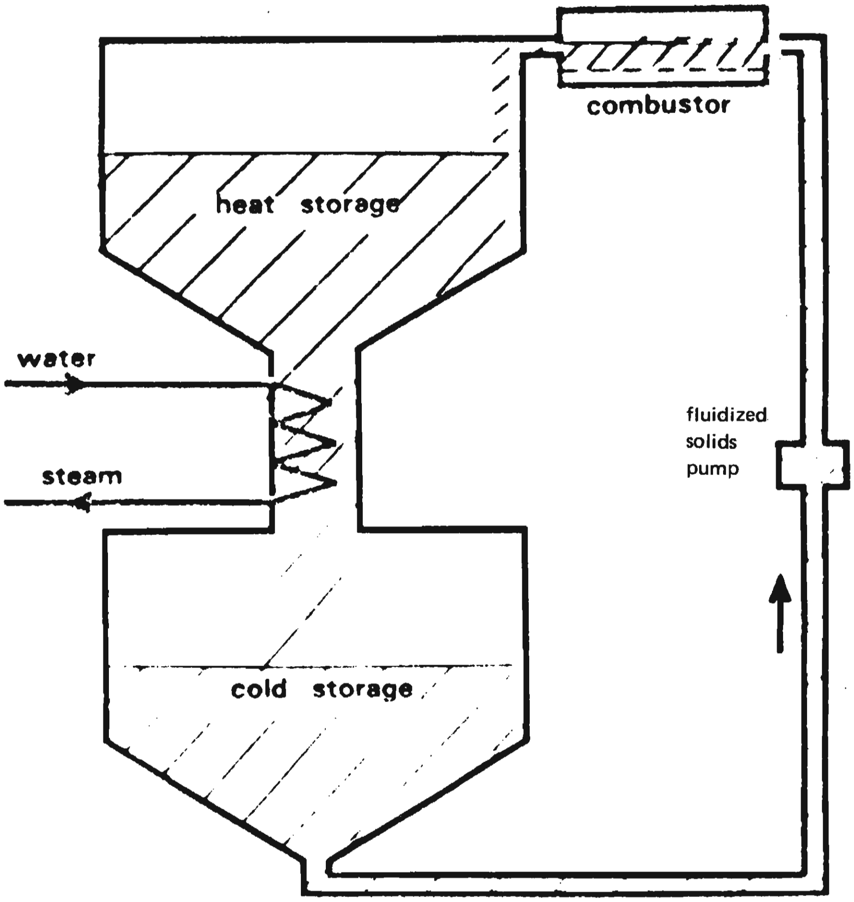

Figure 3.5 Concept of Fluidized Bed Heat Storage System (Ref. 3.16, reproduced with permission)

plant. It is included, however, because the two references which describe it contain an excellent review of the problems associated with underground storage, as well as an analysis of the heat transfer and cost. The construction of the system consists of excavating a cavity, installing a grid of pipes for heat transfer, and then backfilling the excavation. Storage capacity and input rates are high and the cost is low. The second system[3.19] utilized underground formations of limestone or granite. Energy is input or extracted through vertical pipes connected by a manifold system. Amortized costs were given, but there is not enough information to convert these costs to a capital cost. It is not known whether additional work has been done.

3.2 Phase Transformation Systems

Table III.2 is a compilation of proposed and operational systems which utilize phase transformations. The most striking features are the limited number of compounds which have been utilized for storage systems and the small scale of most of the systems. Note that capacities are given in kW_t-hr, rather than MW_t-hr, as was the case in Table III.1.

3.2.1 Passive Heat Exchanger Systems

The first three entries in Table III.2 represent systems designed for space-vehicle solar energy storage. All three utilized lithium hydride because of its extremely high heat-of-fusion. The largest[3.20, 3.21] of the three (1.87 kW_t-hr) is illustrated in Figure 3.6. The LiH was contained between two concentric cylinders;* a conical region at the top was provided to allow for the density change of the storage material which occurs upon melting. Electrical resistance heaters (8-12 kW_t) located within the inner cylinder provided the simulated solar energy input. Energy extraction (43 kW_t) was accomplished with coils on the external cylinder through which Dowtherm A was passed.

The two smaller configurations utilizing LiH are illustrated in Figures 3.7 and 3.8. Both units had optical cavities, and each could operate with solar input as well as simulated solar input (electrical resistance heaters). The design[3.22] shown in Figure 3.7 consisted of a coiled heat exchanger through which mercury (for solar tests) or air (for simulated solar tests) flowed. Capacity, input and output rates were

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*A second configuration which had fins located in the LiH was also tested.

TABLE III. 2

OPERATIONAL AND CONCEPTUAL HEAT-OF-FUSION STORAGE SYSTEMS

Storage Configuration	Storage Medium	Application	Status	T_{MAX}	$T_{MAX}-T_{MIN}$	Capacity			Input Rate kW_t	Output Rate kW_t	Cost $\$/kW_t$-hr	Heat Exchanger	Comments	Ref
						kW_t-hr	$\frac{kW_t\text{-hr}}{m^3}$	$\frac{kW_t\text{-hr}}{kg}$						
Annulus R_I=0. 114m, R_0=0. 127m H=0. 349m	LiH	Orbital Solar Energy Storage	Lab Scale Experiment	688		1. 87	496	0. 71	8-12	43		Inner and Outer Cylinder Surfaces A_I=0. 251 m^2, A_0=0. 279 m^2	Geometry with internal fins also tested. Detailed mathematical modelling	3. 20, 3. 21
Cylinder R=0. 088m, H=0. 042m	LiH	Orbital Solar Energy Storage	Lab Scale Experiment	680		0. 281	381	0. 66	0. 81	0. 53		Coiled Tube with Fins A=0. 037 m^2	Lower capacity/m^3 due to heat exchanger tubes	3. 22
Annulus	LiH	Orbital Solar Energy Storage	Lab Scale Experiment	688		0. 2		0. 75	0. 66	0. 31*		Thermoelectric Convertors in LiH	*Output was electric, 0. 31 is kW_t	3. 23
Cylinder R=0. 037m, H=0. 905m	LiF/LiOH Eutectic	Underwater Propulsion	Lab Scale Experiment	427		3. 51	902	0. 64		1. 17		Single Straight Tube A=0. 031 m^2	Input was electrical resistance heater eutectic has low volume change upon melting larger system designed and built, but never tested	3. 24
Cylinder R=0. 343m, H=0. 914m	NaOH	Space Heater	Lab Scale Experiment	510	458	40	484	0. 31	6. 9	2	?	U-Tubes, A =0. 66 m^2	Input was electrical resistance heater	3. 26
Cylinder R=0. 305m, H=1. 52m	NaOH	Hot Water	Operational Units	482	361	193	434	0. 29	20	20	4. 60	Coiled Tube, A=1. 7 m^2	Input was electrical resistance heater. Extensive field testing	3. 27
Rectangular Models	NaOH	Space Heater	Operational Units	482	361	117		0. 29	12	7. 3	5. 10	External Surface of Modules	Input was electrical resistance heater extensive field testing	3. 27
Cylinder R=16. 8m, H=33. 5m	NaF/FeF_2 Eutectic	Storage for Nuclear Reactor	Conceptual	680		9.6×10^6	423	0. 19	8×10^5	8×10^5	21**	Direct Contact With Molten Lead	**Cost of lead and NaF/FeF_2 only	3. 30
Required Volume = 1622 m^3	KNO_2 - $NaNO_2$ (0. 21 - 0. 79)	Solar Central Receiver	Preliminary Design	254		1.8×10^5	96	0. 043	4.9×10^4	3×10^4	17	Straight Tubes With Scraping	Other salts being considered, small scale scraping experiments promising	3. 31
Large Tank	$Ge_{0.4}S_{0.6}$	Storage for Electrical Utilities	Conceptual	590										3. 32

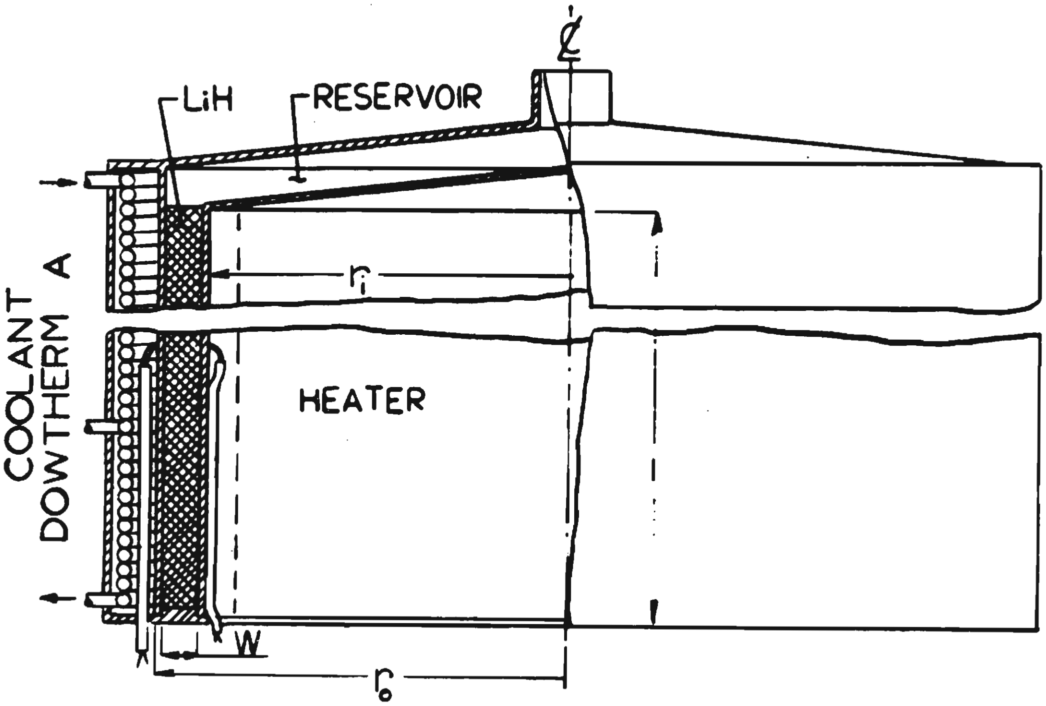

Figure 3.6 Diagram of LiH Heat Storage System
(Ref. 3.21, reproduced with permission)

0.281 kW_t-hr, 0.81 and 0.53 kW_t, respectively. In the design[3.23] shown in Figure 3.8, energy was conducted through the optical cavity walls and absorbed by the LiH. Energy output was electrical and was provided by 12 series connected modules, each of which had 10 thermoelectric couples. Performance characteristics (0.2 kW_t-hr and 0.66 and 0.31 kW_t) were similar to those obtained for the design described in Ref 3.22.

Although a fairly extensive testing program was conducted for the above units, there is no indication that any of them were used in space flight applications.

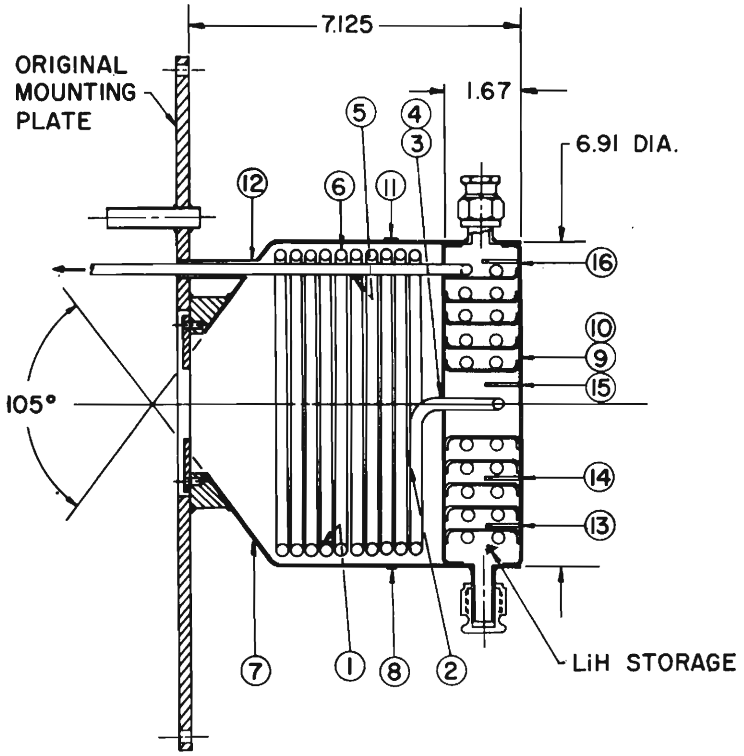

Figure 3.7 Diagram of LiH Storage System with Solar Receiver (Ref. 3.22, reproduced with permission)

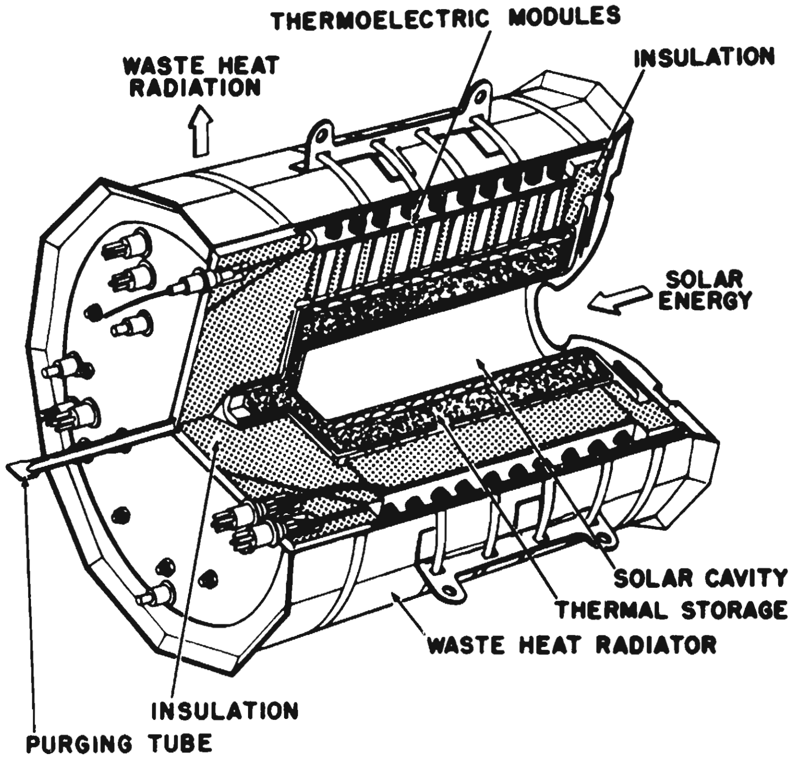

Figure 3.8 Diagram of LiH Storage System with Solar Receiver and Thermoelectric Converters (Ref. 3.23, reproduced with permission)

Figure 3.9 illustrates a configuration[3.24] considered by the Navy as part of a program to develop a thermal storage system for underwater applications. The storage medium utilized was a eutectic mixture of lithium fluoride and lithium hydroxide. This material was selected because it has a very small volume change upon solidification or melting, which greatly simplified the mechanical design. Energy input was accomplished with an electrical resistance heater whose power was not specified. A single, straight tube which passed through the center of the unit was utilized to generate steam. The storage capacity was 3.51 kW_t-hr, and the output power was 1.17 kW_t. There are indications[3.25] that a larger system was designed and constructed, but never tested due to the termination of the program.

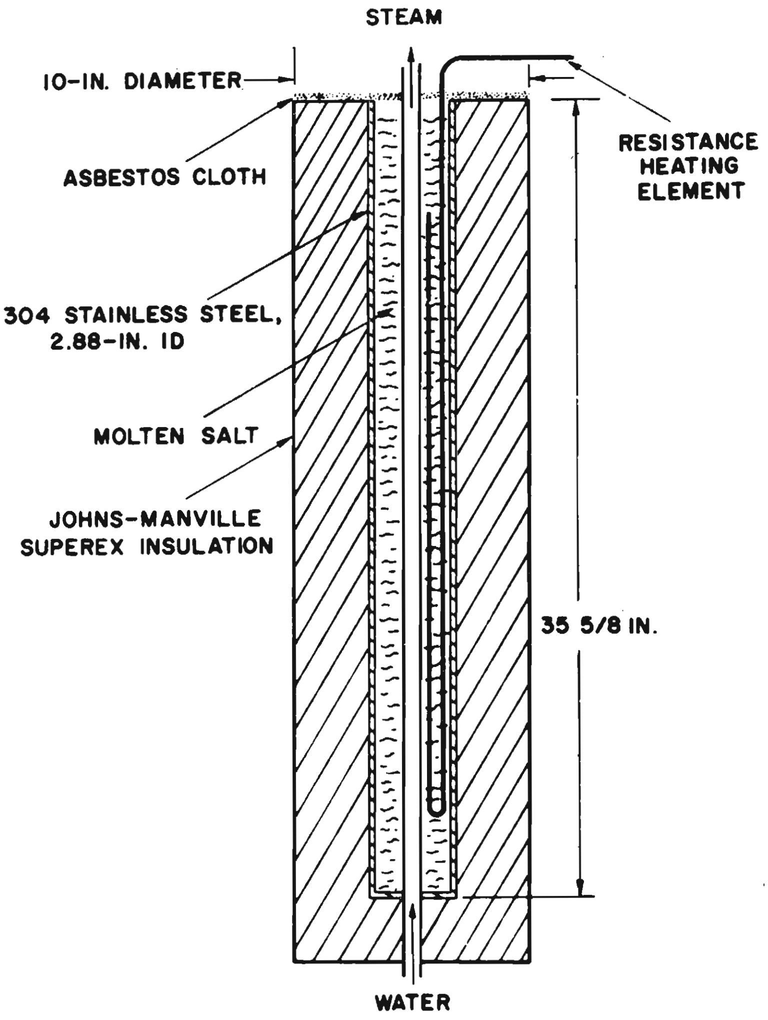

Figure 3.9 Diagram of LiF/LiOH Storage System
(Ref. 3.24, reproduced with permission)

The next three configurations[3.26,3.27] listed in Table III.2 are the largest systems utilizing phase-transformations for which information was found. Sodium hydroxide, which melts at 318°C and has an unusually energetic solid-solid transition at 287°C, was the storage material. The solid-liquid and solid-solid phase transitions, as well as the sensible heat capacity of both the liquid and solid NaOH, were utilized for energy storage.

Figure 3.10 presents the details of an experimental room heater (capacity of 40 kW_t-hr) which was basically a cylindrical tank filled with NaOH; electrical resistance heaters (6.9 kW_t) provided energy input, while copper tubes through which air passed were utilized for output (2 kW_t). No further reference to this system was found, and it is not known if the units were extensively tested or marketed.

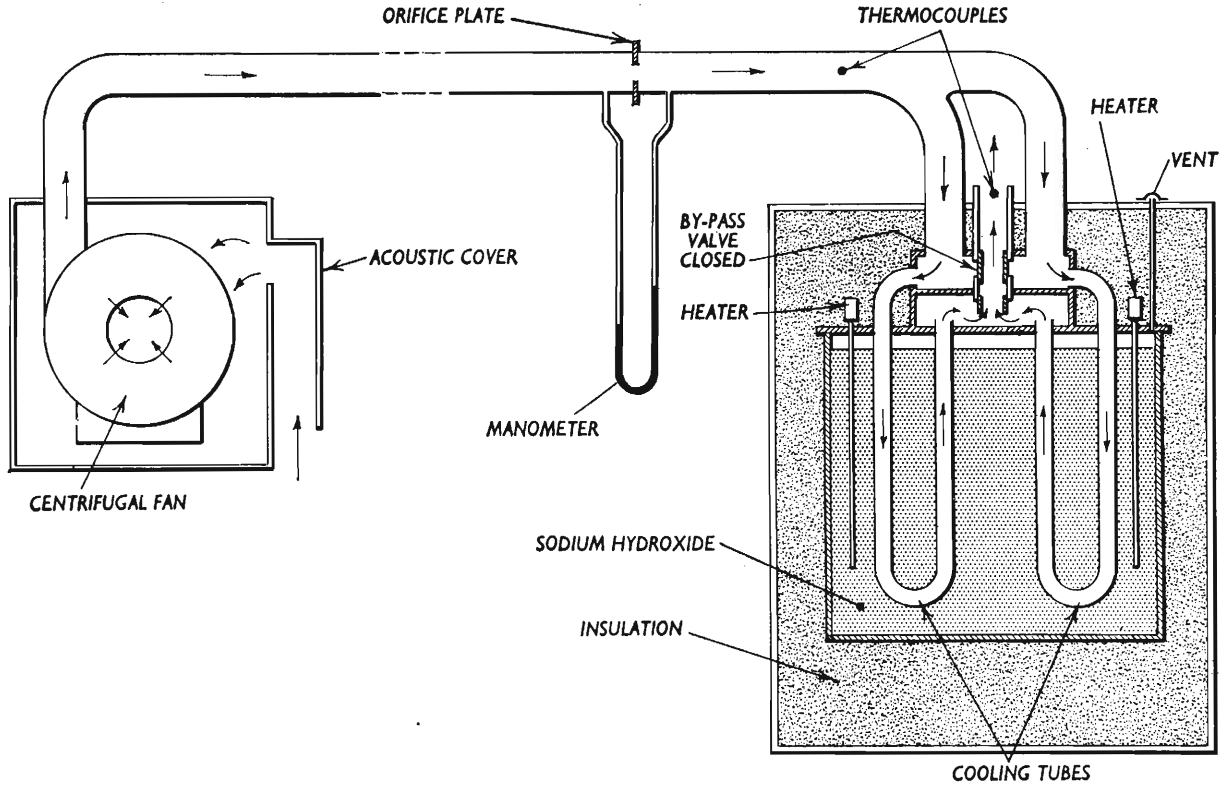

Figure 3.10 Experimental Heater to Store About 40 kWh of Recoverable Heat in Sodium Hydroxide (Ref. 3.26, reproduced with permission)

Two systems which were extensively field tested are shown in Figures 3.11 and 3.12. The first of these is a large hot water heater (193 kW_t-hr), which was charged electrically (20 kW_t). A unique feature of this design was the coiled vertical heat exchanger for energy output. By introducing cold water into the bottom of the coiled tube, a solidification front is formed in the NaOH. This front moves upward as the storage unit is discharged, and output rate (20 kW_t) remains constant with time. Estimated cost for this unit was \$4.60/kW_t-hr. The second system, a 117 kW_t-hr unit designed for space heating, consisted of six modules containing sodium hydroxide which were charged with internal electric resistance heaters (12 kW_t). The modules were arranged to provide channels for heating air as the unit was discharged (7.3 kW_t). This unit was estimated to cost \$5.12/kW_t-hr.

It is important to note that the above systems, which are the largest heat-of-phase-transformation systems built to date, are three orders of magnitude smaller in capacity and input/output rate than required for the 10 MW_e solar central receiver electrical generating plant. Conceptual designs[3.28, 3.29] of two much larger NaOH systems [(1) capacity = 0.88 MW_t-hr, input/output rate = 0.37/0.24 MW_t; and (2) capacity = 1350 MW_t-hr, input/output rate = 450 MW_t] suggest that storage could be provided for approximately \$6.75 and \$5.00/kW_t-hr, respectively.

3.2.2 Active Heat Exchanger Systems

The systems discussed above have utilized conventional passive heat exchangers. The final three entries in Table III.2 are systems which employ active heat exchangers. The first of these, which relies upon direct contact heat transfer between the storage medium and a heat transfer fluid,[3.30] was proposed as a storage system for use with a nuclear reactor. The system is essentially a large cylindrical tank (30,000 m^3) of molten salt through which molten lead passes (a conventional heat exchanger is used to transfer heat from the lead to the turbine working fluid). The proposed system is large (9.6×10^3 MW_t-hr), as are the input and output rates (800 MW_t). One proposed storage medium is a eutectic mixture of NaF/FeF_2. The cost figure of \$21/kW_t-hr is based upon the current price of lead and NaF and the price of the raw materials for manufacturing FeF_2. Some small scale testing using mercury as the heat transfer fluid has indicated that the salt which solidifies on the droplets of mercury during discharge of the system is broken off at the bottom of the tank and that a pool of mercury is formed.[3.31]

Figure 3.13 is a schematic of a storage system described by Severson and Smith,[3.32] which is proposed for use with a central receiver solar power plant. Two different heat exchangers are utilized for energy input and output. A conventional heat exchanger with extended surfaces is used for energy input; energy output is accomplished using a series of straight boiler tubes which are periodically scraped to remove the frozen salt. The performance figures listed in Table III.2 indicate that a 180 MW_t-hr system with input and output rates of 49 and 30 MW_t, respectively, could be constructed for a cost of \$17/kW_t-hr. Small scale experiments with a scraper system have yielded encouraging results. Several other salt mixtures are being considered which show promise of further cost reduction.

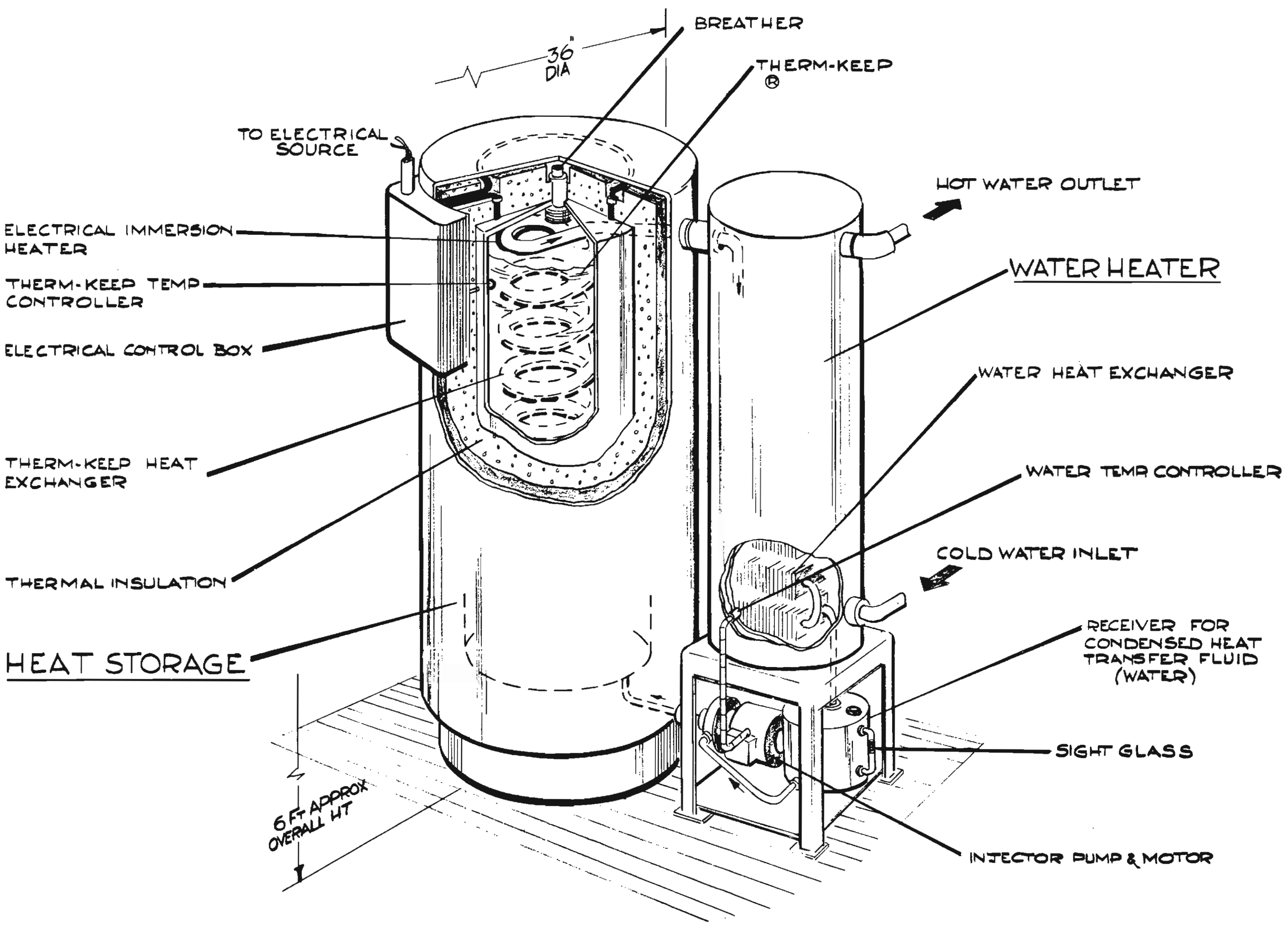

Figure 3.11 "Therm-Bank" Water Heater
(Ref. 3.27, reproduced with permission)

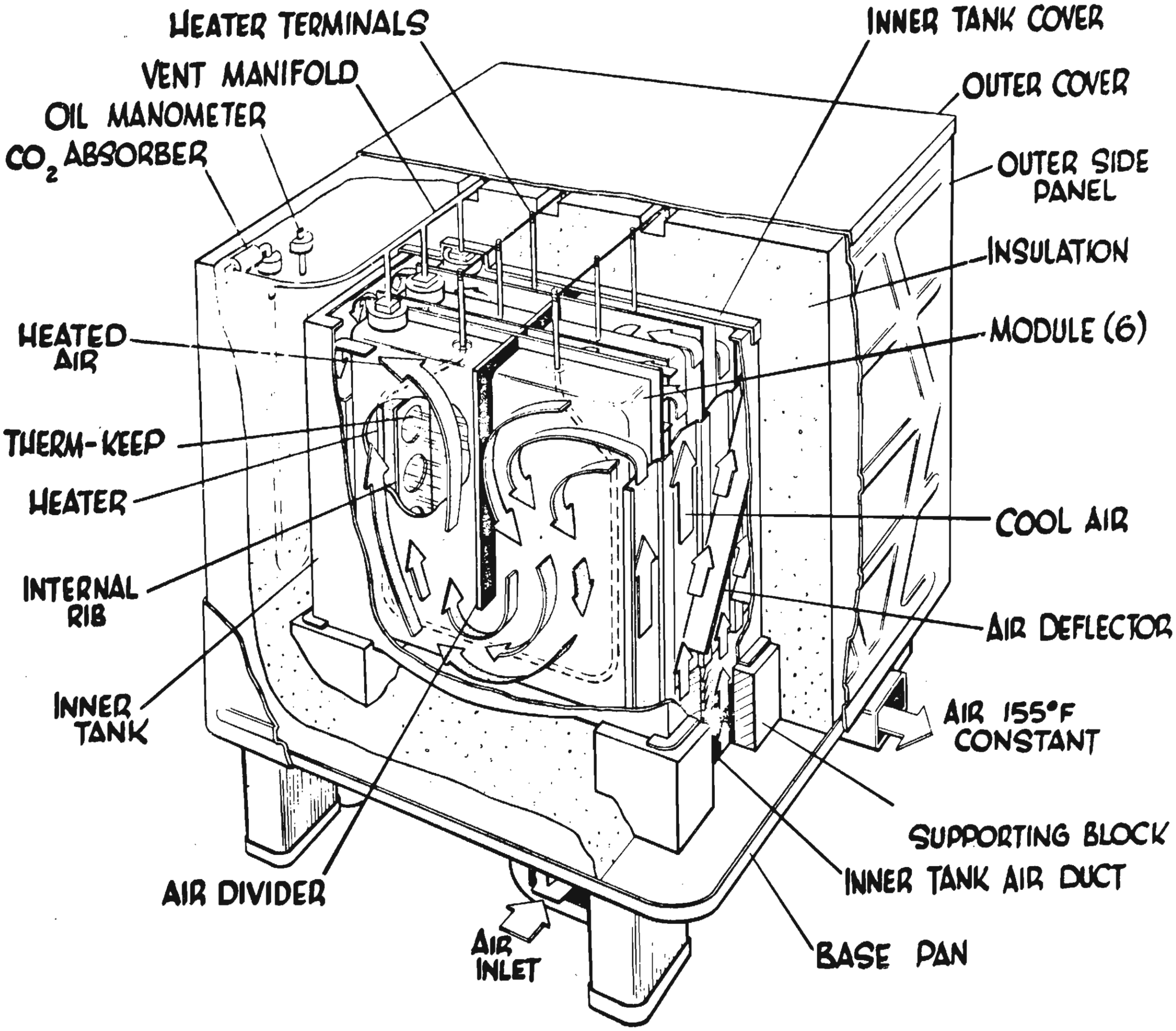

Figure 3.12 "Therm-Bank" Space Heater
(Ref. 3.27, reproduced with permission)

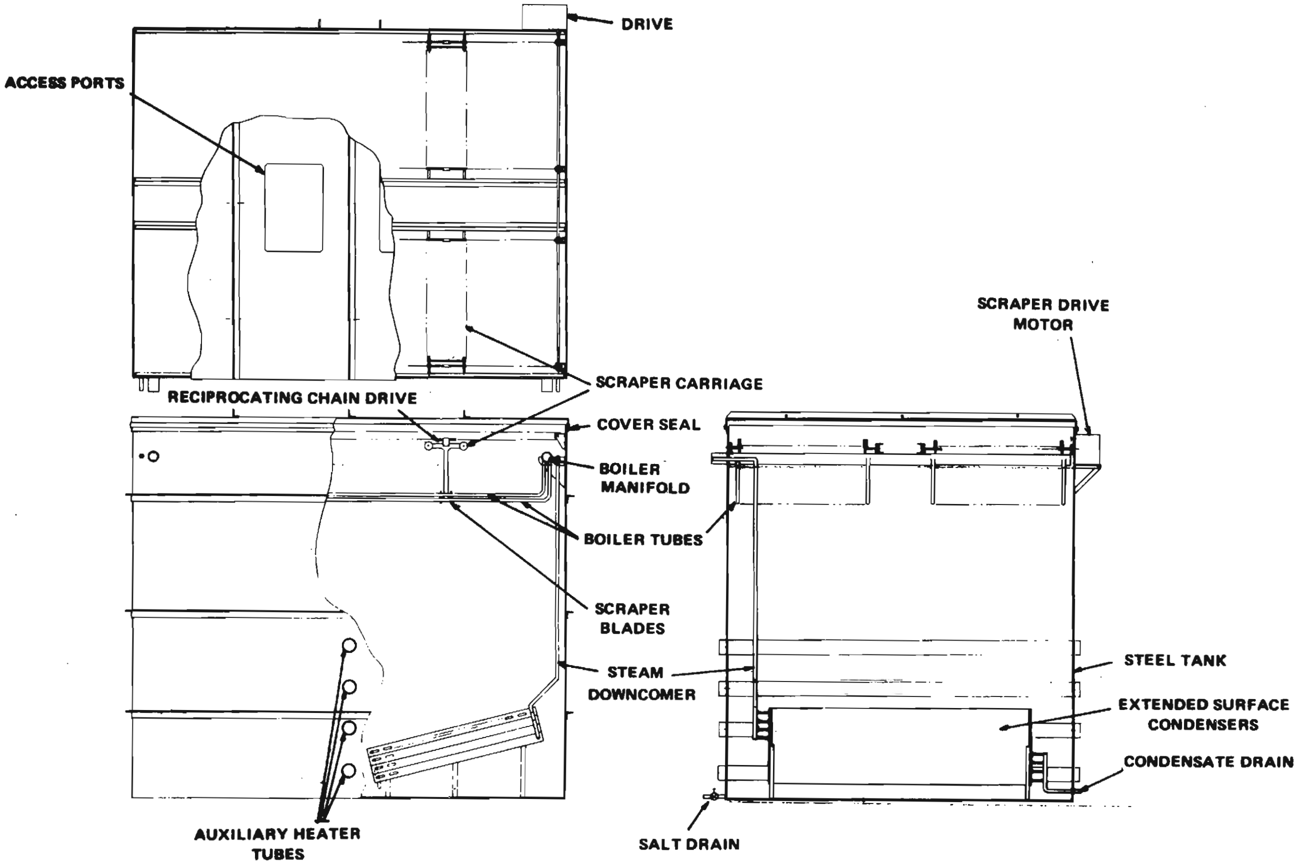

Figure 3.13 Heat-of-Fusion Thermal Storage System with Active Heat Exchanger (Ref. 3.22, reproduced with permission)

The final concept[3.33] in Table III.2 involves the use of a germanium sulfide compound, $Ge_{0.4}S_{0.6}$. This material was selected because it does not have a tendency to stick to the heat exchanger on which it has solidified, and since the solid is less dense than the liquid, it tends to float to the top of the storage tank. Current research is concerned with $Ge_{0.4}S_{0.6}$ property determination and methods for reducing the costs of germanium.

3.3 Reversible Chemical Reactions

The storage of thermal energy using reversible chemical reactions is a relatively new idea which has three advantages as a storage mechanism:

1. the energy stored per unit mass and volume is at least an order of magnitude greater than that possible with phase transformation systems,

2. the energy may be recovered at a constant temperature, and

3. long-term storage at ambient temperature is possible.

In addition to these advantages, there are a number of possibly serious disadvantages. The gaseous products of a reaction must be separated and stored until the reverse reaction is needed, thus necessitating storage tanks and pumps. Any sensible or latent heat of the reaction products which is lost during the storage term will have to be supplied for the reaction reversal; this results in an energy loss from storage which must be accounted for. Finally, some storage schemes involving chemical reactions require an input of energy to cause the reaction reversal which liberates the stored energy (see, for example, the coupled reaction system discussed in Section 3.3.6). Table III.3 summarizes a number of systems which are currently being investigated.

3.3.1 Inorganic Hydroxides

The first entries listed use the heat of dehydration of inorganic hydroxides, e.g., $Mg(OH)_2$ or $Ca(OH)_2$, for energy storage.[3.34, 3.35] The addition of water to the oxides reverses the reaction and liberates the stored energy. Energy densities for these two systems are 0.288 and 0.366 kW_t-hr/kg, respectively. Basic materials costs are low, 0.62 and 0.072 \$/kW_t-hr. Preliminary studies, both experimental and analytical, indicate that the reaction kinetics are favorable for diurnal storage.

3.3.2 Sulfur Trioxide Decomposition

Boeing Engineering and Construction, in conjunction with Rocket Research Corporation, has proposed[3.36] utilizing the catalytic decomposition of sulfur trioxide, which occurs at 723°C, as an energy storage technique. The product species are removed, separated, and stored (SO_2 as a liquid, O_2 as a compressed gas). Upon demand, they are recombined in a catalytic reformer, at a lower temperature than the decomposition step, and the exothermic heat of reaction is recovered (the SO_3 thus formed is also stored as a liquid). Preliminary storage system costs are encouraging (\$16.40/kW_t-hr). The technology associated with the reformation of SO_3 is the well developed step in the "contact process" of sulfuric acid manufacture and therefore is state-of-the-art. The decomposition of the sulfur trioxide requires demonstration to evaluate stability of the catalyst.

TABLE III. 3

REVERSIBLE CHEMICAL REACTIONS FOR THERMAL ENERGY STORAGE

Proposed Reaction	Heat of Reaction, Q		Temp C°	Cost (Material) $\$/kw_t$-hr	Status	Comments	Ref
	kw_r-hr/kg	kw_t-hr/m^3					
$Mg(OH)_2 + Q \rightleftarrows MgO + H_2O(g)$	0.288	340	375	0.62	Lab Scale		3.34, 3.35
$Ca(OH)_2 + Q \rightleftarrows CaO + H_2O(g)$	0.366	411	520	0.07	Experiments		
$SO_3 + Q \rightleftarrows SO_2 + \frac{1}{2} O_2$	0.343	262^+	722	16.4^{++}	Conceptual	$^+$Gas stored at 200 atmospheres $^{++}$Storage system cost	3.36
$CH_4 + H_2O + Q \rightleftarrows CO + 3H_2$	1.8	6.8*	800		Conceptual	*Assumes gaseous products are stored at a pressure of 10 atmospheres and 273°K	3.37
$NiCl_2 \cdot 6NH_3 + Q \rightleftarrows NiCl_2 \cdot 2NH_3 + 4NH_3$	0.29	7.5*	175	7.60	?		3.40
$LaNi_5H_5 + Q \rightleftarrows LaNi + 5/2\ H_2$	0.048	3.5*	100	1060.	Conceptual		
$SmCo_5H_{2.5} + Q \rightleftarrows SmCo_5 + 5/4\ H_2$	0.024	7.4*	100	4410.			3.41
$VH_2 + Q \rightleftarrows VH + 1/2\ H_2$	0.105	9.8*	100	105.			
$FeTiH + Q \rightleftarrows FeTi + 1/2\ H_2$	0.078	14.1	100	28.			
Coupled System:					Conceptual		3.42, 3.43, 3.44
$FeTiH + Q \rightleftarrows FeTi + H_2$	0.118	92	400	17.9			
and							
$MgH_2 + Q \rightleftarrows Mg + H_2$							
$H_2SO_4(dilute) + Q \rightleftarrows H_2O(g) + H_2SO_4(conc)$	0.107	452	238	0.45	Lab Scale Experiments	Concept requires real time use of large amount of energy at 100°C during storage cycle	3.45, 3.46

3.3.3 Water-Gas Reaction

Hanneman, Vakil, and Wentorf[3.37] discussed the thermodynamics of a closed-loop chemical system for energy transmission, conversion, and storage. The system utilizes the reversible reaction.[3.38]

$$CH_4 + H_2O + Q = CO + 3\ H_2$$

At T = 1100°C, the reaction proceeds to the right, storing 1.81 kW_t-hr/kg of CH_4 and H_2O. Catalytic methanation of the CO at T = 800°C is used to recover the stored energy (note the reduction in temperature). The high temperatures necessary can be obtained from a pebble-bed reactor, which can achieve an outlet temperature of 950°C.[3.39]

3.3.4 Hexamine Reaction

Daniels[3.40] cites the unpublished work of Blytas which utilizes the decomposition reaction

$$NiCl_2 \cdot 6NH_3 + Q \rightleftarrows NiCl_2 \cdot 2NH_3 + 4NH_3$$

for energy storage. At a pressure of 1 atmosphere, 0.29 kW_t-hr/kg may be stored or liberated at 175°C.

3.3.5 Metal Hydrides

Libowitz[3.41] has proposed solar thermal energy storage utilizing hydrides. In the charging phase, the metal hydride is decomposed and H_2 gas is stored. Upon demand, the H_2 gas is reintroduced and the stored energy is released through the rehydriding process. Some typical hydrides are indicated in Table III.3.

3.3.6 Coupled Reactions

Recent proposals[3.42, 3.43, 3.44] describe systems in which two chemical reactions are coupled via a common product/reactant species. The charge and discharge cycles may be represented as

$$Q_1 + AB(s) \rightleftarrows A(s) + B(g) \text{ at } T_H$$

$$Q_2 + CB_{(s)} \rightleftarrows C_{(s)} + B_{(g)} \text{ at } T_L$$

In essence, heat Q_1 at high temperature is supplied to AB, which decomposes to $A_{(s)} + B_{(g)}$. B is then removed, cooled to T_L, and reacted with C, which rejects Q_2. Upon demand, Q_2 is supplied to CB, which decomposes to yield $C + B_{(g)}$. After heating, $B_{(g)}$ reacts with A(s) to form AB and liberate Q_1. To maximize the efficiency, Q_1 must be much greater than Q_2. Ideally, Q_2 should be endothermic, while Q_1 highly exothermic.

The proposals have suggested the use of metal hydrides for these coupled reactions, although other chemical systems may be utilized. There exists a number of hydrides which can offer a broad temperature range of storage-discharge conditions. Appropriate control of H_2 overpressure yields the possibility of energy release from storage at a higher quality (temperature) than input (at the expenditure of compression work). Characteristics of a Mg and FeTi system are indicated in Table III. 3.

3.3.7 Heats of Dilution

Utilizing the heat of dilution of concentrated acid solutions is a rather old idea[3.45] that has received new attention.[3.46] Although these aqueous systems are limited in operating temperature range, the combination of H_2SO_4 and water does, in fact, offer advantages in that temperature boosting is possible and material costs are inherently low.

3.4 Summary

This section has reviewed operational and conceptual thermal energy storage systems which utilize sensible heat, latent heat, or the heat-of-reaction of reversible chemical reactions. The discussion has been limited to the general characteristics and status of the various systems. Before proceeding to a discussion of the technical problems associated with each system, it is instructive to summarize briefly the results of this section. Perhaps the most important conclusion which can be drawn from this comparison is the fact that very few large capacity, high input/output rate storage systems have actually been built.

Several large above-ground systems using sensible heat storage in liquids have been proposed. Based upon the relatively low level of technology involved, it is probable that they would perform as anticipated. Most liquid systems will be limited to temperatures less than approximately 300-400°C because of either containment cost or storage medium decomposition. Placing the storage system underground, either in an excavated cavern or through the use of an acquifer, offers the potential of significantly lower costs. The cost of liquid systems utilizing petroleum based heat transfer oils may also be reduced if a hybrid system consisting of both liquid and solid media is considered.

A number of storage systems which rely upon the sensible heat capacity of solids have been constructed. They range in size from small room heaters to relatively large units (0.75 MW_t-hr) for industrial applications. Concepts utilizing fluidized solid particles and underground formations of limestone or granite have also been proposed. Additional analysis is required to determine the viability of these systems.

Several small scale systems based upon the heat of phase transformations have been constructed. These include lab scale units utilizing both LiH and LiF/LiOH and commercial units utilizing NaOH. Passive heat exchangers were used for energy input and output. Several systems utilizing active heat exchangers have been proposed, and some small scale testing has been conducted. As was the case with the sensible heat systems, there is a considerable difference in the performance (capacity and input/output rates) of systems which have been tested and those which have been proposed.

Storage systems based upon reversible chemical reactions are the least advanced. Various reactions have been proposed, and some small lab scale experiments have been conducted. Additional research is required before large storage systems can be designed and constructed.

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SECTION 4. TECHNICAL ASSESSMENT OF MATERIALS CONSIDERATIONS RELATED TO THERMAL ENERGY STORAGE

This section deals with the materials considerations associated with sensible, phase transformation, and heat-of-reaction thermal energy storage techniques. The objective is to discuss the thermophysical characteristics of materials, assess the technical problems which are imposed by the materials, and identify relevant problem areas for which additional research is recommended.

In discussing sensible heat systems, three classes of storage materials are considered. The first class consists of the fluids, such as water and heat transfer oils, which are the materials most commonly used in low and moderate temperature applications. The second class of sensible heat storage materials is made up of liquid metals and molten salt eutectics which are capable of operating at higher temperatures than the heat transfer oils. The final class includes the various solid materials which have been proposed for thermal storage applications. Solids offer the potential of high temperature storage at low material cost. The thermophysical characteristics of some representative materials are presented and comparisons of the various sensible heat storage materials are made.

Phase change thermal storage materials are described next. This classification could potentially include a very large number of substances. It has, however, been restricted to inorganic salts and eutectic mixtures, since these materials appear to be the most attractive at temperatures above 250°C. Even though the discussion is limited to a relatively small number of materials, those chosen are representative of classes of materials with regard to corrosion and containment properties, cost and long-term stability characteristics.

The final topic considered in this section deals with the storage of thermal energy utilizing reversible chemical reactions. Since only limited experience has been garnered to date, the materials considerations must be restricted to broad projections based upon the sparse laboratory results currently available.

4.1 Sensible Heat Storage Materials

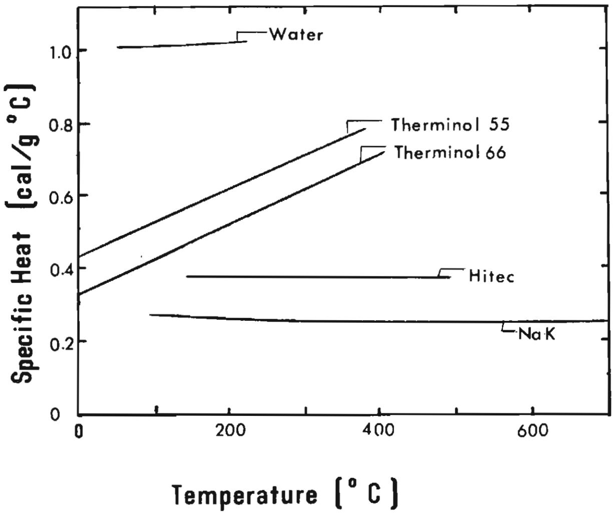
Sensible heat storage, being the least complex of the various modes of thermal storage, probably places the least restrictions on the characteristics of the storage medium. In general, it is desirable that the material have a high specific heat capacity, a high temperature capability, a high density, and a low cost. In addition, a low vapor pressure at elevated temperature can result in lower containment costs. Also affecting containment costs is the compatibility between the storage medium and container. Clearly, if corrosive storage materials require expensive containment materials, the cost of storage will increase. Finally, it is important that the material be stable in the cyclic high temperature environment in which it is required to operate.

The selection of a storage medium in the design of a thermal storage system requires a rather thorough understanding of the thermophysical and chemical characteristics of the material in order that performance estimates and material response predictions can be made. Specifically, it is important to have information on such properties as the density, specific viscosity, and thermal conductivity. Furthermore, a system design requires the analysis of a material's reactivity with containment materials and surrounding substances with which it may communicate. All of this information is needed in a complete design of a thermal storage system.

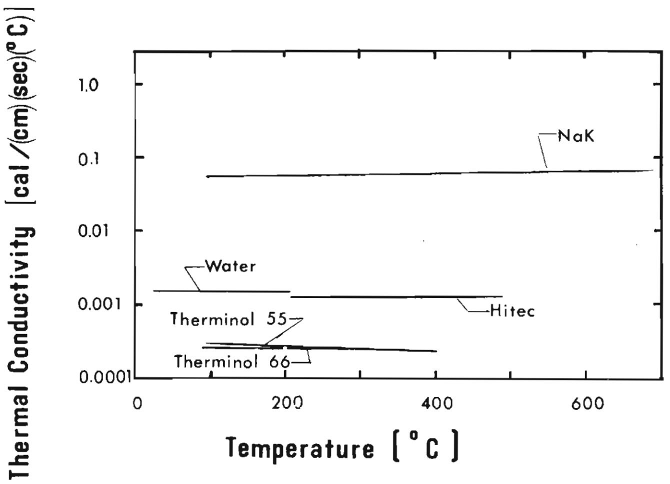
4.1.1 Fluid Storage Materials

At the lower operational temperature levels water is one of the best storage materials. As illustrated in Figure 4.1(a), water has a specific heat nearly twice that of the other materials shown, while its other characteristics (see Figures 4.1(b), 4.1(c), and 4.1(d)) are comparable or better. Unfortunately, water has a relatively high vapor pressure at high temperatures. At 240°C an overpressure of nearly 33 atmospheres is required to maintain the liquid phase. The liquid phase is much preferred to the vapor phase since its volumetric heat capacity is so much greater than that of the vapor. Thus, due to the containment problems, water loses its attractiveness as a sensible storage material at higher temperatures.

Heat transfer oils have been considered for thermal storage applications because of their relatively low vapor pressure at high temperature. The physical properties of a number of heat transfer oils are illustrated (along with those of water) in Figure 4.1. For the most part, these materials have fairly similar properties which are not as good as those of water; however, these materials are capable of operating at temperatures exceeding 300°C. Rocketdyne[4.1] has examined various heat transfer



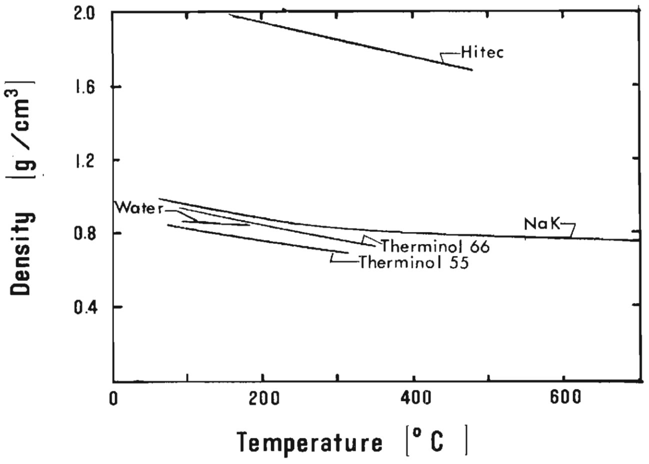
(a) Heat Capacity



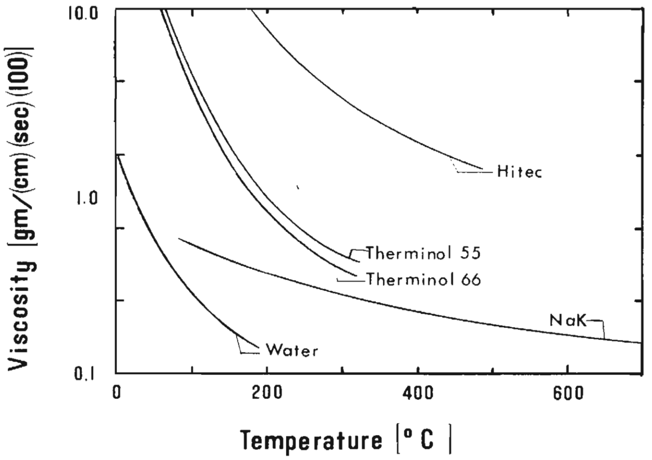
(b) Thermal Conductivity (from Ref. 4.2)

Figure 4.1 Properties of Various Heat Transfer Fluids

X



(c) Density



(d) Viscosity

Figure 4.1 (continued)

fluids and has selected four materials considered prime candidates for thermal storage applications. These fluids are the last four entries in Table IV. 1 in which the temperature limitations and auto-ignition temperatures have been compared to that of water. "HITEC," a molten salt having a high temperature capability, is discussed below. It is evident from Figure 4. 1 and Table IV. 1 that the physical properties of these materials are fairly well defined;[4.2] what remains is the examination of their safety, stability and compatibility characteristics. As with most organic materials, flammability must always be accommodated. Although the auto-ignition temperatures of the fluids in Table IV. 1 are above the operational temperature limit, the flash points are not. Therefore, with the ever-present possibility of leaks, ignition sources should be isolated from any storage system utilizing these materials.

TABLE IV. 1

PHYSICAL CHARACTERISTICS OF FLUID SENSIBLE HEAT STORAGE MATERIALS

Material	Maximum Temperature Limit (°C)	Maximum Temperature Limit (°F)	Auto Ignition Temperature (°C)	Auto Ignition Temperature (°F)	Remarks
Water	240	464	-	-	This temperature was arbitrarily chosen for a steam pressure of 475 psi; the maximum upper limit for liquid water is determined by the critical temperature of 374°C and a corresponding pressure of 3184 psi.[4.4]
Na-K (54-46)	860	1500	-	-	Inert environment required; vapor pressure = 4.5 psi at 700°C[4.5]
Therminol-55 (Monsanto)	316	600	358	675	Non-oxidizing environment required[4.2]
Therminol-66 (Monsanto)	344	650	374	705	Non-oxidizing environment required[4.2]
Caloria-HT-43 (Exxon)	316	600	404	759	Non-oxidizing environment required[4.2]
HITEC	425	800	-	-	Melting point 145°C.

The possible stability difficulties associated with the organic heat transfer oils center primarily around the decomposition of the material itself rather than reaction with containment materials. Hydrocarbon fluids are subject to spontaneous cracking--reduction of the average molecular weight--and formation of volatile species and oxidation. These degradation processes are temperature dependent, and near the maximum operational temperature limit, the rate of degradation of organic heat transfer fluids has been observed to double for each 10°C increment.[4.3] Oxidation, either from air leakage into a sealed system or from impurities such as water, results in the formation of peroxides which catalyze the polymerization of the fluid. Consequently, the viscosity of the fluid increases and coating of heat transfer surfaces or containment materials can occur. It is apparent that a system employing organic heat transfer fluids may require the monitoring of the condition of the fluid along with in-situ regeneration or the addition of new fluid as required to compensate for degradation.

For temperatures above the limits of the organic heat transfer oils, liquid metals have been suggested for use as heat transfer fluid. In some nuclear reactor applications considerable operating experience has been obtained with liquid metals. It follows that liquid metals might also be applicable as a sensible heat storage medium. Reference to Figure 4.1 and Table IV.1 shows that while most properties of liquid metals are similar to those of water and the organic fluids, the liquid metals have a rather low specific heat; they do, however, have a distinctly higher thermal conductivity. In these illustrations the properties of NaK were used, being typical of most liquid metals.

The reactivity of sodium, potassium, and their eutectics requires careful consideration of the container design. Type 304 stainless steel is the most common material used for containment with special attention usually given to the maintenance of an oxygen and oxide-free environment in order to prevent corrosion. In any application involving the use of liquid metals, the possibility of their contact with water must be considered due to the vigor with which the liquid metals react with water.

Another class of materials capable of high temperature operation are the molten mixtures of inorganic salts. These systems have found widespread application as heat transfer fluids in many industrial processes. HITEC is a good example of heat transfer salt systems developed by duPont in the thirties[4.6] for use in the chemical and petroleum industries. It is made up of 40 wt. % $NaNO_2$, 7 wt. % $NaNO_3$ and 53 wt. % KNO_2, and has a low melting point (145°C) and a relatively high upper temperature limit in air (425°C). Notice in Figure 4.1 that while the specific heat of HITEC is somewhat lower than that of most of the other fluids, its density is a factor of two higher than the others and its thermal conductivity is as high as that of water. Since this eutectic has been in use for some time, consideration of the methods developed for maintenance of the material is instructive, as similar procedures may be necessary for many liquid sensible heat storage systems. As Bohlmann[4,7] has extensively reviewed the available literature relevant to HITEC, only some of the more significant points will be discussed here.

At high operational temperatures, T > 425°C, the principal concern is the decomposition or oxidation. Depending upon environment, the following reaction has been proposed:

$$5\ NaNO_2 \rightarrow 3\ NaNO_3 + Na_2O + N_2\ . \qquad (1)$$

This reaction is expected to occur over the temperature range 454°C to 538°C. At higher temperatures, the decomposition is so rapid that the mixture appears to boil. In an oxidizing environment, the nitrite converts to nitrate via the reaction

$$2\ NaNO_2 + O_2 \rightarrow 2\ NaNO_3\ . \qquad (2)$$

Inhibition of (2) can be accomplished by blanketing the eutectic with nitrogen, thus eliminating the reactive oxygen. It is suggested that a blanket of nitrogen will also inhibit (1) by shifting the equilibrium to the left. The return of the eutectic mixture to the correct composition requires regeneration of the nitrites and removal of reaction products. This is accomplished in industrial applications by the addition of $NaNO_2$, or the addition of HNO_3 or NO_2 to convert hydroxides formed by reaction of Na_2O with water, and carbonates formed by pickup of CO_2, to nitrates and nitrites.

The discussion of molten salt systems for sensible heat storage has considered only HITEC because of its well known characteristics and the scarcity of data on other candidates. It is strongly recommended that other inorganic salt systems having low temperature melting points and high temperature capability be investigated for possible use as heat transfer fluids or sensible heat storage media.

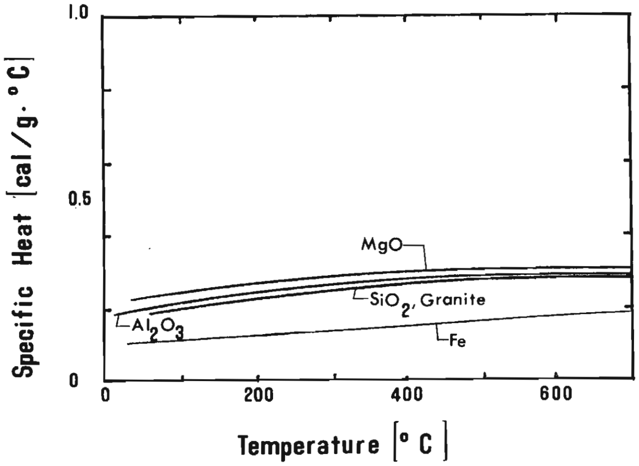
As illustrated by the discussion in the previous paragraph, the identification of decomposition and oxidation mechanisms can provide the means of compensation and regeneration. As thermal energy storage materials will undoubtedly be required to meet longevity requirements, proposed storage materials will have to be evaluated with regard to stability and compatibility and based upon results from these studies, material makeup and reformation processes should be developed.

4.1.2 Solid Storage Materials

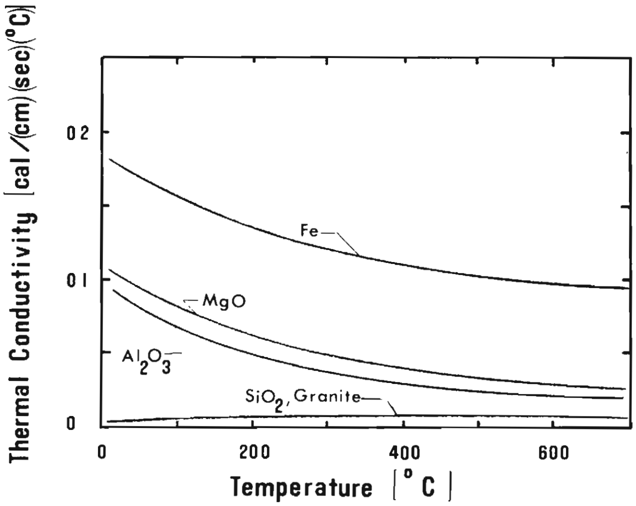
As a thermal storage medium, inorganic solid materials offer some distinct advantages. Solids typically have quite low vapor pressures at very high temperatures; there are many inorganic solid compounds available which are chemically inert; and, perhaps most important, many readily available solid materials are quite inexpensive. On the other hand, most inorganic solids have a low specific heat and thermal conductivity which can result in sizable systems with complex heat exchanger subsystems. Although the heat transfer problem can be alleviated by using the solid in a particulate form, as in a packed bed arrangement, the direct contact heat exchange between the solid and the heat transfer fluid creates potential compatibility and fluid stability problems.

In Figure 4.2 and Table IV.2 some of the thermophysical properties pertinent to the storage of thermal energy in solids are presented. The materials selected for this illustration are representative of those used in past applications or currently being considered for thermal storage. The specific heat, thermal conductivity, density, and melting point of these materials are typical of the properties of most low-cost, inorganic solid materials which appear attractive for thermal storage application. The importance of a thorough understanding of these properties for purposes of engineering cannot be overstressed. Currently there is a remarkable lack of accurate data for many inorganic solids; indeed, in many cases only room temperature thermal conductivity data exist. When obtaining this thermophysical property data it is important to note that most of these properties are strongly dependent on the nature of the preparation of the materials (e.g., melted or pressed) and their purity. These effects must be dealt with in the characterization of the materials.

An attractive solid storage concept is the packed bed solid/liquid system. In this configuration, the solid storage material, in the form of small, variable-size particles, constitutes a particle bed within the container; a heat transfer fluid flowing through the bed transfers heat to and from the solids via direct contact between the fluid and the solid particles. When the organic heat transfer fluids are placed in contact with a solid storage material, it should be anticipated that the decomposition mechanisms discussed in relation to the organic fluids will be enhanced. For example the typical water content of rocks is 0.77 to 3.23 percent by weight.[4.8] Thus, in a packed bed of rocks operating with an organic heat transfer fluid, the aforementioned fluid polymerization reaction would be expected to proceed. There are variations in the high temperature ($T > 500°C$) properties of solids with regard to decomposition; however, numerous materials exist (SiO_2 and Al_2O_3) which are extremely stable and inexpensive. If technical grade quality is sufficient, materials such as SiO_2 and Al_2O_3 offer a distinct economic advantage. The principle difficulties to be expected are those of the influence of impurities upon



(a) Specific Heat



(b) Thermal Conductivity

Figure 4.2 Properties of Various Solid Storage Materials

TABLE IV. 2

PHYSICAL CHARACTERISTICS OF SOLID SENSIBLE HEAT STORAGE MATERIALS

Material	Melting Point (°C)	Density (g/cm^3)
Al_2O_3	2015	3.97
MgO	2800	3.58
SiO_2 (quartz)	1728*	2.65
Granite**	~1200	~2.7
Fe	1535	7.9

*Softening point of cristobalite.

**Many common granites melt in the vicinity of 1200°C; melting points are highly dependent on chemical composition.

the behavior of these solids at the high temperatures typical of a thermal energy storage system. Experimental evaluation of the stability, compatibility, and corrosion characteristics of these technical grade solid materials is desirable.

At this point it is instructive to examine the relative attractiveness of the various sensible heat storage materials which have been described. One measure of the potential usefulness of a storage medium is its specific storage capacity (energy stored per unit mass). This quantity has been plotted versus temperature swing for the fluid storage materials in Figure 4. 3 and for the solid storage materials in Figure 4. 4. Comparing the two figures it is clear that the fluids, as a group, have a better storage capacity potential than the solids. This, however, is not the complete picture; it is necessary to include some measure of the economics of the system. In order to provide this measure, the storage capacity per unit material cost can be used. This parameter has been plotted versus temperature swing for fluids and solids in Figures 4. 5 and 4. 6, respectively. A comparison of these figures illustrates that the inclusion of material costs greatly modifies the relative comparison based on capacity alone. Notice, in this case, that most of the solid materials compare quite favorably with the fluids, and that the extremely low cost of SiO_2 (sand) and granite makes them appear quite attractive. Thus, it is important to remember that system economics are quite critical to the material considerations.

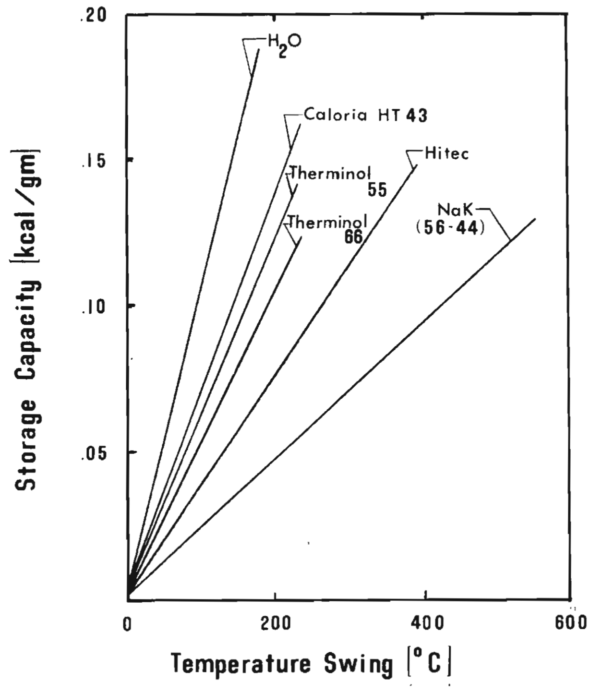


Figure 4.3 Thermal Storage Capacity Comparison for Various Fluid Storage Media

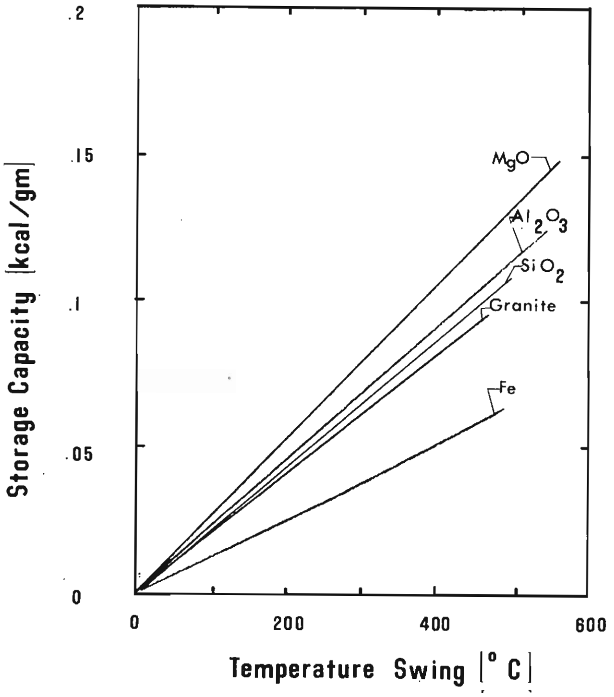


Figure 4.4 Thermal Storage Capacity Comparison for Various Solid Storage Media

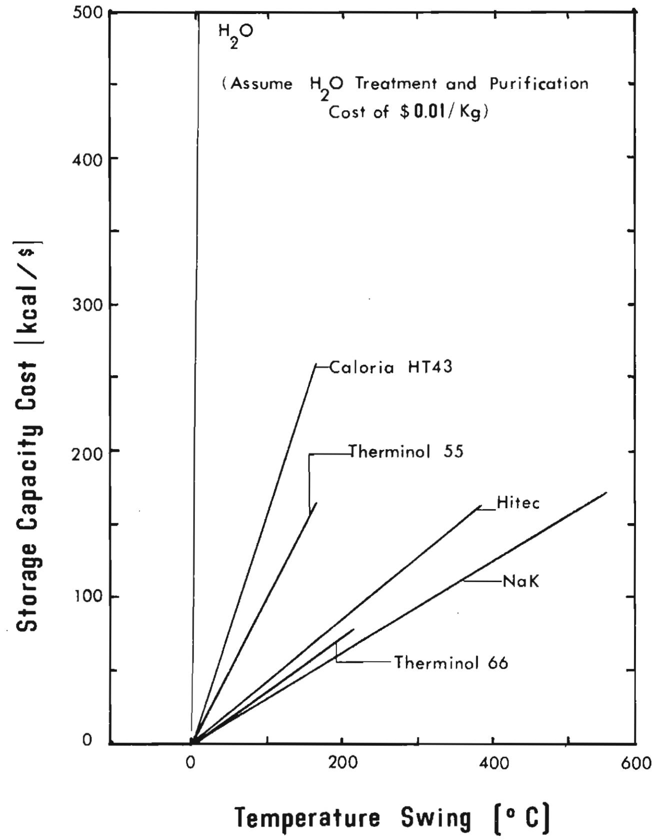
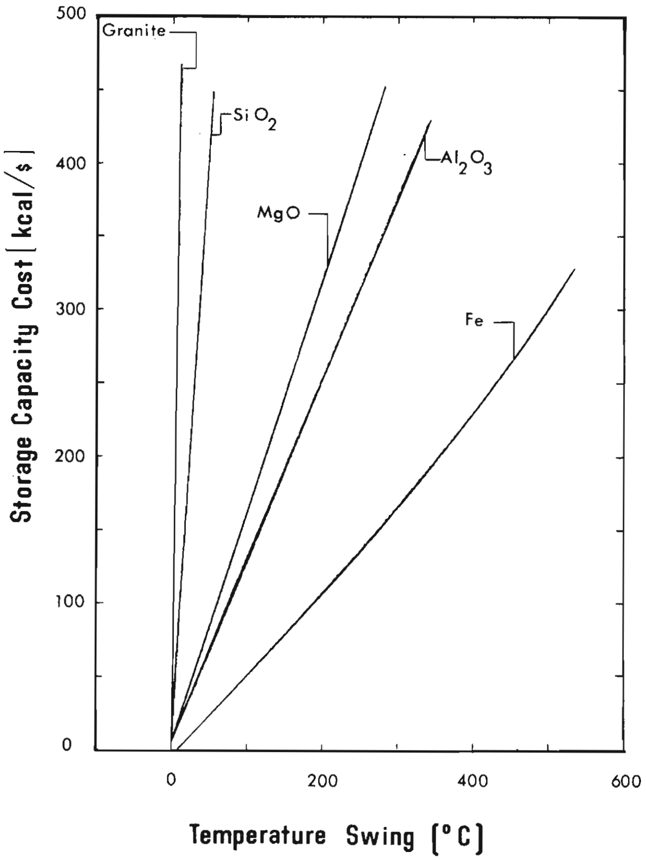


Figure 4.5 Capacity-Cost Comparison for Fluid Storage Media

Figure 4.6 Capacity-Cost Comparison for Solid Storage Media



Relative to sensible heat storage materials, the areas requiring additional investigation include the following:

1. The thermophysical properties of prospective materials should be well understood; this includes such effects as variation with temperature.
2. The phenomena of high temperature stability, compatibility, and corrosion need investigation.
3. The problems of material condition monitoring and material replacement should be carefully analyzed.

4.2 Inorganic Materials for Latent Heat Thermal Energy Storage

A large number of materials can be considered for application in latent heat thermal storage systems. Barin and Knacke[4.9] have compiled the thermodynamic properties of over a thousand inorganic compounds which could, in principle, be considered for thermal storage. Combinations of these various compounds to form binary and ternary eutectics greatly increases the number of candidates. The first task is, therefore, to reduce the number of materials by selecting those most appropriate to thermal storage and to discuss representative materials where possible.

We have chosen to eliminate those substances which are expensive (e.g., silver salts, most salts of transition metals, the rare earths and actinides). Likely candidates are those materials which are commonly available, such as nitrates, fluorides, sulfates, chlorides, carbonates, etc. In many cases, the paucity of thermophysical property data has further limited the number of the materials which can be considered.

In this subsection the status of thermodynamic data sources appropriate to the evaluation of latent heat thermal storage is examined. This is followed by discussion of the general characteristics of phase transformations including volumetric changes, impurity effects and kinetic properties, with specific systems being examined in some detail. Although experience with latent heat materials for thermal storage is limited, the research in molten salt chemistry, various high temperature battery programs and the molten salt reactor experiment has provided results which are relevant to the present study. These data have been found to be spread diffusely throughout the primary literature and there are presented in some detail here.

Since there is a wide variation in physical and chemical properties of the many fused salts which have been studied to date, a more detailed examination of representative systems will be presented following the general discussion of fused salts. Many fused salt systems possess similar chemical behavior; thus, discussion of these systems can be arranged within the format of molten salts with a common anion. Accordingly, fluorides, chlorides, hydroxides and oxides, and oxyanions of the non-metals such as carbonates, nitrates and nitrites, phosphates, and sulfates are described as classes of material. Not considered due to their high costs are the heavier halides, most oxyanions of metals, and cations of most transition metals, rare earths, and actinides.

Previous estimates of heats of fusion for salt eutectics have largely been weighted arithmetic averages of the heats of fusion of the pure components. This method of estimating ΔH_f (eutectic) can be very inaccurate; values calculated by this method are generally 30 to 50% higher than experimentally measured values. The much more accurate Kirchoff method for calculating ΔH_f for eutectics is presented in Appendix B; estimated values in the present discussions have been calculated by this procedure.

4.2.1 Thermodynamic Data Sources

To evaluate candidate latent heat storage materials, the basic thermodynamic information required includes the heats of fusion and melting temperatures. The determination of this information for eutectic mixtures requires knowledge of the heat capacities of the pure components in order to calculate the heat of fusion of the mixture (cf. Appendix B). A variety of data sources can be used to obtain this basic data. Standard handbooks[4.4, 4.10] supply rudimentary thermodynamic information. NBS publications,[4.11, 4.12] while in some cases dated, have tabulated properties of many pure compounds and elements. The classic complilations of K. K. Kelly[4.13] and the Bureau of Mines[4.14] are still pertinent although hard to find. The JANAF Tables,[4.15] Barin and Knacke,[4.9] and Thermophysical Properties of Materials Data Tables[4.16] are the most current compilations of thermophysical data. The "Bulletin of Thermodynamics and Thermochemistry"[4.17] annually surveys the field of thermodynamics and thermochemistry, and, while not furnishing actual data, supplies information about research published, in progress, and about to be published. The open literature, through Chemical Abstracts, Physics Abstracts, and Nuclear Science Abstracts can be searched for fundamental data; many specific reports contain details of thermophysical properties relevant to specific systems.[4.18-4.20]

In the area of the chemistry of fused salts, Sandia Laboratories has published a comprehensive compilation[4.24] of over 8000 eutectic mixtures with melting points ranging from -138°C to 2800°C. This data collection includes chemical composition, melting point temperature, and literature reference citation. This survey could provide a valuable guidance in the initial selection of fused salts for a thermal storage application.

Heat capacity studies disclose solid state polymorphic phase transitions and non-equilibrium phenomena such as glassy-phase formation and the existence of metastable phases which can affect the thermal characteristics of solid-sensible as well as latent heat storage media. Although the data base is greater with regard to heat capacity measurements than that of thermal conductivity, there still remains a significant lack of information when, for example, compared to the number of phase diagrams. The situation regarding this paucity of data is not improving since many laboratories which have specialized in thermophysical measurements have ceased functioning or are continuing at a reduced level of funding as are data collection and analysis groups (JANAF, for example).

The evaluation of a latent heat storage material on the basis of equilibrium thermodynamic data may overlook a number of serious non-equilibrium effects. These can include kinetics of the phase transformation, the possibility of superheating and supercooling, and the self-decomposition of the storage material due to thermal cycling. Systems considered for long-term usage will be subjected to changes in properties due to impurity effects. The sources of such impurities can be numerous--low purity starting materials, corrosion of containment materials, products of decomposition and admission of reactive substances such as air or water. The presence of impurities can affect the salt in a number of ways which will influence the operational characteristics of thermal storage systems. Miscible impurities can lower the latent heat and melting temperature of a pure compound; melting may occur over a temperature range rather than isothermally. A positive effect of impurities, immiscible ones specifically, is that they can act as nucleation sites to speed crystallization or fusion and minimize supercooling or superheating.

In addition to impurity considerations associated with single component systems, the maintenance of the composition of molten eutectic salts is important. As a system deviates from the eutectic composition, the possibility of precipatation of the components from the melt exists. In a latent heat storage system this results in reduced storage capacity, although the molten phase can be used as a suspension if the settling-out of the solids is prevented. Although these effects are usually considered undesirable, the work of Severson and Smith[4.22] on a $NaNO_2$-NaOH mixture suggests that slight deviations from a eutectic composition may aid a system design. Since the molten salt surrounding a heat transfer pipe solidifies as a slush or slurry, it is maintained that removal of the salt and maintenance of high heat transfer rates are facilitated.

Transformation from the solid to liquid phase has an associated volumetric change. For inorganic salts this typically amounts to a 10 to 40% expansion which must be accommodated in the system design, since stresses can be induced which might cause container failure. The situation is complicated by the fact that upon recrystallization the density of the bulk solid should be maintained close to theoretical, maintaining reasonable thermal conductivity, as the formation of voids or gaps in the solidifying material can reduce heat transfer rates and should be avoided. There is a significant lack of dilatometric data applicable to inorganic salts, especially in the region of phase transformations. Vapor pressure data for eutectic salts are also in the classification of necessary, but unavailable, data. Since the temperature of a phase transformation can be greatly affected by pressure, the boundaries of phase diagrams may "move" depending upon the experimental conditions (e.g., closed versus open systems). In addition, high vapor pressures can, of course, result in loss of material and selective distillation of components in near-eutectics. The net result of these processes can be changes in the heat of fusion and melting temperature.

Transport property data for the molten phase of most latent heat storage materials are sparse. Qualitative observations have been made however; for example, molten hydroxides are known to have such high wetting characteristics that they will, in fact, flow out of containers. Measurements of viscosity, thermal conductivity and density variations as a function of temperature are not to be found for most salt eutectics. The necessity for such measurements is paramount since, unfortunately, there is no proven theoretical basis upon which reasonable estimates of these characteristics can be made.

4.2.2 Characteristics of Representative Salt Systems

In this section, the relative merits of several representative inorganic salt systems as thermal storage media are measured in terms of the characteristics of an ideal latent heat storage material. There are basically three categories of desired characteristics. First, the basic goal in a heat of fusion system is to maximize the material's heat of fusion, heat capacity, and thermal conductivity. Although it would be desirable to achieve this goal on both a weight and volume basis, individual system requirements may dictate the greater importance of one over the other. Other desirable attributes of storage systems are that the material vapor pressure be low at elevated temperatures, that a minimum of thermal decomposition occur over the system lifetime, that inadvertent contamination of the storage system not result in a hazardous situation, that any contamination be easily and economically reversed, and that the components of the system not be toxic during any phase of the operation.

Another consideration is that there should be a minimum of physical and chemical interaction between the storage media and the containment system. It might be of little avail to use an abundant and cheap eutectic salt mixture if one were forced to employ a very expensive super-alloy to contain it. As will be discussed, this requirement presents severe difficulties for a number of fused-salt categories.

The economic availability of the salt material is the final major requirement to be met. Bulk quantity prices vary dramatically for the various inorganic salts. A major concern in the pricing of inorganic salts is the acceptable impurity level for each system. Impurities affect not only the cost of the materials, but also the thermophysical properties, the kinetics of phase transformations and side reactions, and the chemical interactions of the molten material with the containment system.

With these basic requirements in mind, a detailed discussion of several chemical classes of inorganic salt systems is now presented.

4.2.3 Fluoride Salt Mixtures

One of the most exhaustive studies of molten salt mixtures in recent times has evolved at Oak Ridge National Laboratory (ORNL) in connection with the Nuclear Aircraft Propulsion and Molten Salt Breeder Reactor programs. During these programs, a multitude of fused fluoride systems were examined for their heat transfer capabilities in a radiation environment.[4.23]

The use of fluoride mixtures as a latent heat TES material immediately encounters the difficulty of high melting points. Of the fluoride mixtures which are stable up to 750°C, only those containing large amounts of LiF, BeF_2, or MBF_4 (where M = alkali metal) melt below 500°C. These three low-melting fluoride mixtures possess many desirable qualities and long-term stability for TES applications. However LiF and BeF_2 are expensive (BeF_2 possessing the additional disadvantage of being highly toxic), while MBF_4 has a significant vapor pressure of BF_3 at elevated temperatures and can be extremely corrosive to even high nickel content alloys in the presence of small amounts of oxide impurities or water.

The values listed in Table IV.3 for eutectic composition, melting point, heat capacity of the liquid, and thermal conductivity have been experimentally determined for all three systems. Only the ΔH_f listed for the NaF-$NaBF_4$ systems was obtained from experimental data; the values listed for the other two systems were calculated using the Kirchoff method as described in Appendix B. The value for the LiF-NaF-KF system is probably accurate to ±10%, as the heats of fusion and heat capacities for both liquid and solid states are well known for all the pure constituents of the mixture, as is the heat of mixing for LiF-KF. The ΔH_f value calculated for the NaF-BeF_2 is considerably less accurate, since ΔC_P values for the pure BeF_2 liquid and solid were indeterminable, and ΔH_{mix} has not been determined for NaF-BeF_2. Some of the calculated values of ΔH_f presented here and in following discussions were based on properties of chemically similar materials. These are noted in the text and the reader is cautioned against indescriminate usage.

TABLE IV. 3

THERMOPHYSICAL PROPERTIES OF SOME LOW-MELTING TEMPERATURE FLUORIDE SYSTEMS

System	M. P. (°C)	ΔH_f (cal/g)	C_p (liq) (cal/g/°C)	K (cal/cm/sec/°C)	Ref.
LiF-NaF-KF (46.5-11.5-42)	454	99	0.45	0.011 (455°C)	4.15, 4.24, 4.25
NaF-BeF_2 (57-43)	360	78	0.44	0.010 (400°C)	4.15, 4.24, 4.25
NaF-$NaBF_4$ (8-92)	384	31	0.36	0.010 (455°C)	4.26

Some energy storage processes may be able to utilize molten salt systems with fusion temperatures in excess of 500°C. This possibility, which was considered recently by Schroeder,[4.27] expands the number of usable fluoride eutectics. The thermophysical properties for two fluoride eutectics melting below 800°C discussed by Schroeder are presented in Table IV. 4. The remaining fluoride eutectics cited in this reference

TABLE IV. 4

THERMOPHYSICAL PROPERTIES OF SOME HIGH-MELTING TEMPERATURE FLUORIDE SYSTEMS

System	M. P. (°C)	ΔH_f (cal/g)	C_p (ave)* (cal/g/°C)	Ref.
KF-NaF-MgF_2 (58-35-7)	685	138	0.38	4.27
NaF-CaF_2-MgF_2 (65-23-12)	745	133	0.36	4.27

*Average value for C_p over the temperature range 150 to 860°C.

which melt below 800°C all contain a significant proportion of LiF; their thermophysical properties closely resemble those given in Table IV. 3, and they likewise suffer from the same cost disadvantage as the low-melting temperature fluoride systems.

Turning now to chemical properties of molten fluoride eutectics, it has been conclusively demonstrated[4.26, 4.27] that these mixtures are stable for many years up to 750°C if maintained under an inert gas atmosphere. Suitable containment materials are Hastelloy N, titanium modified Hastelloy N, and Inconel. Corrosion of the Hastelloy materials is approximately 2 mil/year at 750°C and is somewhat greater for Inconel. Schroeder[4.27] states that the addition of small amounts of aluminum to the molten fluoride completely inhibits corrosion of 18/8-type stainless steel at 850°C; the nature and duration of these tests were not specified, however.

The dominant long-term corrosion mechanism in these systems is mass transfer from hot to cold zones in non-isothermal systems. This becomes quite severe above 700°C for most materials other than the three mentioned above and has caused line clogging due to the precipitation of metallic crystals in circulating fused salt loops. It was shown[4.28] that if these salts could be purified sufficiently of oxidizing impurities, the container corrosion rate correlated well with the maximum system temperature and the diffusion rate for Cr from the bulk alloy into the molten salt. Such purification procedures generally consist of alternately sparging the molten salts with HF and H_2 at elevated temperatures.

If oxidizing impurities are present in the molten fluorides, then the initial corrosion rate is considerably higher than the rate for mass transfer and eventually decreases as the oxidizing species are reduced. If these impurities (usually reactive fluorides, oxides, and water) are present in sufficient amounts, leaching of Cr from the metal along grain boundaries can lead to the formation of subsurface voids. The present thermal storage application does not require the presence of the oxidizing UF_4 species as in the ORNL studies, and the possibility of using stainless steels as containment materials might profitably be re-examined.

The ORNL corrosion studies have further shown the importance of circulating molten salt test loops versus static tests. The dynamic tests are much more severe than static tests in that many corrosion processes can come to a steady state which might have been masked in a static configuration by slow diffusion rates.[4.23, 4.26, 4.28, 4.29]

In conclusion, it appears that the physical and chemical characteristics of molten fluorides may be suited to high temperature latent heat TES systems. The impact of material economics on the overall effectiveness of fluoride eutectics will be examined at the conclusion of this section.

4.2.4 Chloride Salt Mixtures

Mixtures of molten chlorides probably have been the most widely studied of the fused salts. Pure chlorides are generally characterized by high melting points, and thus their eutectic mixtures are often considered for phase change thermal storage. The physical properties of three representative and economically attractive eutectics are presented in Table IV. 5. In addition these systems are non-toxic and have no significant vapor pressure up to 800°C.

TABLE IV. 5

THERMOPHYSICAL PROPERTIES OF SOME CHLORIDE SYSTEMS

System	M. P. (°C)	ΔH_f (cal/g)	C_p (liq) (cal/g/°C)	Ref.
$NaCl-MgCl_2$ (52-48)	450	77	0.26	4.15
$NaCl-CaCl_2$ (48-52)	500	44-67	0.25	4.15
NaCl-KCl (50-50)	658	91	0.26	4.15, 4.30

As for the fluoride eutectics, the present heats of fusion were calculated using Kirchoff's method. ΔH_{mix} for molten $NaCl-MgCl_2$ and molten NaCl-KCl is known; however, this property has not been measured for the $NaCl-CaCl_2$ system, and for the present calculation has been estimated. Again, the necessity for accurate calorimetric studies is emphasized. A realistic evaluation of these systems must await these experimental investigations. Heat capacities were calculated by averaging weighted $C_p(\ell)$ values for the pure constituents at the appropriate temperatures. These data were taken from the JANAF tables.[4.15]

Thermal conductivities have not been determined for these three systems (and indeed have not been determined for most inorganic salt eutectics). Reliable thermal conductivity data for these systems are of the greatest importance as the dynamics of heat exchange within the storage system are critically dependent on the thermal conductivity of the storage media. At this time the thermal conductivity data available for metal chloride eutectics is so fragmentary that even speculation on a possible range of values for these eutectics is fruitless. This is clearly an area where research is urgently needed.

Studies of fused chloride systems within industry[4.31, 4.32] are primarily oriented to the use of salt baths for heat treatment of metals. These baths are open to the atmosphere and the salt bath is renewed by the addition of appropriate "rectifying agents" while corrosion products are removed. For thermal storage applications it may thus prove necessary to enclose the fused chlorides within an inert environment to attain prolonged container lifetime. System design and cost effectiveness studies should therefore take into careful consideration the means necessary to prevent accidental contamination of the storage material and the procedures required to renew the chloride salt's purity.

The molten salt heat treatment baths used for heat treating metals are generally contained in cast pots of Fe-Ni-Cr alloys. It was shown by Jackson, et al.[4.31] that under such highly oxidizing conditions the dominant corrosion mechanism in these systems is intergranular attack rather than mass dissolution and transfer. The salt baths studied were binary and tenary mixtures using NaCl, KCl, $CaCl_2$, $BaCl_2$, and Na_2CO_3. Alloys with higher Cr compositions were severely attacked, and additions of Ni were beneficial only above 30 wt.%. These tests were conducted at 870°C for 50 hours, and the extrapolated corrosion rates for all the alloys tested were several inches per year. Extended tests at a series of lower temperatures with carefully controlled atmospheres are necessary to establish accurate corrosion rates for thermal storage applications.

The work most pertinent to the topic of molten chlorides enclosed in controlled environments is a series of papers by Littlewood, et al.[4.33-4.36] It was shown that the corrosivity in an equimolar NaCl-KCl was dependent on the redox potential of the melt, which in turn depended heavily on the presence of very small amounts of water and oxygen in the melt. In melts containing very small amounts of impurities, it was shown that if the metal was sufficiently noble (e.g., Ni, Fe), the redox potential could be reduced to a value very near the Nernst potential of the metal with only slight corrosion taking place. Even trace amounts of silicates and other oxides from glasses or ceramics were sufficient to prevent the redox potential of the melt from falling and thus rendering the metals immune.

The reduction of oxidizing impurities in the melt through a rapid initial corrosion reaction followed by immunity is apparently analogous to the process occurring in the ORNL studies of molten fluorides. Littlewood notes that the elimination of oxidizing impurities by such a process is efficacious only if their initial concentration in the salt is low. Several hundred hours were required before a nickel coupon of 0.3 cm^2 surface area reduced the impurities in 5 g of NaCl-KCl (dried by fusion "in vacuo") to bring the redox potential of the melt within 10 mV of the Nernst potential of nickel. This indicates that stringent pre- and in-situ purification procedures may be necessary to insure long-term compatibility of chloride melts with their containers; detailed studies are clearly required to determine the required purity of constituent chlorides and the handling procedures necessary to avoid subsequent contamination. For the chlorides: NaCl, KCl, $MgCl_2$, and $CaCl_2$, these studies are of the utmost importance as they are among the cheapest inorganic salts available in bulk quantity today.

4.2.5 Hydroxide and Oxide Salt Mixtures

Of the inorganic hydroxides, sodium hydroxide is abundantly available in bulk quantities and is inexpensive. Much effort has been expended in recent years to assess NaOH as a possible material for fused salt reactors or as an electrolyte in regenerative fuel cells. With regard to thermal storage, NaOH is the one inorganic molten salt to be found in a moderate temperature storage system which is presently available commercially.[4.37]

From the standpoint of their physical properties, alkali metal hydroxides appear to be excellent candidates for moderate to high temperature thermal storage. Representative systems are summarized below in Table IV.6 along with a stable oxide, B_2O_3. The measured values for the heats of transformation and fusion of NaOH are comparable with ΔH_f values calculated for the chloride systems. Furthermore, the measured heat capacity is larger than that of most fluoride eutectics and is considerably greater than that calculated for the three chloride systems. The measured value of thermal conductivity is much lower than that of the fluorides listed earlier but is twice that of HITEC and other nitrates. Heat content parameters were calculated for the NaOH-KOH system and also compare very favorably with other eutectics.

TABLE IV.6

THERMOPHYSICAL PROPERTIES OF
SOME HYDROXIDE AND OXIDE SYSTEMS

System	M.P. (°C)	ΔH_f (cal/g)	C_p (liq) (cal/g/°C)	K (cal/cm/sec/°C)	Ref.
NaOH	318	76*	0.50	0.0022	4.25
NaOH-KOH (50-50)	170	64*	0.40	not measured	4.15
B_2O_3	450	76	0.43	0.0026	4.15

*This quantity includes a solid-solid phase transformation.

The thermophysical properties of B_2O_3 are on a par with those of the hydroxides. One difficulty in implementing B_2O_3 as a storage medium is its tendency to supercool and the formation of a glassy solid. The presence of impurities in the oxide may greatly improve its nucleation properties and decrease the viscosity of the liquid.[4.38]

These hydroxide and oxide systems are chemically stable to very high temperatures. However, a critical design feature which must be taken into account with the alkali metal hydroxides arises from a possible chemical interaction of the storage media with water or steam which might be used as heat transfer fluids. A highly exothermic reaction occurs between water and these hydroxides, and any system failure resulting in the accidental contact of these two materials could result in a catastrophic increase in steam pressure. This danger of accidental water contact does not give rise to such grave consequences for systems using salts which form neutral water solutions and have low heats of dilution.

Exposure of molten hydroxides to the atmosphere should be avoided as the absorption of carbon dioxide and the precipitation of carbonates result. According to at least one source,[4.39] the presence of 1 wt.% Na_2CO_3 in molten NaOH accelerated the mass transfer rate of nickel from the containment system. The effect of mass transfer in molten hydroxides was most clearly revealed in thermal and forced convection nickel test loops in which non-isothermal conditions prevailed.[4.40, 4.41] The test loops were typically plugged or severely constricted by the transfer of nickel from hot to cold zones in a matter of hours for peak temperatures of 650 to 810°C.

Static tests in molten NaOH revealed[4.42] corrosion rates for Inconel and Hastelloy D which were nearly the same, but greater than that for nickel. It was also observed that iron and chromium were selectively leached in the Inconel samples. The leaching of these more reactive metals has been hypothesized to occur by the reduction of the hydroxide to H_2 gas and the formation of a sodium oxymetallic salt. In particular, nickel corrosion in fused NaOH has been markedly reduced by the presence of a blanketing H_2 atmosphere.[4.43-4.45] The use of such a corrosion inhibitor for molten hydroxide systems introduces the possible long-term problem of hydrogen embrittlement of the alloys and weldments of the containment unit. Although embrittlement in a pure hydrogen environment is well documented, possible difficulties associated with the molten hydroxide systems discussed have not been addressed in the literature surveyed.

Further corrosion experiments revealed that Inconel stressed by prior cold work was significantly more susceptible to corrosion than unstressed Inconel.[4.46] Effects of specimen stress are generally ignored in most static coupon tests, and these results indicate the importance of such effects, particularly with regard to heat exchanger elements where high stress levels may be introduced in forming operations and where minimum wall thicknesses may be desirable.

Investigations of B_2O_3 have shown[4.47-4.49] that this material is highly corrosive to high temperature cobalt, nickel, and iron alloys above 900°C. Dynamic, cyclical tests of these and more common structural alloys at lower temperatures are necessary to establish the usefulness of B_2O_3-based systems as thermal storage media.

It has been shown[4.38, 4.46] that the removal of all traces of water from both the molten hydroxide and B_2O_3 systems is extremely difficult. In some cases the procedure for water removal may actually introduce other impurities into the system which are even more deleterious in terms of corrosiveness than systems containing water. The effect of impurities on the chemistry of these molten salts is, in general, poorly understood, and the consequences of accidental contamination of the melt and subsequent repurification may be severe.

4.2.6 Carbonate Salt Mixture

Molten carbonates have received a considerable amount of attention in recent years due to their use as electrolytes in high-temperature fuel cells. These studies have been primarily limited to carbonates of the alkali metals and their respective eutectic mixtures.

Carbonate systems generally have rather high melting points although a few mixtures are molten below 500°C. Physical properties of some representative eutectics are given below in Table 4.7.

The ternary eutectic Li_2CO_3-Na_2CO_3-K_2CO_3 possesses excellent thermophysical properties for latent heat storage applications. The presence of a lithium salt, however, will have an adverse effect on this system's energy storage capacity in terms of material cost. It should also be noted that this mixture has an equilibrium CO_2 vapor pressure of approximately 10.5 torr at 750°C.[4.50]

The heat of fusion for the K_2CO_3-$MgCO_3$ system is not known and cannot be calculated from existing data. A value of C_p(liq) was estimated from data in the literature. Pure molten $MgCO_3$ is not stable at CO_2 pressures less than 1 atm., and it seems reasonable to expect that a sizeable CO_2 overpressure would be necessary to stabilize this eutectic at temperatures much greater than the melting point.

TABLE IV. 7

THERMOPHYSICAL PROPERTIES OF SOME CARBONATE SYSTEMS

System	M. P. (°C)	ΔH_f (cal/g)	C_p(liq) (cal/g/°C)	Ref.
Li_2CO_3-Na_2CO_3-K_2CO_3 (43.5-31.5-25)	397	99	0.40	4.50
K_2CO_3-$MgCO_3$ (57-43)	460	unknown	0.35	4.15, 4.21, 4.25
KCl-Na_2CO_3 (50-50)	588	64	0.33	4.15, 4.21, 4.25
K_2CO_3-Na_2CO_3 (44-56)	710	38	0.36	4.51

ΔH_f and C_p(liq) were calculated for the KCl-Na_2CO_3 eutectic, and although they are considerably smaller than the values determined experimentally for the ternary system discussed above, the low material cost of the KCl-Na_2CO_3 mixture considerably enhances its attractiveness, as will be discussed at the conclusion of this section.

Physical properties of the Na_2CO_3-K_2CO_3 system were determined experimentally. This eutectic also possesses the virtue of low material cost and a rather high melting point.

The characteristics of the thermal decomposition of carbonates into CO_2(g) and the corresponding metal oxide has been alluded to above. This phenomenon must be addressed for each individual system; however, the decomposition reaction is, in general, a reversible equilibrium process for most molten carbonate systems, and the maintenance or regeneration of the original mixture should not represent too severe a difficulty within certain decomposition limits.

The work of Janz, et al.[4.52-4.57] in particular has treated the corrosion of materials in relation to the chemical composition within the melt and the atmosphere above the melt. The ternary Li_2CO_3-Na_2CO_3-K_2CO_3 eutectic discussed above was the molten system employed in these studies. The corrosive properties of molten carbonates were found to be quite different from those of the molten fluorides and chlorides discussed earlier.

It was observed that both 347 and 304 type stainless steels were considerably more resistant to corrosion by molten carbonates than pure nickel. The steel surfaces were passivated in the 600 to 700°C temperature range when the ambient atmosphere was CO_2.

Micrographic examination of steel specimens before and after exposure to the molten carbonates emphasized the importance of carefully considering the consequences of structural alloy compositions. Considerable amounts of carbon were formed in the metal specimen. This carbide formation was well dispersed in the niobium stabilized 347 type stainless steel; however, the carbide formation in the non-stabilized 304 specimen was largely localized at the grain boundaries, which eventually could lead to a drastic reduction in this material's elastic properties.

It is clear that molten carbonates may be excellent thermal storage candidates by virtue of their compatibility with low-nickel ferrous alloys. However, extensive tests with different carbonate systems will be required to determine whether adequate passivity is conferred to steels by molten carbonates not containing Li_2CO_3. This is certainly a valid concern, as studies discussed above[4.54] indicated that Li_2CO_3 is the species responsible for the formation of a $LiFeO_2$ passivating layer. Dynamic loop testing should be performed to reveal any slow diffusion controlled or non-equilibrium phenomena which might have been obscured in the static tests.

Passivity of ferrous alloys might be achieved in molten salts consisting of CO_3/X mixtures, where X is another anion. In the discussion of chloride systems, a study of material compatibility with the molten KCl-Na_2CO_3 system revealed marked differences in the corrosion resistance of several iron-nickel-chromium alloys compared to mixtures consisting entirely of molten chlorides.[4.31] Static tests at 870°C indicated that intergranular corrosion of the alloys was an order of magnitude less for the chloride-carbonate system than was observed for the all-chloride systems.

On the other hand, the results of a study[4.44] on molten NaOH with 1 wt. % Na_2CO_3 indicated that the presence of the carbonate accelerated container corrosion. Clearly, further studies are necessary to resolve the complicated chemistry involved at the metal salt interface for these various mixtures. As total system costs could be considerably lowered by the use of a passivated steel instead of a high percentage nickel alloy, these studies are of paramount importance.

4.2.7 Nitrate and Nitrite Salt Mixtures

A mixture of alkali nitrates and nitrites marketed commercially under the name "HITEC" was discussed earlier in the section devoted to sensible heat storage. This eutectic and others of similar chemical composition exhibit rather low melting points; the thermophysical properties of two typical systems are given in Table IV. 8

TABLE IV. 8

THERMOPHYSICAL PROPERTIES OF SOME NITRATE/NITRITE SYSTEMS

System	M. P. (°C)	ΔH_f (cal/g)	C_p(liq) (cal/g/°C)	K (cal/cm/sec/°C)	Ref.
"HITEC"	145	31	0.37	0.0013	4.7
$NaNO_3$	307	41	0.44	0.0013	4.25

Heats of fusion for the nitrates and nitrites are typically rather low; however, certain processes may be well suited to an isothermal storage system operating at the somewhat low melting temperatures of these mixtures. Heat capacities and thermal conductivities for these mixtures fall into the general range of values for salt systems discussed above.

An upper limit to the useful operating temperature for nitrates and nitrites is imposed by thermal decomposition. In general, this phenomenon becomes severe around 500°C, although the addition of various materials to act as stabilizers can increase the upper temperature by perhaps 50°C.[4.58] The ultimate useful temperature range of these mixtures will thus depend on the chemical nature of the individual systems and the maximum acceptable loss rate of storage media for the overall system.

The limitation of such systems to temperatures under 500°C is unfortunate, as nitrates and nitrites appear to passivate a wide range of common structural steels by the formation of surface oxide layers.[4.7] Such mixtures can be operated in a variety of ambient atmospheres (subject of course to varying upper temperature limits), and the presence of water as an impurity in the melt does not materially enhance the corrosion rate of containers.

4.2.8 Sulfate Salt Mixtures

Sulfate systems tend to possess quite high melting points; however, eutectics composed of sulfates and other anions do exhibit some melting points below the 800°C limit covered in this discussion. Two representative mixtures are described below in Table IV. 9.

TABLE IV. 9

THERMOPHYSICAL PROPERTIES OF SOME SULFATE SYSTEMS

System	M. P. (°C)	ΔH_f (cal/g)	C_p (liq) (cal/g/°C)	Ref.
Na_2SO_4-$CaSO_4$-NaCl (45-3-52)	485	56	0.27	4.15, 4.25
Na_2SO_4-KCl (39-61)	517	53	0.26	4.15, 4.25

ΔH_f and C_p values for both systems were calculated using the Kirchoff method. These quantities are comparable to the values obtained for the great majority of systems discussed above. These sulfate-chloride mixtures should exhibit no significant vapor pressure within the temperature range under discussion. Likewise, these systems should be chemically stable if maintained under an enclosed, inert atmosphere.

The very corrosive nature of molten sulfates toward most alloys renders these systems much less desirable for thermal storage applications than the classes of compounds discussed earlier. Much of the recent experimental work on the compatibility of molten sulfates with structural materials has been done by Umland, et al.[4.59-4.61] Static corrosion of a variety of alloys was studied between 550 and 900°C. In general it was found that the presence of oxygen in the test atmosphere was necessary to prevent the formation of sulfides. Once sulfide formation began, the attack on the metal was very rapid and even catastrophic. The addition of NaCl to the melt increased the corrosiveness. The work of Geobel, et al.[4.62] supports the above conclusions. It was found that molten Na_2SO_4 at temperatures of 650 to 1000°C dissolves any protective oxide layer resulting in accelerated corrosion of the metal even under an oxygen atmosphere.

Considering the severely negative aspects of sulfate salt corrosion, it is recommended that little effort be expended in the development of this class of compounds as thermal storage media.

4.2.9 Other Salt Mixtures

Of the remaining fused salts, perhaps the phosphates come the closest to meeting the general criteria set out earlier for latent heat thermal storage media. Most phosphates have very high melting points even in eutectic mixtures. A survey failed to find a phosphate-containing system with a melting point below 500°C and a cost under $0.50/kg.

Some work has been done on material compatibility with molten phosphates; the work of Finell and others[4.63-4.66] is notable in this respect. Several ferrous alloys were tested at 700°C in molten sodium polyphosphate. The alloys contained varying amounts of chromium, nickel, and molybdenum; it was observed that the corrosion rate increased with increasing iron concentration.

The silicates and borates are inorganic salts that conceivably might be used in thermal storage applications. Many systems containing one or more of these anions do indeed cost less than $0.50/kg; however, a search of such mixtures failed to reveal any possessing a melting point below 500°C. Melting points for these mixtures were in general much higher than for any of the systems discussed previously.

It is felt that further work on the category of "other salt systems" for TES applications up to 800°C should be limited to characterizing the phase diagrams of economically attractive systems which have either been overlooked or unstudied, and which might reasonably be expected to have a melting point less than 800°C.

4.2.10 Economic Considerations of Inorganic Salt Mixtures

The important economic factors accompanying the use of inorganic salts as latent heat storage materials require consideration. Five representative systems have been chosen from the previous section for the purposes of comparison. Figure 4.7 illustrates the enthalpy content for these five salt systems as a function of temperature on a weight basis. From this plot it is clear that the NaOH and LiF-NaF-KF systems are superior to the carbonate-chloride and chloride-chloride systems in terms of specific storage capacity. The relative position of the KF-NaF-MgF_2 system depends on whether its large heat of fusion at 685°C has been utilized.

From such plots one might draw the conclusion that fluorides and hydroxides are superior to chlorides and carbonates as thermal storage materials. Economic considerations greatly modify these preliminary judgments. The primary source used for the assessment of current market prices of these salt systems in bulk quantities is the Chemical Marketing Reporter;[4.67] this publication lists the prices of merchant producers accounting for at least 80 percent of the annual US production of all chemicals. An attempt was made to price these salt systems with the component chemicals in roughly the same state of purity (typically 95 to 99% pure); from the discussions above it seems likely that these bulk materials would not be of sufficient purity upon receipt for direct use in thermal storage units. Purification procedures cannot be defined nor their price estimated at this time; consequently the system prices used in this section represent a minimum material price as of June 1975.

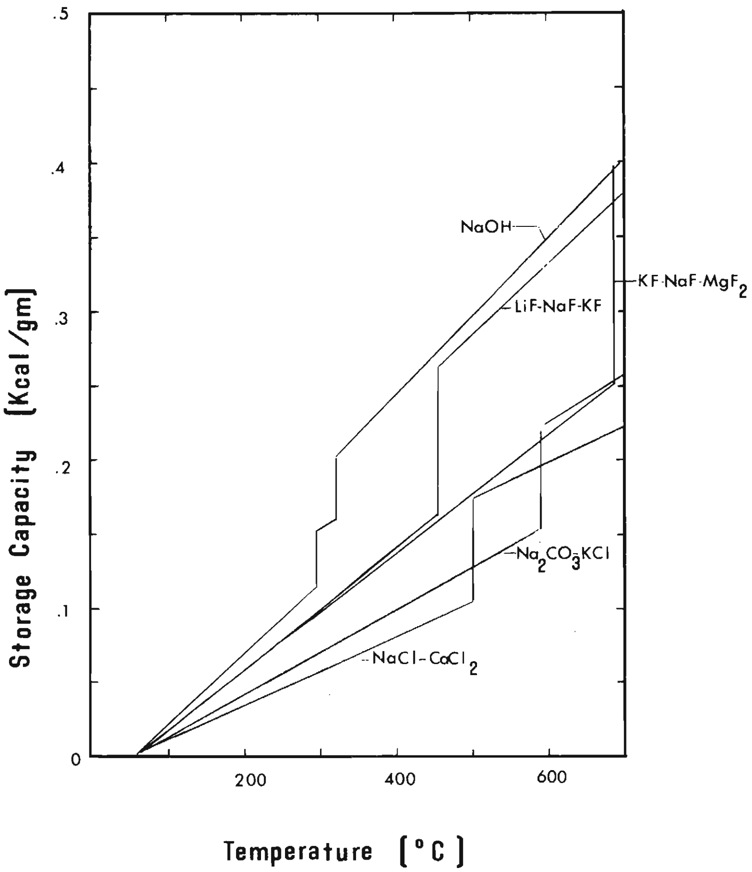


Figure 4.7 Thermal Storage Capacity Comparison for Various Inorganic Salt Mixtures

A plot of system energy content per unit cost of the material as a function of temperature is given in Figure 4.8. It is clear that a drastic reordering of the systems considered in Figure 4.7 has occurred. The effect of material cost differences has completely overwhelmed variations in salt system heat of fusion and heat capacity; the basic lesson to be gathered from this plot is that fluorides are expensive, hydroxides are moderately priced, and chlorides and carbonates are quite cheap.

Nevertheless one must not be misled into assuming that a detailed analysis of material costs for inorganic salts will resolve the question of which salt system will best serve as a latent heat storage material. The cost of the storage media represents only a portion of the total system cost. As was noted above, however, the choice of the storage media has a very great influence on the materials necessary for the containment system and heat exchangers, and these components do represent a sizable portion of the total system cost. Thus, the need for a total systems analysis is necessary in order to select the optimum materials for an inorganic salt storage system.

The very large differences in corrosion characteristics for the various classes of molten salts, their importance in structural material definition, and the variations in salt costs combine to favor carbonates, and possibly carbonate-chloride systems, as high temperature latent heat storage media.

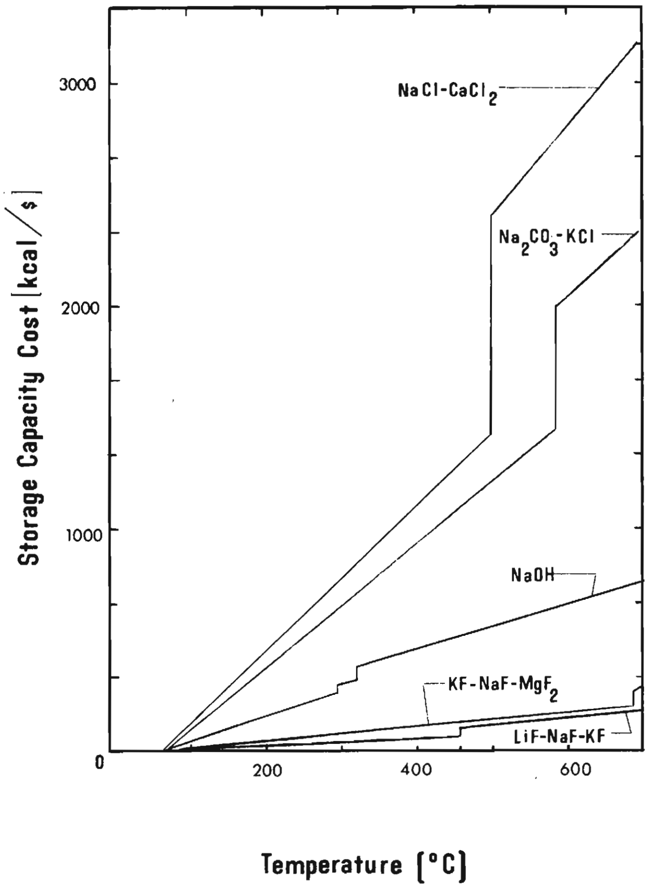


Figure 4.8 Capacity-Cost Comparison for Inorganic Salt Mixtures

Possibly less desirable are hydroxide systems with more corrosive and expensive components, and chloride systems also with more corrosive but very cheap constituents. Nitrates and nitrites appear to be good choices for applications under 500°C, being noncorrosive and fairly inexpensive. Fluorides may be important where high heat storage densities are required; however, their high price and fairly corrosive nature (unless enclosed in an inert atmosphere in an ultra-pure state) render these materials considerably less attractive for latent heat storage systems than the salt mixtures discussed above.

4.3 Material Considerations for Heat-of-Reaction Storage Systems

The state of the technology associated with reversible chemical reaction thermal storage has not sufficiently advanced to a point where very many specific materials problems can be identified. Indeed, relatively few reversible reactions have even been identified conceptually as having application to thermal energy storage. Thus the discussion in this section must be limited to general remarks and some specific examples arising from a few representative proposed systems.

The nature of this mode of thermal energy storage places some unique requirements upon the storage media in addition to the usual criteria. The reaction must be as close to being reversible as possible so that the storage cycle does not consume storage material. The requirement of quantitative cycling is considerably more stringent for heat-of-reaction systems than for the sensible and latent schemes discussed above. As chemical reaction schemes involve the continual breaking and forming of chemical bonds, they are more prone to side reactions than processes involving fusion or sensible heat storage. The economic consequences of nonquantitative cycling for H_2 production in proposed closed-loop water splitting schemes has been amply demonstrated by Joly.[4.68]

The reversible thermal storage reactions should proceed with rates consistent with the charge and discharge conditions at the appropriate temperatures, and should proceed as close to completion as possible. If a catalyst is required to obtain acceptable reaction rates, the effects which might cause its poisoning and premature replacement must be understood and minimized. Possible difficulties could be caused from impurities in the reactants of a given system indicating the need for high purity chemicals. Another source of contamination could arise from the leaching or outgassing of reactive species from an improperly chosen containment material. These considerations could dramatically alter the economic attractiveness of certain catalytic processes. Of course, the problems of stability, compatibility and corrosion must be thoroughly evaluated for the materials in any system which is considered.

Table IV. 10 presents a compilation of the principal types of reversible reactions which have been considered for thermal storage applications. Also included are the heats of reaction and the temperature range where reasonable kinetics and equilibrium states can be expected. A common feature of all these reactions is the formation of at least one gaseous product of the decomposition. This allows a means of controlling the reaction via control of the pressure of the gaseous species, but also introduces the possible complications of gas handling, pumping, and storage. Another means of system control may be available, if a catalyst is necessary to achieve reasonable reaction rates and can be removed or introduced into the system to control the reaction.

It should be noted that a considerable amount of energy can be tied up in sensible and latent heats of products and reactants. This energy must be accounted for in a heat balance for this type of storage system. Finally, the problem of separation and storage of the reaction products may be formidable and deserves serious consideration.

TABLE IV. 10

POSSIBLE REVERSIBLE CHEMICAL REACTIONS FOR THERMAL STORAGE APPLICATIONS

	Temperature Range, °C		ΔH /cal* g	Ref.
$SO_2(g) + 1/2\ O_2(g) \rightleftarrows SO_3(g)$	727	650	360.	4.69, 4.70
$CaCO_3(c) \rightleftarrows CO_2(g) + CaO(c)$	554	527	420	4.69
$Ca(OH)_2(c) \rightleftarrows CaO(c) + H_2O(g)$	520	490	240	4.71
$Mg(OH)_2(c) \rightleftarrows MgO(c) + H_2O(g)$	375	350	166	4.71
$CH_4(g) + CO_2(g) \rightleftarrows 2CO(g) + 2H_2(g)$	676	538	980	4.72
$C(c) + CO_2(g) \rightleftarrows 2CO(g)$	827	649	741	4.72
$CH_4(g) + H_2O(g) \rightleftarrows CO(g) + 3H_2(g)$	676	538	1451	4.72
$COCl_2(g) \rightleftarrows CO(g) + Cl_2(g)$	517	482	140	4.69
$CuCl_2(c) \rightleftarrows CuCl(c) + \frac{1}{2} Cl_2(g)$	475	427	140	4.69
$NiCl_2 \cdot 6NH_3 \rightleftarrows NiCl_2 \cdot 2NH_3 + 4NH_3$	175	125	250	4.73
$AH_2 \rightleftarrows A + H_2$			varies with hydride	

*Based upon total weight of reactant species

Many advantages may be realized in heat-of-reaction schemes utilizing reactions found in current process chemical technology. These manufacturing processes involve chemical reactions which are well understood and have been commercialized on an immense scale for many years. The problem of developing workable reversible reaction schemes which would incorporate basic processes is reduced to achieving a thorough understanding of the reverse reactions and resolving the difficulties of product separation and storage. An example of the use of process chemical technology as applied to chemical reaction storage schemes is the utilization of the $SO_2 + 1/2\ O_2 \rightarrow SO_3$ reaction; this is a manufacturing step in the "contact process" method of sulfuric acid production. Other examples which might be considered in a similar manner are the steam reforming of methane, $CH_4 + H_2O \rightarrow CO + 3H_2$, and the Haber synthesis of ammonia, $N_2 + 3H_2 \rightarrow 2NH_3$.

As was the case with the other modes of thermal storage discussed previously, a performance analysis of these storage concepts requires the specification of the thermophysical properties of not only the reactants but also the products. Specifically required information is density, heat capacity, thermal conductivity and viscosity (of the gaseous species), and in some cases reaction kinetics, all as functions of temperature.

The problems of containment of these types of systems will undoubtedly introduce some phenomena which have not been experienced in other thermal storage systems. The use of aqueous systems such as salt hydrates, inorganic hydroxides, and sulfuric acid and their compatibility with structural materials must be individually evaluated. Close attention should be paid to the tendency of these storage media to cause stress corrosion cracking in the containment materials. Otherwise-inexpensive bulk chemicals may require repurification procedures to remove concomitant low-level impurities. Likewise, great care must be exercised in the design of aqueous heat-of-reaction systems in order to avoid inadvertent electrochemical corrosion.

The use of transition metal coordination complexes in heat-of-reaction schemes appears to be both expensive and prone to undesirable side reactions. For instance, the reaction involving the thermal decomposition of $NiCl_2 \cdot 6NH_3$ must be carefully studied to assess the possible effects due to accidental contamination of the system with water. Such occurrences could be economically undesirable both from the standpoint of reactant replacement and the possible production of corrosive substances within the system.

As a final example of materials problems, schemes involving metallic hydrides are considered. These systems offer quite high energy storage densities but are considerably offset in their advantages by the very high costs of most metal hydrides. Compatibility of hydrides and hydrogen with containment materials is of widespread interest today. Much effort has been expended over the past few years to develop an understanding of hydrogen embrittlement of structural materials, and a current program at Sandia Laboratories is endeavoring to assess compatibility problems of hydrogen in existing steel natural gas pipelines. Similar studies are needed to examine the long term effects of hydrogen on containment systems.

The economic considerations relating to reversible chemical reaction storage are quite difficult to assess due to the very limited technology development in this area. Such effects as the "degree-of-completion" of the reaction and its dependence on temperature have not yet been evaluated in terms of storage system cost; thus, realistic cost estimates are difficult to make. Table IV. 11 compares the material cost per unit capacity based on the utilization of the full heat-of-reaction. Notice that these costs vary over four orders of magnitude from \$0.07/kW_t-hr for $Ca(OH)_2$ to \$928/kW_t-hr for $LaNi_5H_5$. Clearly, further analysis of these systems is required before better cost comparisons can be made.

TABLE IV. 11

COST COMPARISON OF HEAT-OF-REACTION STORAGE MATERIALS

Base Material	Cost (\$/kW_t-hr)
$Mg(OH)_2$	0.62
$Ca(OH)_2$	0.07
H_2SO_4	0.45
$NiCl_2 6NH_3$	7.60
SO_3	0.16*
MgH_2	2.88
$FeTiH_2$	28.00
$LaNi_5H_5$	928.00
Coupled Hydride System $FeTiH_2$ and MgH_2	17.90

*Based upon H_2SO_4 at \$0.025/lb

The foregoing discussion of reversible chemical reaction storage systems has illustrated the serious need for basic studies aimed at the understanding of the various materials related problems. These studies must include not only the stability and compatibility considerations as in other thermal storage modes, but also the kinetics and equilibrium phenomena which are critical to the performance of these types of systems.

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SECTION 5. ASSESSMENT OF THE HEAT TRANSFER AND FLUID MECHANICS PROBLEMS ASSOCIATED WITH THERMAL ENERGY STORAGE SYSTEMS

This section is concerned with the heat transfer and fluid mechanics aspects of the thermal energy storage systems discussed in Section 3. The purpose of the section is to identify the key technical problems associated with each method of energy storage, review the relevant theoretical analyses and experimental results, and identify required additional research.

5.1 Sensible Heat Storage Systems

5.1.1 Liquid Storage Systems

The storage of thermal energy as the sensible heat of a liquid storage medium has, over the years, found widespread application due to the low level of technology required in implementation and low cost. The most commonly used storage medium has been water, and most applications have been at relatively low temperatures. As the storage temperatures of these systems increase, the required technical sophistication of their design also increases. Specifically, due to the high vapor pressure of water at high temperatures, the problem of containment becomes formidable; if other fluids are used as the storage medium, then heat exchangers may be necessary for transferring the energy into and out of storage. In this section these technological problems are discussed relative to storage in tanks and caverns, steam accumulators, and acquifers.

The storage of thermal energy in liquids may be accommodated by either "mixed" or "non-mixed" systems.* A "mixed" system using a tank or underground cavern is the simplest of the liquid storage concepts. Heat can be adequately transferred to and from storage using simple, commercially available heat exchangers immersed in the tank or by the

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*In a "mixed" system the bulk temperature of the storage medium varies continuously as energy is added or removed; in a "non-mixed" system, the hot and cold portions of the storage medium are separated.

continuous circulation of the storage medium through external heat exchangers. Predicting the performance characteristics of a simple, mixed liquid storage system is technically straightforward. The calculation of the thermal response of the system to energy input and removal is discussed in detail by Brumleve,[5.1] Duffie and Beckman,[5.2] and Yang and Lee.[5.3] All three of these studies set up simple procedures for estimating the performance; in addition, the first two discuss the problem of energy losses from the system. The technology required in the design of a mixed liquid thermal storage system is adequately understood and well documented, and the implementation of this type of system should not be difficult.

In non-mixed liquid systems the hot and cold portions of the storage fluid are either stored in separate containers or in a single container where separation is accomplished by natural thermal stratification (i.e., the formation of a thermocline) or by the use of a movable baffle. The design of the systems based on the multiple tank configuration is simple and straightforward. On the other hand, the single vessel, natural thermocline configuration requires that fluid input and output be handled carefully to maintain thermal stratification and to avoid deleterius effects of mixing on system performance. Brumleve[5.1] discusses the performance of non-mixed systems (relative to mixed systems) and presents a simple theoretical analysis of the spreading of the thermocline based on thermal conduction in the fluid only. Duffie and Beckman[5.2] also describe procedures for predicting the performance of the system, but do not deal specifically with the problems of mixing at the thermocline. Due to the complexity of the natural thermal stratification problem, most of the work addressing it has been experimental. Davis and Bartera[5.4] discuss an experimental program dealing with a stratified storage tank for use in a solar water heating application. Data are presented which illustrate the performance of the system for two types of fluid input and output configurations. In one case a thermocline was formed having a width which was 20 to 30 percent of the height of the tank. Using the second configuration, no thermocline was formed thus illustrating the sensitivity of the system to the fluid removal and input configuration, as well as diffuser design. Milby[5.5] presents some preliminary results of experiments carried out using the Sandia storage system described in Section 3. The thermocline obtained with this system was not as sharp as expected, and in addition, its width was quite sensitive to the rate at which energy was added to the system. Unfortunately, these results were inconclusive due to some experimental difficulties in that the input-output diffusers were suspected of causing excessive mixing. Miller and Fong[5.6] have conducted an experimental program aimed at the investigation of the effect of conduction in the container wall on the problem of mixing in the fluid. They found that this effect could have a significant impact upon the width of the thermocline in a small tank. Thermocline widths an order of magnitude greater than those predicted by conduction in the fluid alone were observed.

As far as the theoretical treatment of this problem is concerned, there is very little information available that is directly applicable. Miller[5.7] is currently developing a numerical model of the thermocline mixing problem, including wall effects; results, however, are not yet available. Theoretical models and correlations of experimental data have been developed[5.8, 5.9] for the similar problem of the thermal stratification in liquid hydrogen fuel tanks. Some of this work may be applicable to the thermal storage program. The application of this concept to a thermal energy storage system will require a thorough understanding of the thermal stratification problem. Especially critical is the effect of system size on the various mechanisms which can cause mixing; e.g., as the size of these systems are scaled up, some of the adverse effects may diminish.

The steam accumulator is a class of liquid storage systems wherein energy is input by condensing steam in water (the storage medium) and extracted by allowing some of the water to flash back to steam. Since the issuance of the first patent on this type of system in 1873, a great deal of development work has been carried out. A text by Goldstern[5.10] provides an excellent review of this development in addition to current design practice for, and applications of, steam accumulators. The large economic benefits projected by Margen[5.11, 5.12] for the underground storage of liquids is a strong motivation for studying the possibility of using an underground steam accumulator. The advantages of low cost and available technology make this concept appear quite attractive.

The technology needed to design and engineer a liquid thermal storage system using a tank or underground cavern for containment appears adequate with the exception of the incomplete understanding of the nature of the mixing problem in thermally stratified systems. In this regard it is important that the factors which affect the formation of a thermocline be identified and quantified. The problem of thermal losses from these types of storage systems does not seem to pose any serious development problems as illustrated by discussion presented by Brumleve.[5.1]

A liquid storage concept that has received a great deal of attention recently is the use of an acquifer formation for the underground storage of hot water. The main reason for this interest is the projected potential for very low-cost energy storage. In this concept, hot water at high pressure is injected into an underground layer of porous rock and water, which has a very low ground-water velocity. The hot water displaces the ground-water as it is injected into the porous rock with the artesian pressure head of the ground-water being sufficient to prevent flashing.

The problems to be dealt with in developing and implementing this concept involve two general areas: the general characteristics of the acquifer such as geometric configuration, thermophysical and physical properties, and geochemistry; and the interaction between the injected water and the ground-water, and the performance of the storage system. The former area involves basic geological questions, while the latter involves the heat transfer and fluid mechanics of flow in a porous medium. In order to evaluate the feasibility of this storage concept, a simple, one-dimensional performance analysis was performed.[5.13, 5.14] Meyer, Hausz, and Kleinecke[5.15] have refined the simple, one-dimensional analysis to include mixing of the hot and ground-waters, conduction in the porous solid, heat transfer to the surrounding rock formation, and two-dimensional fluid flow in a porous medium. Unfortunately, there exist no experimental data with which to verify the analysis. The encouraging performance characteristics indicated by the results of the analysis illustrate the need for supporting experimental work (such a program is being initiated at Auburn University under ERDA sponsorship). This type of data will either verify the analysis or point out the need for a more rigorous theoretical treatment.

Future studies of underground thermal storage systems might benefit from work which has been carried out for related technologies. As an example, the petroleum industry has been using hot water injection to improve oil production for some time; much of this technology can be obtained in the open literature[5.16, 5.17] and some of it may be applicable to the acquifer storage problem. Another example is the area of geothermal energy.[5.18, 5.19] These related technologies should be examined in order to identify common areas of study.

5.1.2 Above and Belowground Solid Systems

Thermal energy storage in a solid material may be the simplest of all the sensible heat storage system concepts. The technologies that apply to this problem are the fluid mechanics of the flow field, the heat exchange at the fluid/solid interface, and the conduction of heat within the solid. The geometric configuration of a solid material thermal storage system can vary from an insulated block of material with fluid channels running through it to an underground solid rock formation which has been drilled for fluid channels or fractured in such a way as to form channels, or even to a bed of large rocks with a fluid flowing through it. Because of the large number of geometrical configurations possible, it is difficult to present a generalized discussion of the various classes of technical problems. In many cases the problems will be directly related to classical problems, such as the flow of a fluid through a rectangular channel[5.20] (Couette flow) or the conduction of heat in a spherical solid.[5.21] The nature of this type of storage system is such that the technology required for its application is not particularly complex. This fact will become obvious in the next few paragraphs where a number of solid storage concepts are described.

In a recent study, Schmidt and Szego[5.22] analyzed the performance of a sensible heat solid storage system which consisted of a series of channels formed by parallel planes and separated by the storage material. By considering the fluid thermally mixed and specifying a heat transfer coefficient between the fluid and solid, an energy conservation equation for the fluid was written. This, along with the heat conduction equation in the solid, was integrated numerically to give the temporal and spacial temperature distributions in the system. This simple method was shown to yield acceptable results for design considerations. Sreenivasan and Altman[5.23] present an analytical solution for the thermal response of a cylindrical solid storage device; this solution, along with a specification of the rate of heat transfer to or from the fluid flowing in a pipe located concentrically within the device (the classical Graetz Problem)[5.24] provides a complete solution for the performance of the system.

Another attractive method of sensible heat solid storage involves the use of underground rock formations. Brun[5.25] has performed a simple engineering analysis of such a system applied to the storage of solar energy for electric power production. This system consists of vertical holes (bored in the rock) into which a pair of concentric casings are inserted to transport the heat transfer fluid. The heat is then transferred between the fluid and the rock through the outer casing. Again, the technical problems surrounding this concept are basically of the classical fluid mechanics and heat transfer category; specifically, the heating and cooling of a fluid flowing in a pipe (the Graetz Problem)[5.24] and the diffusion of heat in a semi-infinite medium bounded internally by a circular cylinder. The most serious technical problem (aside from material compatibility problems) appears to be the provision of a suitable means for achieving a low thermal resistance between the outer casing and the rock.

Other studies have also dealt with various technical problems of underground thermal storage. Garg[5.26, 5.27] describes a system for the disposal of the waste heat from an underground power generation system. This system consists of a network of buried pipes through which a fluid carrying the waste heat is flowing. The heat is disposed of by allowing it to diffuse out of the pipes into the earth. The reports describe the thermal properties of different kinds of earthen materials as well as the diffusion of heat from the pipes. The results are applicable to low temperature systems; at higher temperatures the losses are likely to become unacceptable. In addition, due to the low conductivities of the materials involved, the heat transfer rates are likely to be quite low. Nonetheless, the analytical methods described in the study could be applied to underground storage systems. Shelton[5.28] discusses the losses from underground storage systems. For low-temperature applications, he shows that the losses are so small that the use of insulation is not justified.

The preceding discussion has covered the subject of sensible heat storage in solid materials only so far as previous work has been carried. Extensions to this previous work might include the application of the thermal stratification technique in order to obtain constant fluid output temperatures. However, even though the direct contact between the heat transfer fluid and the solid storage material is a favorable condition for heat transfer, the thermal conductivities of solids are typically so low that reasonable heat transfer rates may be unattainable. Certainly, the application of advanced technological concepts such as heat pipes can improve the situation, but the cost of these technologies might be prohibitive. It does not appear that the development of sensible heat systems based upon solid storage is technology limited. The nature of the problems is such that well-known methods of analysis and commonly used engineering techniques can adequately be applied. What is needed, however, are new and ingenious concepts and applications that will take advantage of the low-cost potential of solid storage systems.

5.1.3 Combined Liquid/Solid Systems

Packed beds of particulate solid materials have, for a long time, been used in various applications such as low-temperature energy storage for space heating of buildings, high temperature test gas preheaters in aerodynamic wind tunnels, and reactors in many chemical processes. All of these applications involve the flow of a liquid or gaseous fluid through the bed, as well as the transfer of heat between the bed and the fluid. Thus, much of the basic technology needed to design a packed bed, high-temperature thermal energy storage system has been developed (to various degrees) for these applications.

An excellent example of the application of the packed bed concept to high-temperature thermal storage is the recent proposal by the Rocketdyne Division of Rockwell International for a storage system for the ERDA sponsored Solar Thermal Central Receiver Program.[5.29] This particular system is sufficiently refined so as to include most of the technological disciplines likely to be faced in the design of any packed bed storage system. Specifically, the system consists of a vertical column of crushed granite (packed to a porosity of about 25%) through which flows a heat transfer oil (Caloria HT-43). The charging process involves the flow of heat transfer fluid downward through the bed, while during discharge, the flow is upward through the bed. This manner of operation is intended to achieve a thermal stratification within the bed so that the heat transfer fluid has a nearly constant output temperature during discharge. The energy transfer to and from the heat transfer fluid is accomplished in commercial tube-in-shell counterflow heat exchangers.

The major technical problems to be encountered in designing a system of this type involve the flow of the fluid through the bed and the transfer of heat between the fluid and the solid particles. Of primary concern in the area of fluid mechanics are the problems of pressure loss (pumping costs) of the flow through the bed; the "channeling" of the fluid due to non-isotropy in the packing of the bed; and the distribution of the fluid at the entrance to the bed. The determination of the pressure loss in flow through a packed bed of solids have been the subject of numerous investigations.[5.30-5.34] Typically, empirical correlations of experimental data are used to relate pressure drop to the various physical parameters involved. However, the effects of particle shape, roughness, distribution, manner of packing and other difficult-to-define parameters cause a great deal of difficulty in correlating data. Thus, these effects should be carefully considered when making predictions of pressure loss in packed beds.

The problem of fluid channeling in the bed is usually a result of non-uniform packing densities. Particle size distribution and shape can have a significant effect on the uniformity of packing density. If the particle size is small relative to the container size (this is necessary in a packed bed storage system in order to achieve reasonable heat transfer surface areas), and the packing density is high, the probability of having channeling problems is reduced as long as the high packing density does not cause localized increased flow restrictions. The nature of the physical problem of channeling prohibits its analytical treatment; however, intuition suggests that it could only have a detrimental effect upon a packed bed thermal storage system and, thus, should be avoided. One method for reducing the probability of channeling difficulties is to insure that the heat transfer fluid is introduced into the bed in a uniform manner. Since the fluid channel must undergo a rapid increase in cross-sectional area at the entrance to the bed, it is possible that a non-uniform flow distribution might be induced at this section. Thus, the use of some sort of diffusing device might be necessary to eliminate these effects.

The fluid mechanics technology needed to facilitate the design of a packed bed thermal storage system appears to be adequate. The technical problem areas described above are minor in nature and do not represent any significant difficulty in the application of packed bed technology to thermal energy storage. This is not to say that the predictive capabilities discussed above can be expected to eliminate the need for laboratory or pilot scale experimental systems. Indeed, the empirical nature of the analyses implies the need for these experiments; however, it appears that the analyses can be used to make good first-cut predictions and then allow the confident extrapolation of the experimental results.

The primary area of concern in the transfer of heat between the fluid and the solid is the understanding of the characteristics of the stratification layer. What is important is the thickness of the zone, the velocity at which it moves in the bed, and the rate at which it spreads out. The latter of these characteristics is probably the most important since the understanding of this phenomenon is critical to the prediction of how long the fluid being removed from the system during discharge can be expected to be at the peak bed temperature. Another heat transfer problem is the effect of the wall on the heat transfer process. If this effect is confined to the close proximity of the wall, then the transfer of heat in the core of the bed is basically one-dimensional and the problem of scaling experimental results from one bed size to another becomes simple. The more pronounced the wall effects become, the less scalable the data obtained from the bed become.

A solution to the problem of fluid/solid heat transfer in a packed bed has been available for quite some time. In 1929, Schuman[5.35] published a solution which he developed in terms of a fluid/solid particle heat transfer coefficient. The solution assumes that the effects of the walls and of axial conduction in both the fluid and the solid are negligible. Similar results have been reported by Hung and Nevins,[5.36] Rao and Suri,[5,37] and Yang and Lee[5.3] who, after applying the same assumptions, merely obtained the solution via different methods.

In 1940 Saunders and Ford[5.38] reported a comprehensive experimental program dealing with heat transfer in packed beds of solids. In their work they discuss the effects of particle size and shape and indicate methods of correlating experimental data. The problem of the determination of the fluid/solid particle heat transfer coefficient has, thus far, received only empirical treatment. Rao and Suri made their determination by curve fitting their theoretical analysis to their experimental data. A more sophisticated approach to the problem was made by both Close[5.39] and Turner[5.40] who empirically determined the heat transfer coefficient by a method based upon the harmonic response of the bed to a cyclic temperature input. There exist quite a few attempts at correlating experimental data for the purpose of predicting the heat transfer coefficient. These efforts are reviewed in References 5.30, 5.32, and 5.34. It appears that most authors have concluded that the correlations of fluid/solid-particle heat transfer coefficient for systems much different than those upon which the correlations were based might not be satisfactory.

Another area of heat transfer in packed beds that deserves mention is that of the conduction of heat within the solid particles. Most analyses of packed bed heat transfer assume that the thermal conductance within the solid is large when compared with that of the film at the solid particle surface, and thus has little effect of the flow of heat to or from the solid. For systems of "small" particles, this is usually true; however, it is recommended that this problem always be evaluated, since, if it is important and neglected, serious errors in the analysis could be generated.

The discussion in the previous paragraphs has reviewed the state-of-the art of the heat transfer technology needed in the design of a fixed bed thermal storage systems. It is clear that little or no attention has been given to the problem of wall effects on the performance of packed bed storage systems.

The impact of these effects is difficult to estimate; however, it can be safely stated that the one-dimensionality, and thus the scalability, of the problem becomes questionable as wall effects become significant. Additionally, thermal losses from the system can be closely related to the wall effects. The one-dimensional analyses carried out to date have shown a consistent discrepancy with experiment which appears to be attributable to longitudinal conduction in the fluid and/or the solid. This effect should be evaluated through an extension to the one-dimensional analysis. The most important parameter required in an analysis of fixed bed heat transfer is the fluid/solid particle heat transfer coefficient. The current technology includes empirical correlations for rough predictions; however, experimental determination is needed for more accurate results. It seems that some basic work is needed in this area in order to improve predicative capabilities.

5.1.4 Fluidized Solid Systems

As an extension to the packed bed solid storage concept, the use of a fluidized bed heat exchanger has been considered.[5.41, 5.42] Instead of the simple direct-contact heat exchange between a fluid and stationary solid particles in a packed bed, the fluid is used to fluidize the particles, carry them to a fluidized particle heat exchanger, and participate in the exchange of heat between the particles and the heat exchanger wall. Fluidized bed heat exchangers are known to be capable of very high heat transfer rates, which makes the application of this technology an attractive alternative to the packed bed system where the heat transfer rate may be limited.

The use of a fluidized particle heat exchanger has a number of advantages in thermal energy storage applications. In addition to the possibility of attaining high heat transfer rates with reasonable sized equipment, very high temperature operation can be accomplished in unpressurized systems by using a gas for the fluidization medium. Moreover, inexpensive simple materials can be utilized which will result in the capital costs consisting of mainly the container and heat exchanger and the operating costs consisting primarily of the pumping cost.

In 1964 Botterill and Elliott[5.41] proposed a thermal energy storage concept based on a fluidized particle heat exchanger. During heat exchange processes the solid-particulate storage medium is removed from its static containment vessel and fluidized by the flow of a working fluid; the fluidized particles then pass through a heat exchanger where their stored sensible heat is removed (or heat is added); finally, the particles are sent to a second containment vessel for storage until the process is reversed. The primary technological problems related to this storage concept are the transfer of heat to and from a flow of fluidized solid particles, the process of fluidizing the solid particles, and the control of the heat exchange process.

The subject of solid particle fluidization has, to date, received a great deal of attention. A number of books have been written on the subject[5.30-5.32, 5.43] and in addition, numerous papers have been published dealing with many of the specific problems of fluidized bed heat transfer, such as particle-to-fluid heat transfer[5.43, 5.44] and heat transfer between fluidized beds and boundary or immersed surfaces (see, for example, References 5.45 through 5.55). These studies deal mainly with the development of empirical models and the presentation and correlation of experimental data, and provide a good foundation for the design of a fluidized bed heat exchanger. Although a great deal of work has been carried out in this area, the complex nature of the problem is such that final engineering design must be backed up by some small-scale experimental work.

The use of fluidized particle heat exchangers appears to offer a number of advantages in thermal storage applications. The idea, however, has not progressed beyond the conceptual stage; thus, the advantages cannot be quantified. As a first step, a storage system should be synthesized around a fluidized bed heat exchanger and a thorough systems analysis carried out to evaluate such factors as pumping costs and to determine the associated system impact. The technological background appears adequate to support preliminary designs of this type of thermal storage system.

5.2 Phase Transformation Storage Systems

Systems utilizing the heat of fusion of a material undergoing a solid/liquid change-of-phase have received a great deal of attention in the last ten to fifteen years. Application of phase change technology to space flight systems has involved both high-temperature concepts for solar energy storage (for use during shadowed portion of the orbit) and low and moderate temperature concepts for thermal environment control. Low-temperature heat-of-fusion (HOF) thermal storage systems have been developed for use in heating and cooling applications, and in one case a system is already being marketed. The heat exchange processes used in nearly all HOF storage systems have been of the passive type, even though a number of active systems have been proposed. The heat transfer and fluid mechanics technology associated with HOF thermal storage systems involves some complex phenomena such as the moving solid/liquid boundary and the large density changes which may occur during solidification. In some situations quite refined methods of analysis have been developed, while in others the methods may be very limited. The object of this section is to discuss the state of development of these technologies.

5.2.1 Passive Heat Exchange

Practically all HOF thermal storage systems conceptualized or developed for the purpose of storing solar energy in space flight applications have been high-temperature devices using either lithium hydride or lithium fluoride as the phase-change material (PCM) (References 5.56 to 5.61). In addition, due to weight and volume constraints, the storage system has been an integral part of the solar energy receiver and passive heat exchanger processes have been used. McKinnon[5.56] and McKinnon et al.[5.57] describe the analysis and experimentation carried out in support of the NASA sponsored SUNFLOWER program. Their system consisted of both cylindrical and spherical cavity receivers surrounded by a jacket of PCM for energy storage. Heat was input to storage through the wall separating the receiver from the PCM and removed by a heat transfer fluid (HTF) flowing through tubes running through the PCM. The analysis used in this study was based on the determination of the thermal resistance of the solid PCM by an "electrical resistance" analogue, and was developed for making predictions of the thermal performance of the system. It is limited to predicting the heat removal rate from storage for a non-simple two dimensional geometry. The experimental program, along with verifying the applicability of the concept, illustrated that the effects of natural convection in the liquid phase can significantly alter the heat transfer rates. Martinek[5.59] presents a comprehensive analytical and experimental treatment for a similar storage/receiver configuration. He develops the conservation equations describing the heat storage and removal process and the numerical algorithms required for a computer solution. The analysis considers the effects of such things as internal fins as well as the changes of density with temperature (causing mass flows of both solid and liquid) of the PCM. Not considered were the effects of gravity induced natural convection. The results of the analysis specify the performance characteristics of the system, which compare quite favorably with the experimental results.

Young et al.[5.60] present a study of methods of impoving the heat transfer rates in passive thermal control systems using a PCM as a thermal capacitor. It is shown that the use of finned heat pipes can improve the heat transfer rates into and out of the PCM; this improvement must be balanced against the volume of PCM and surface area displaced by the heat pipe. It is also shown that the use of selected heterogeneous mixtures of PCM's can result in improved heat transfer rates through convection currents induced by differences in the surface tension of the components of the mixture. The fundamental mechanics involved in this problem are poorly understood; thus the extent of the improvement cannot be predicted.

Another class of lower temperature HOF thermal storage systems have applications including storage for solar thermal electric power production systems at moderate temperatures as well as thermal storage for cooling-load leveling at low temperatures. These systems, as in the case of the space flight systems all utilize passive heat exchange concepts.

A team of investigators from the University of Minnesota and Honeywell Corporation[5.62] has discussed the application of HOF thermal storage to a solar thermal power system. In their system, a bundle of horizontal tubes containing PCM is submerged in a larger container of pressurized water. In order to discharge the storage system, the pressure of the water is lowered causing the water to boil on the surface of the PCM tubes. An analysis of the heat transfer rate from the PCM tubes is presented which shows that the temperature difference between the liquid PCM and the saturation temperature of the water can be limited to a few degrees using reasonably sized tubes if not all of the PCM is required to solidify. Turner[5.63] is investigating a similarily configurated system for the purpose of superheating steam. He stresses that the problem of shrinkage of the PCM upon solidification and possible separation at the PCM/tube interface could create a serious increase in thermal resistance which would retard the heat removal.

HOF thermal storage systems have been under investigation for application in solar heating of buildings for some time.[5.64-5.66] Most of this work has dealt with materials problems and economic considerations and has included very little thermal analysis. The nature of this particular application does not warrant the use of high technology concepts in the storage system designs, thus, the systems investigated have utilized simple configurations such as drums filled with PCM around which air flows,[5.65] or trays of PCM separated by channels through which a heat transfer fluid flows.[5.64]

A low-temperature application of HOF thermal storage has been proposed by Dudley[5.67] in which the storage system is used in an air conditioning system in such a way as to distribute the cooling load over a 24 hour period. Thus, in this application the "charging" of storage involves the removal of heat or the freezing of the PCM. Nevertheless, the technological problems of this system are nearly the same as any other HOF storage system. In this study the storage system is configured as layers of PCM separated by thin sheets of aluminum with fluid passages distributed over their surfaces. An analysis of the heat transfer, carried out to facilitate the design of the system, illustrated that the use of simple, approximate heat transfer models could be justified if the assumption of uniform, constant properties could be made. The effects of density changes and convection were not investigated.

5.2.2 Active Heat Exchange

The use of active heat exchange processes is intended to reduce the heat transfer areas required to meet heat removal specifications placed on the storage systems. In 1957, Etherington[5.68] designed, built, and tested a storage system based upon an active heat exchange process. The process consisted of allowing a heat transfer oil to flow through, in direct contact with, a molten salt PCM. The results obtained from this system were promising in that good heat transfer rates were obtained and the agitation created by the flowing oil seemed to prevent the sub-cooling of the PCM and the formation of an undesirable crystal structure. The investigation uses simple heat balances in its analysis, but there is no attempt at the identification of the actual heat transfer mechanism occurring between the oil and the freezing salt or complex fluid mechanical phenomena which are taking place. A similar concept was patented recently by Bundy[5.69] for the purpose of "off-peak" energy storage in nuclear reactor electric power plants. In this system, the heat is removed from the molten PCM by flowing a liquid metal (again in direct contact) through the PCM. As a cool globule of the liquid metal flows through the PCM, heat is transferred to the metal by the PCM freezing on the surface of the globule. The heated metal will expand, cracking and sloughing-off the solid PCM crust; the heated liquid metal is collected at the bottom of the storage vessel and pumped to a heat exchanger. Again, only simple heat balances have been performed to estimate the performance characteristics of the system, and no comprehensive heat transfer modeling has been performed in order to evaluate the sensitivity of the system to various parameters.

An active heat exchange process proposed by Van Vechten[5.70] uses a germanium sulfide compound as the PCM, since its density increases upon melting, and its melt has a positive coefficient of thermal expansion. With these properties, and the provision that the solid material will flake away from the surface of a heat exchanger onto which it has been frozen, a thermal storage system can be designed with the heat exchangers at the bottom of the tank. Thus, during heat removal from the system, the solid PCM will separate from the heat exchanger and float to the surface of the liquid PCM. To date this system has only been conceptualized and some rough economic predictions made. However, the engineering design of this system does not appear to pose any serious technical problems (other than material related problems).

The most recent concept of a HOF storage system using an active heat exchanger comes from the Honeywell Corporation proposal for the Solar Thermal Central Receiver Program.[5.71] This concept uses a eutectic salt mixture contained in a storage tank. The system is charged through a finned heat exchanger at the bottom of the tank and discharged through pipes at the top of the tank around which the solid PCM forms. A mechanical scraping mechanism removes the solid periodically to reduce the thermal resistance of the solid PCM; the solid phase material, being more dense than the liquid, sinks to the bottom of the tank. Preliminary estimates of heat transfer rates were made using a simplified analysis. The design and analysis of this system have not yet been carried to a point where serious technological problems (other than those that are material related) can be said to exist.

The technical literature contains considerable information on the modeling of the heat transfer in melting and freezing processes. Much of the work is related to one-dimensional problems involving the passive type heat exchangers. Only one[5.59] of the papers reviewed considered the density changes which occur during freezing or melting (this effect can be as great as 20% and, thus, could be quite important to the heat transfer process). The studies reviewed below by no means exhaust the work available in the literature; the intent here is to illustrate the kind of modeling studies available in the literature which are directly applicable to HOF storage systems.

In 1959, Murray and Landis[5.72] published a study of methods of solution of the transient heat conduction in materials undergoing melting and freezing. Their methods involve both numerical and analog machine calculations and are represented as being quite accurate. The paper also includes a survey of previous similar work. Altman et al.[5.73] describes an analysis specifically applied to a spacecraft solar energy storage system. They use an energy integral method whose ultimate solution rests on the finite difference numerical solution of a differential equation; included also is the standard numerical solution to the partial differential equation of heat conduction. Good agreement between the two methods was found. Matveev[5.74] presents a simple approximate solution for the problem of a thermal storage system being operated with a "stratified heat transfer zone" which moves down the heat exchanger (i.e., the "non-mixed" operation). A similar problem was solved by Yang and Lee[5.3] who obtained a more refined solution using numerical techniques. They determined the storage system response to both step and periodic input functions; the sensitivity of the frequency response and phase shift to physical parameters was investigated. Griggs et al.[5.75] present a numerical two-dimensional transient solution for the passive heat exchange in a HOF energy storage system while Saito and Shimomura[5.76] present a similar one-dimensional solution along with some experimental data.

Summarizing, the technology of HOF thermal storage systems appears, for the most part, to be adequate for the design of simple systems. The term "simple systems" is intended to indicate systems using the passive-type heat exchangers (the above statement does not include materials-related technology). There are, however, some areas which deserve additional investigation. These areas include:

1. The effects of large density changes during melting and solidification of PCM.

2. The interface thermal resistance between solid or liquid PCM and heat exchanger surfaces.

3. The effects of natural convection upon the process of melting the PCM.

4. The ability of the available heat transfer models to predict the performance of large scale systems.

More complex HOF storage systems such as those using active heat exchange processes and/or direct contact heat exchange are at a lower stage of technological development. Among the primary needs are new ideas and concepts for accomplishing these processes in an efficient and economical manner. In addition to the ideas, the development of supporting analytical and experimental work is necessary.

5.3 Heat-of-Reaction Thermal Storage

Storing energy in the form of the heat of reaction of a material which undergoes a reversible chemical reaction is a concept which deserves consideration for application in advanced thermal storage systems. This class of thermal storage systems has the potential capability of storing as much as an order-of-magnitude more energy per unit mass or volume than either sensible heat or heat-of-fusion systems, offering the advantage of a compact storage system. In addition, the energy is released from storage nearly isothermally, thus maintaining the availability of the energy stored. On the other hand, in addition to the heat transfer process, most systems will also be undergoing a mass transport process caused by the reaction, thereby increasing the level of complexity of the operation of the system.

Typically, these systems use a storage medium which, upon the addition of thermal energy, reacts reversibly to form one or more substances which can be separately stored. To recover the energy, the reaction is made to proceed in the opposite direction. Currently under consideration are systems using the processes of hydriding of metals, ammoniating of certain salts, and hydration of particular chemical compounds. The application of the use of heat of reaction to thermal storage has not yet passed the very early conceptual stage, although metal hydride systems have been designed, tested, and evaluated for the purpose of hydrogen storage,[5.77] and much of this work can be directly applied to thermal storage systems.

The development of a heat-of-reaction thermal storage system will very likely require some advancement in the state-of-the-art in several technological areas. One of the most significant technological problems will be related to the materials used in the system and their thermophysical properties. A discussion of this area was presented in Section 4. The other important problem area will be associated with the transfer of heat to and from the storage medium, as well as the related mass transfer problems internal to the system.

As mentioned previously, metal hydrides have been proposed as a means for storing hydrogen in applications where the hydrogen is being used as a fuel. Much of the chemical kinetics data and heat and mass transfer analyses developed for this problem can be applied directly to thermal energy storage systems. Powers and Cummings[5.78] present an analysis of the conduction of heat in a planar hydride bed. Arguing that the reaction rate is at least an order of magnitude higher than the heat transfer rate, the reaction zone can be considered quite narrow and the problem is reduced to a form quite similar to the heat-of-fusion problem discussed in Appendix A (i.e., heat conduction with a phase-change). Noticeably missing in this analysis is any mention of the convective or other effects of the hydrogen which is released (or absorbed) during the reaction. Yu, Suuberg, and Waide[5.79] present a similar analysis in which they also reduce the conduction bed problem to a state which is analogous to heat conduction with a phase-change. In addition, however, they describe an analysis of a convection bed wherein the heat is transferred from the hydrogen gas (which is flowing through the bed and participating in the reaction) by direct contact with the solid particles. The resulting mathematical formulation is similar to a packed bed model with the addition of heat source or sink terms. The work accomplished by these investigators provides a solid framework from which the analyses of heat-of-reaction thermal storage systems can be initiated.

A limited amount of work has been carried out in the application of the heat-of-reaction concept to thermal energy storage. Libowitz[5.80] describes a metal hydride thermal storage subsystem for a solar heating application in which the gaseous hydrogen driven off during charging is stored in a tank. The basic conceptualization of the system is presented and some simple thermodynamic arguments are applied to the hydriding and dehydriding reactions. No effort is expended toward defining the problems of heat transfer to and from the reacting hydride bed. Ervin[5.81] has proposed a system to store thermal energy using the heat of hydration of certain inorganic oxides, such MgO and CaO, which form hydroxides as a result of hydration. These reactions occur at relatively high temperatures (375 and 520°C) and were proposed for use with concentrating solar collectors. A number of experiments have been performed to observe the chemical behavior of the material and some data on rates of hydrating and dehydrating are presented. The application of this storage system to a solar energy system is proposed using a fluidized bed heat exchanger, although no estimates of performance are made. A simple model of the heat transfer and chemical reaction response of a spherical particle is presented.

It seems that even though the concepts proposed for heat-of-reaction thermal storage are technologically advanced relative to most sensible or phase-change systems, little effort has gone into attempts to understand the transport processes which are necessary in the operation of the system. This area will have to be dealt with so that performance predictions, cost estimates, and engineering design calculations can be performed. Specifically, it will be necessary to develop analytical models describing the transport of heat and mass in these chemically reacting systems. These models can then be used to predict performance, evaluate convective effects and optimize such variables as particle size and distribution or packing density. Finally, special attention will have to be given to the problems involved with the control of these storage systems as well as the monitoring of their operation. This aspect of system design and development has been noticeably neglected and may turn out to require the application of advanced technological concepts.

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SECTION 6. SOLAR CENTRAL RECEIVER SYSTEMS ANALYSIS

The three previous sections have dealt specifically with storage subsystems without regard to particular applications. The purpose of this section is to present the results of a systems analysis which illustrate some of the factors which must be considered when incorporating storage into an energy conversion system.

Before presenting specific results, some general comments regarding the impact of storage on the total system may be made. Incorporating storage into a solar system in general adds a series of indirect costs to the system in addition to the obvious direct storage costs (storage material, heat exchangers, piping, siting, etc.). The indirect costs include the expenses associated with the additional collectors required to charge the storage, increased thermal power handling capability (receiver, pumps, piping, tower size, etc.), power cycle compromises, parasitic losses, and additional overhead and maintenance. Associated with these additional costs, of course, are certain benefits. These benefits may include a reduction in the size of the electrical equipment, increased capacity displacement, continuity of operation, and increased market penetration. The purpose of a systems analysis is to maximize these benefits while minimizing their cost.

The system considered for illustrative purposes, shown pictorially in Figure 6.1 and schematically in Figure 6.2, is very similar to that discussed in Reference 6.1. It is a supercritical, high efficiency, 250-MWe (minimum) steam power plant with a central receiver energy collection system and a sensible heat storage system. The solar collection system is a series of 200- to 300-meter towers each surrounded by a field of uniformly spaced heliostats subtending a 10° to 60° angle annular area centered at the tower bases.

Solar energy is collected in the central receiver at a temperature of approximately 510°C. A heat transfer fluid called HITEC (discussed in Sections 3 and 4) is heated in the solar receiver, piped to ground level, and used to produce steam in an unfired boiler. The net thermodynamic efficiency of the system when operating in the solar mode is about 43%. When operating from the auxiliary fossil-fired HITEC heater, the efficiency is reduced to about 36% because of stack losses.

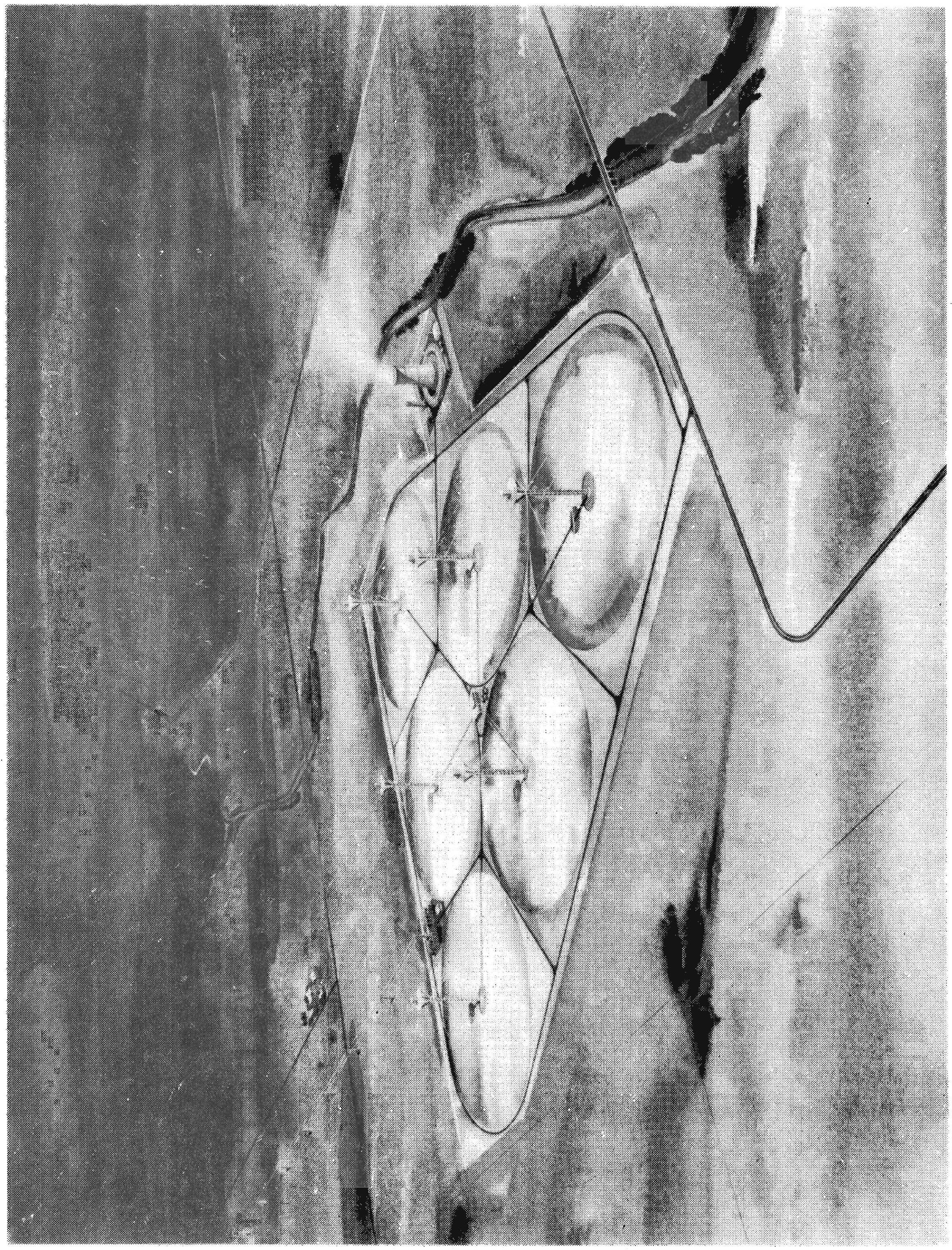

Figure 6.1 Solar Electric Power Plant

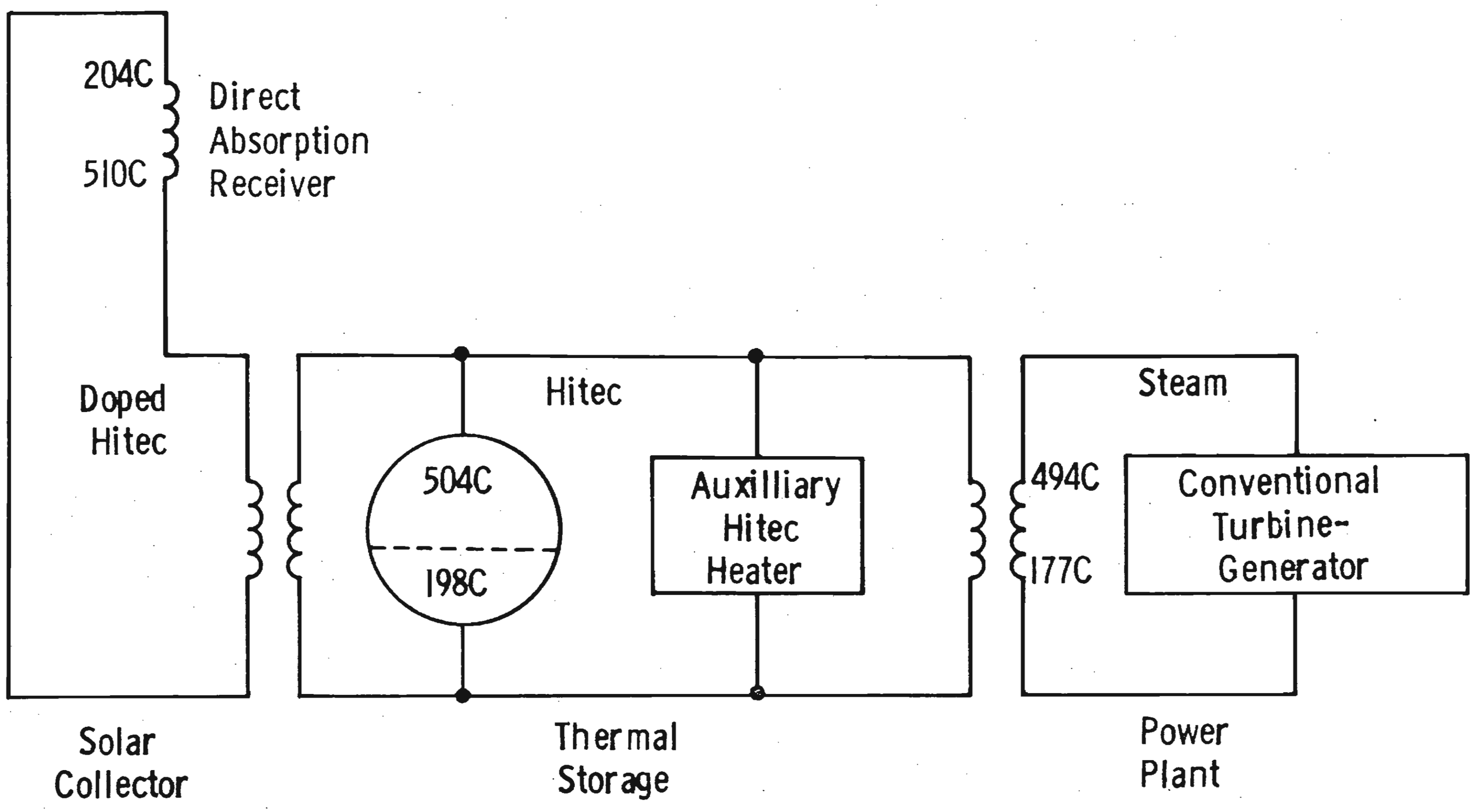

Figure 6.2 Schematic of Solar Electric Power Plant

The solar insolation used in the analysis was derived from the Aerospace tape, Reference 6.2, for Albuquerque, New Mexico. This solar data was used in an SLL Solar Input Computer Model (DAZZLE--Reference 6.3) to calculate mirror field and receiver performance. The model accounts for mirror field reflective shadowing and blocking losses and receiver reflective and radiative losses. Tower height and mirror field density are variables in the optimization process. Thermal energy available to the power plant is calculated on an hourly basis.

6.1 Storage Analysis Methodology

The storage analysis examined the trade-offs between storage capacity, tower height, mirror area and density, auxiliary HITEC heater capacity, and fuel consumption in terms of meeting the demand criteria. The storage process computer model (STOR), written for this storage study, takes the hourly solar insolation data from a DAZZLE run and produces total annual electrical energy, annual fossil fuel use, and power plant capacity displacement information. The function of the STOR program is to determine the combination of direct solar energy, storage thermal energy, and fossil fuel energy which best meets a given demand profile, under various conditions. Cost and performance functions are utilized for the principal subsystems. Two demand profiles were defined for this study. The base load demand was assumed to be 24 hours a day for January through November, with the month of December used for scheduled maintenance on the power plant. The intermediate load demand was assumed to be from 7 a.m. to 11 p.m. for Monday through Friday and 5 p.m. to 11 p.m. on Saturday and Sunday. Excess collected energy was assumed to be sold when not necessary to meet the intermediate demands if the turbine was available. Storage was assumed to be full on January 1, 1962, and the first day of the year was assumed to be Monday for all computer runs. The assumption of starting the year with full storage is based on the solar collection system being operational during the last part of the month of December when the turbogenerator was assumed to be shut down for maintenance.

This storage analysis evaluated the ability of both pure solar plants and hybrid solar plants to meet the base load and intermediate load demand profiles. (A hybrid solar plant is a plant that has both solar and some fossil fuel backup capabilities for running the same turbine.)

6.2 Analysis Results

6.2.1 Pure Solar Plants with Base Load Demand

The interrelationship between storage capacity and collection area is illustrated in Figure 6.3 for a pure solar plant that is attempting to meet the base load demand. As shown, "energy displacement" is plotted as a function of the "solar multiple" for various amounts of storage. The energy displacement term is defined as the percentage of fossil-fuel energy displaced by the solar plant compared to an equivalent fossil-fueled plant. The solar multiple is the ratio of the maximum solar energy available from the mirror field in any hour during the year to the amount of solar power required to run the electrical power plant directly at full output. For example, a base load plant with a solar multiple of 1 would be able to run at full power only 1 hour per year, and would never have any excess energy available for storage. Similarly, a plant with a solar multiple of 3 would be able to run at rated capacity and provide energy at twice the rated capacity to a storage system during 1 hour per year; at other times during the year, the plant could still run at rated capacity, but less energy would be available for storage. The solar multiple for a system is thus a measure of the amount of solar energy that can be collected and is directly related to the size of the collection area.

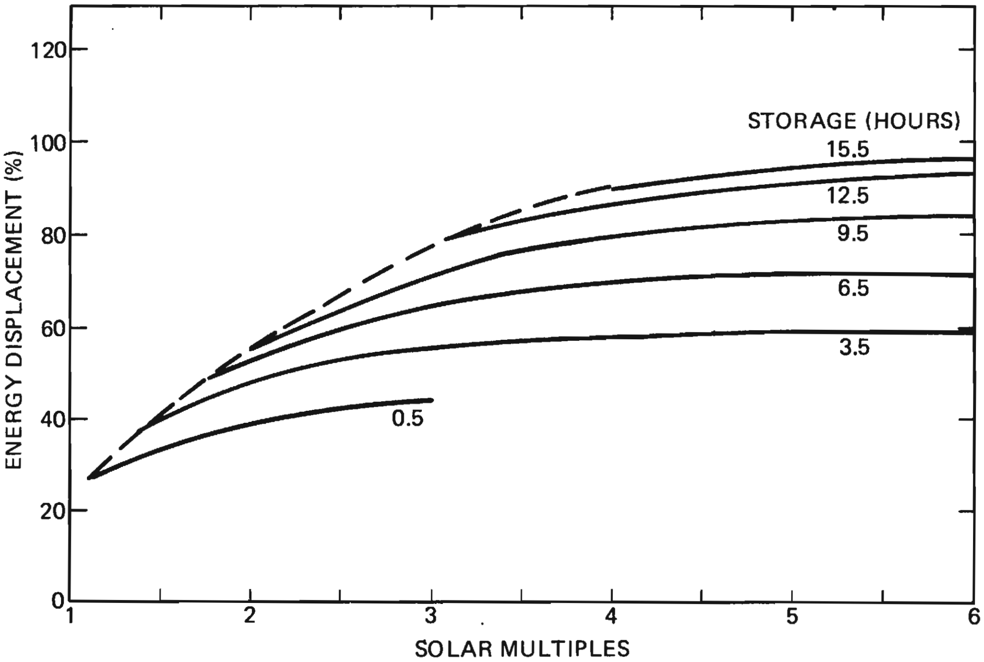

Figure 6.3 Solar Base Load Energy Displacement

Capacity displacement and energy displacement are essentially equal for pure solar plants with a base load demand and will be treated interchangeably. Figure 6.3 presents energy displacement curves for various amounts of storage. This figure illustrates the interrelationship between storage capacity and collection area. Notice that the curves terminate at the dashed line to the left. A design that is on this line never fills storage completely. For example, a 12.5 hour storage design with a solar multiple of 2 displaces no more energy than a system with only 9.5 hours of storage. Thus, for a given solar multiple, there is a maximum amount of storage which can be effectively utilized.

Figure 6.4 shows the effect of incorporating very large amounts of storage in the system. It illustrates the very important fact that considerably more storage is required to achieve the same effect as increasing the mirror field size (solar multiple). For example, note that the same displacement can be obtained to compensate for seasonal variations by increasing storage by a factor of 15 from 48 hours to 30 days (720 hours) or by increasing the mirror field by a factor of 1.4 from 3.75 to 5.25. These results indicate that storage would have to be very inexpensive compared to mirror area before seasonal storage would be economic. This might not be true, however, in non-Southwestern location where the weather gets much worse in the winter (colder or less sunny, or both).

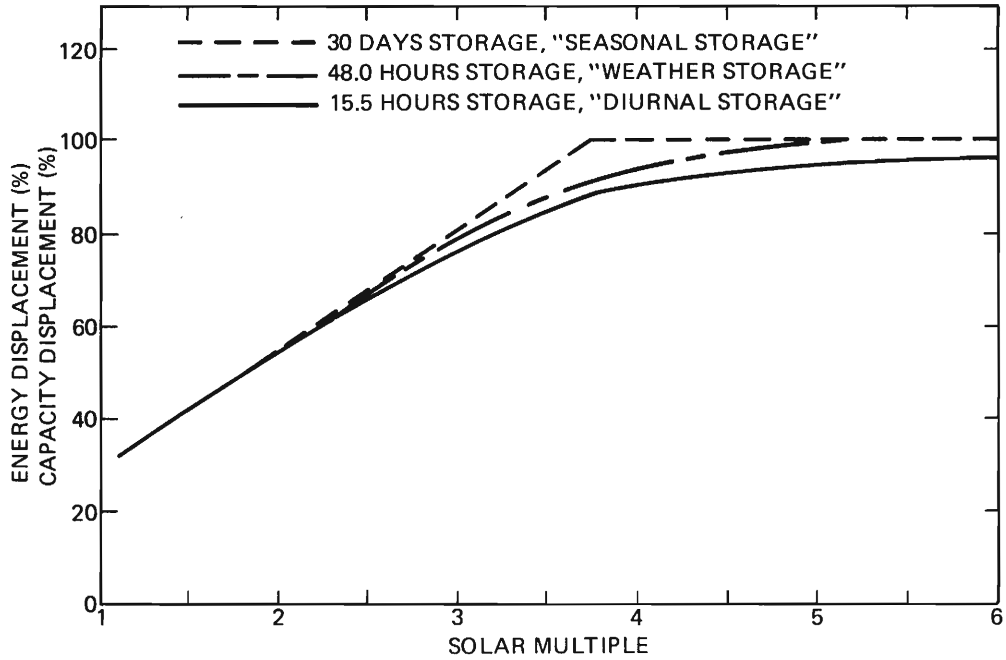

Figure 6.4 Effect of Large Amounts of Storage

The economics of storage are illustrated in Figure 6.5 which plots busbar energy cost (mills/kW_e-hr) versus energy displacement for various amounts of storage. The storage is estimated to cost \$3.86/kW_t-hr (at 1974 prices), and the busbar energy cost is computed assuming a 15 percent levelized annual fixed charge. Costs* for a pure fossil fuel plant are also indicated. Note that a minimum in busbar energy costs exists for each storage capacity. There is a physical explanation for this minimum. Each point on a given curve represents a different plant design. Subject to the constraints imposed, the model selects the combination of design parameters and subsystem sizing which minimizes the initial investment per unit of fossil energy displaced. Designs to the left of the minimum on a given curve have more storage than can be utilized with the collection area available; designs to the right of the minimum achieve higher energy displacement by adding more collection area. Thus, for a given energy displacement, there is an optimum amount of storage (and collection area) which is defined by the locus of minima. With the estimated storage cost, this locus of points is essentially constant for up to 12.5 hours of storage, after which an increase in busbar energy cost is indicated.

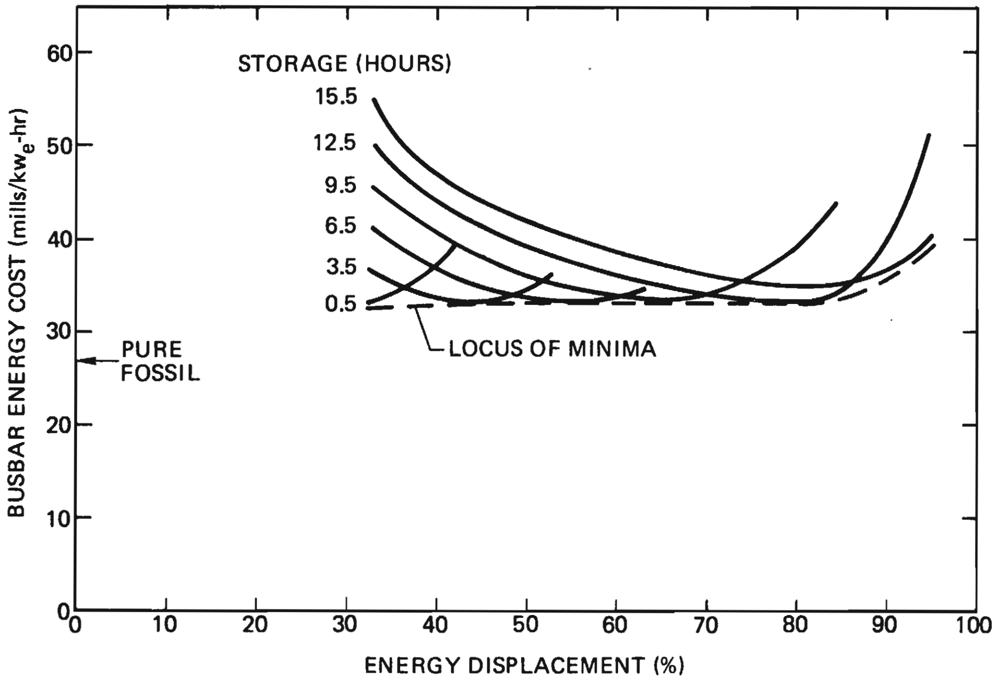

Figure 6.5 Base Load Busbar Energy Costs for Pure Solar Plant

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*The cost of busbar energy is determined as 15% of the initial capital cost of the plant plus the annual cost of fossil fuel burned divided by the annual amount of electrical energy produced.

In comparing pure solar and hybrid plants, busbar energy cost is not necessarily the best criterion for optimization because for hybrid plants it can be highly dependent upon predicted fuel costs. Given that a plant is to be built, a better criterion, and one which removes the dependence on fuel costs, is to minimize the investment required to displace a given amount of fossil fuel each year. Figure 6.6 shows the relationship between initial investment and energy displacement for three different storage costs. This figure illustrates two points. First, the optimum amount of storage, defined as that which yields the minimum initial investment cost of the total system is quite sensitive to the cost of storage, since progressing to the right on one of these curves reflects increasing amounts of storage (the optimum storage capacities are 15.5, 12.5, and 0.5 hours for storage costs of \$1.93, \$3.86, and \$7.72/kW_t-he, respectively). Second, for a plant with a given energy displacement, a factor of four increase in storage cost can result in up to a factor of two increase in the initial investment cost. This again demonstrates the advantage of (or requirement for) inexpensive storage.

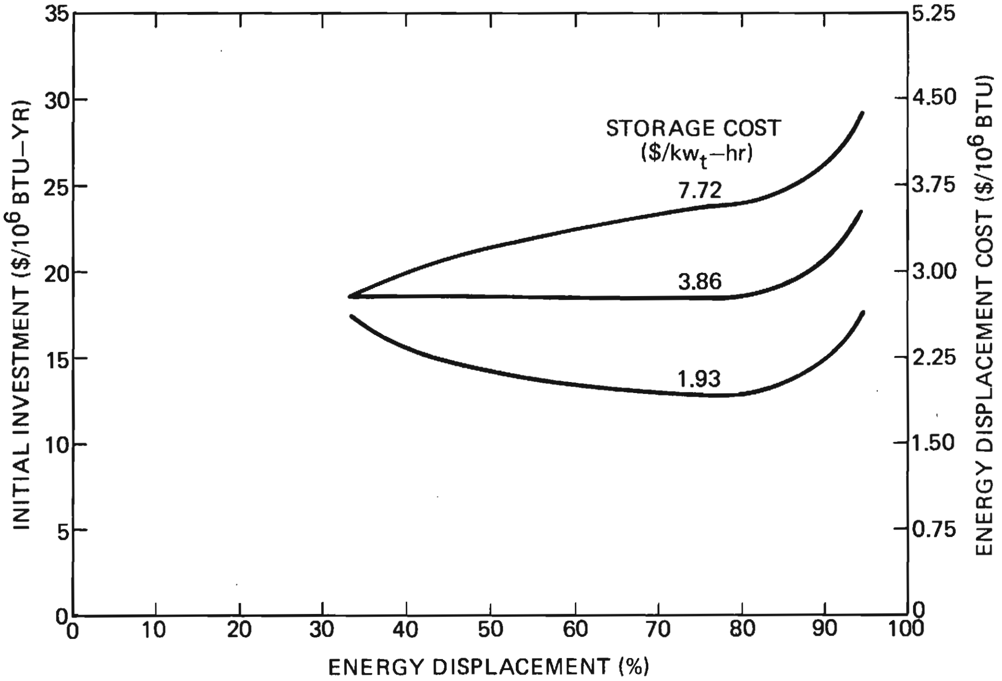

Figure 6.6 Locus of Optimum Designs for Various Storage Costs for Base Load Solar Plant

The design for the present solar plant included a heat exchanger to put energy into storage. This exchanger would not be necessary if the collection fluid could be stored directly. The baseline design used a heat exchanger with a cost of \$7.56/kW_t. Doubling this cost resulted in only a five percent increase in total system capital cost.

6.2.2 Hybrid Solar Plants with Base Load Demand

A hybrid solar-fossil plant has a "capacity displacement" close to 100% (that is, the hybrid plant would be equivalent to a fossil-fueled power plant in terms of satisfying the demand load) at a cost somewhat higher than a pure solar plant. For this analysis, a fossil burning capability of 100% was assumed to be equivalent to 100% capacity displacement, although it probably would have higher availability than its fossil counterpart because of the dual energy source.

Figure 6.7 presents the base load hybrid plant busbar energy costs (mills/kW_e-hr) versus energy displacement for various amounts of storage. Storage is assumed to cost \$3.86 kW_t-hr, and fossil fuel is assumed to cost \$2.00/10^6 BTU. Also indicated on this figure is the locus of optimum designs for a pure solar plant. For modest energy displacements (30-70 percent), the hybrid plant busbar energy cost is lower than that for a pure solar plant. For energy displacements greater than 70 percent, the costs are comparable. These conclusions are highly dependent upon the fossil fuel cost, however, as is indicated in Figure 6.8. At fuel costs of \$3.00/10^6 BTU, the pure solar plant is always less expensive.

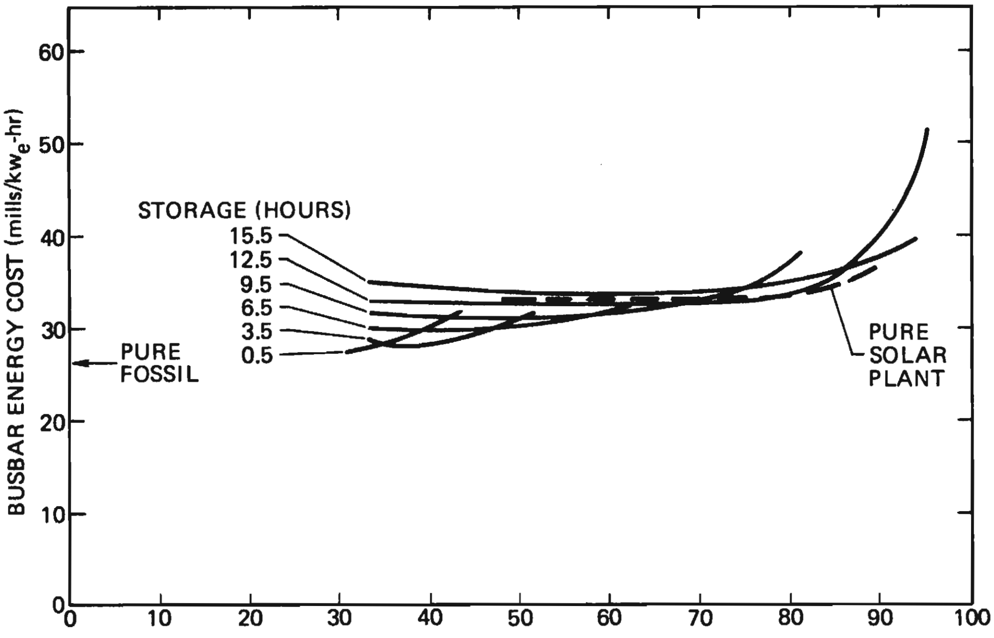

Figure 6.7 Base Load Busbar Energy Cost for Hybrid Solar Plant

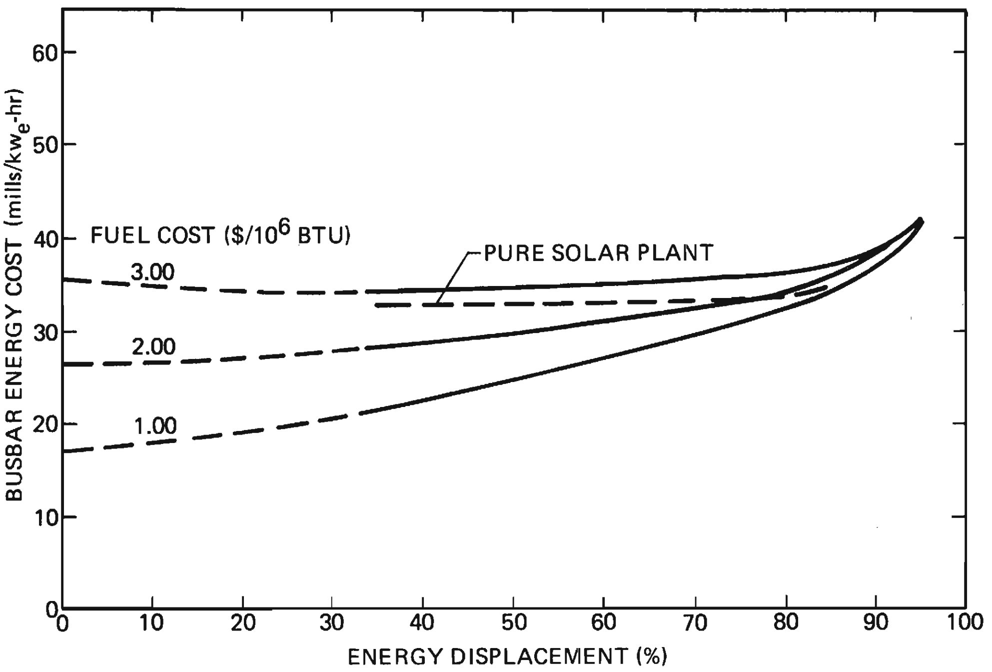

Figure 6.8 Effect of Fuel Cost on Busbar Energy Cost for Hybrid Solar Plant

As mentioned earlier, the effects of fuel cost may be eliminated by considering only the capital investment of the power plant. These results are presented in Figure 6.9, along with the capital investment required for a pure solar plant. As may be seen, the hybrid base load plant with 100% backup always cost more than a pure solar plant, except for very low energy displacement. It should be noted, however, that the hybrid plant has a 100% capacity displacement, whereas the pure solar plant has a capacity displacement approximately equal to its energy displacement.

The results presented thus far have been for a hybrid plant with a 100% fossil fuel backup capability (burner capacity equivalent to turbine power rating). Figures 6.10 and 6.11 illustrate the reduction in burner size possible for various amounts of storage. In these figures, the capacity displacement is plotted versus the solar multiple (collector area) with burner size as a parameter. The capacity displacement is the percentage of an equivalent fossil fueled power plant that would be displaced by the hybrid solar plant; it is assumed to be equal to the ratio of the percentages of the demand window filled by each plant. Note that for 3.5 hours of storage (Figure 6.10), 100% capacity displacement may be obtained with an 80% burner. For larger amounts of storage (Figure 6.11), considerably smaller burners may be utilized.

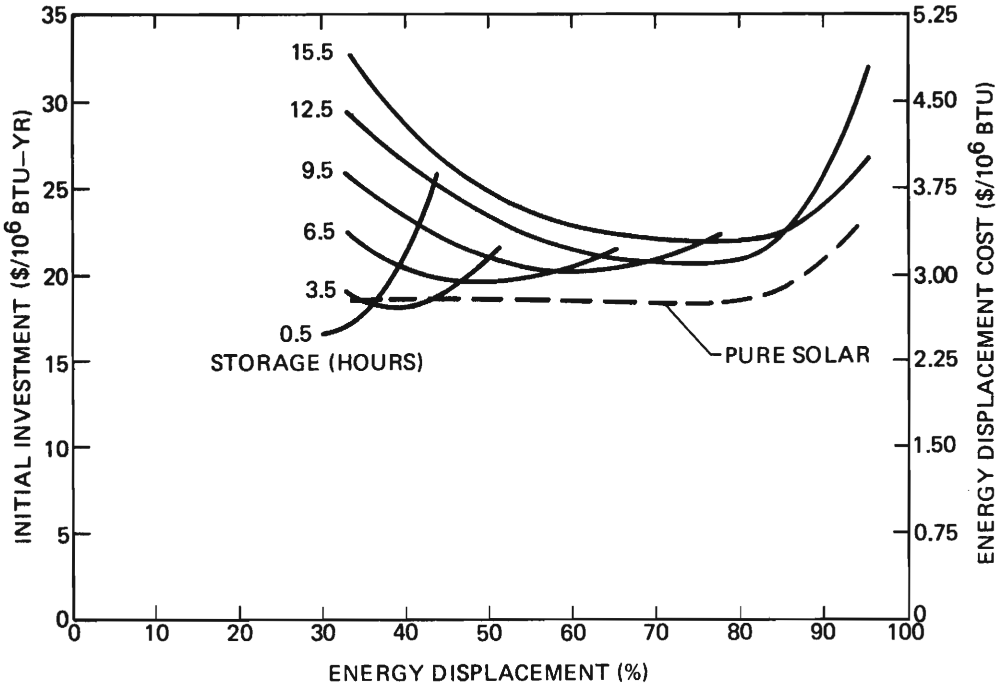

Figure 6.9 Initial Investment and Energy Displacement Costs for Hybrid Base Load Plant

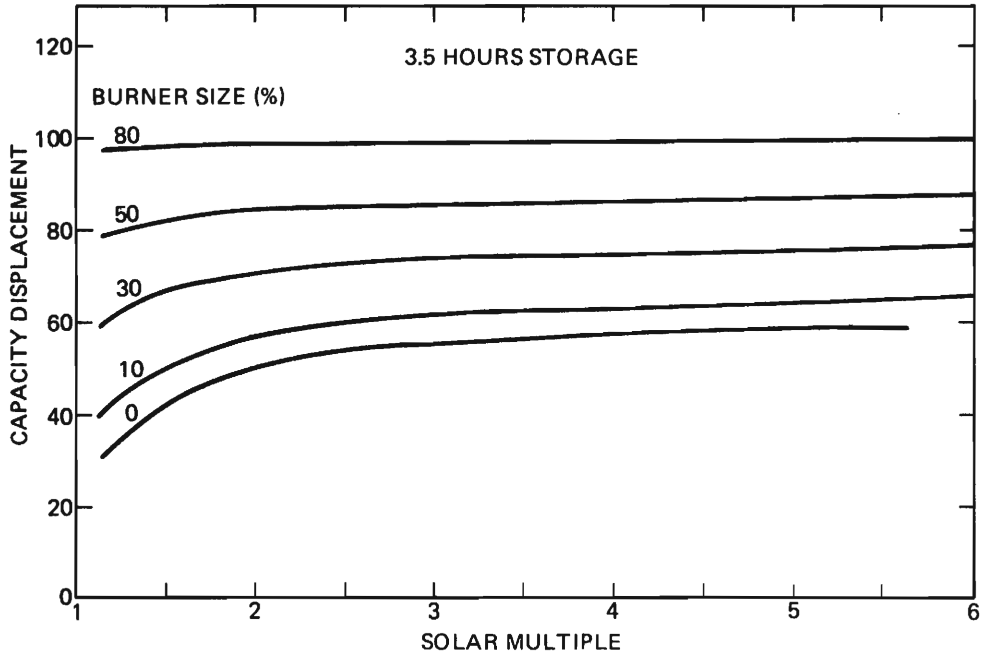

Figure 6.10 Hybrid Base Load Capacity Displacement for 3.5 Hours of Storage

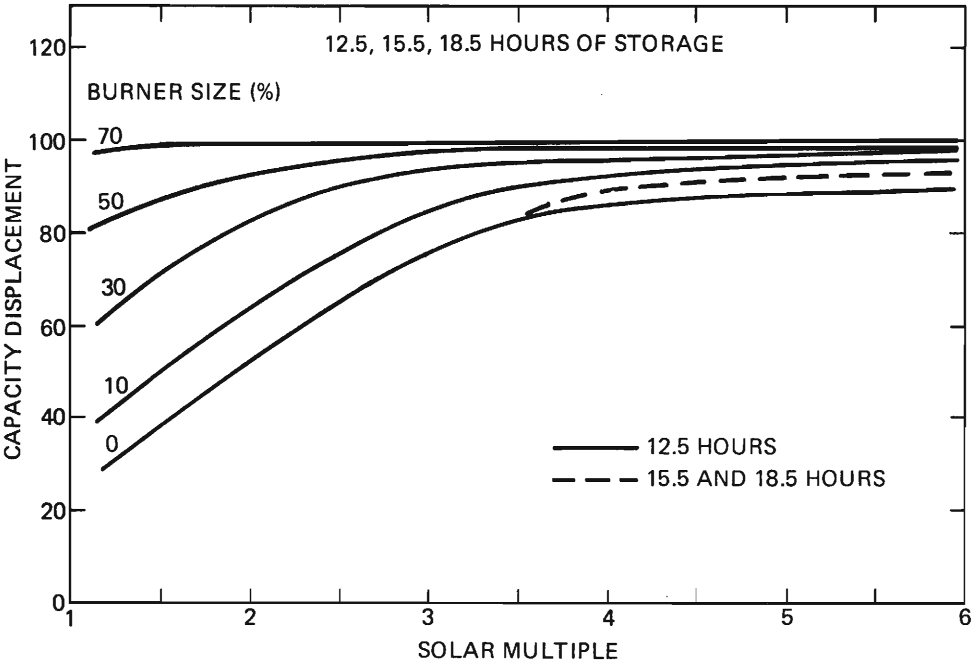

Figure 6.11 Hybrid Base Load Capacity Displacement for 12.5, 15.5, and 18.5 Hours of Storage

Figure 6.12 presents the initial investment costs for base load plants with various burner sizes. Also indicated is the pure solar plant (capacity displacement ≈ energy displacement). This figure illustrates three points. First, by decreasing the burner size, the same performance (capacity and energy displacement) may be obtained at a lower capital cost (c.f. Figure 6.9). Second, more storage than about 15.5 hours is not warranted. Third, for the same initial investment, 100% capacity displacement can be achieved with a hybrid plant, while the pure solar plant has a capacity displacement equal to its energy displacement.

6.2.3 Pure Solar Plants with Intermediate Load Demand

The intermediate load more closely matches actual insolation than does the base load so that the capacity displacement is higher than the energy displacement for the same design. This allows smaller storage capacity to achieve close to 100% capacity displacement.

Figure 6.13 is a plot of the output of the STOR program showing the capacity displacement for various solar multiples. Comparing this plot with Figure 6.3, there is no corresponding upper bound (dashed line) for intermediate load plants, where more storage ceases to gain more capacity displacement with the same solar multiple. However, storage in excess of 9.5 hours was not examined extensively since with more than about 9.5 hours storage there is little distinction between a base load plant and an intermediate load plant.

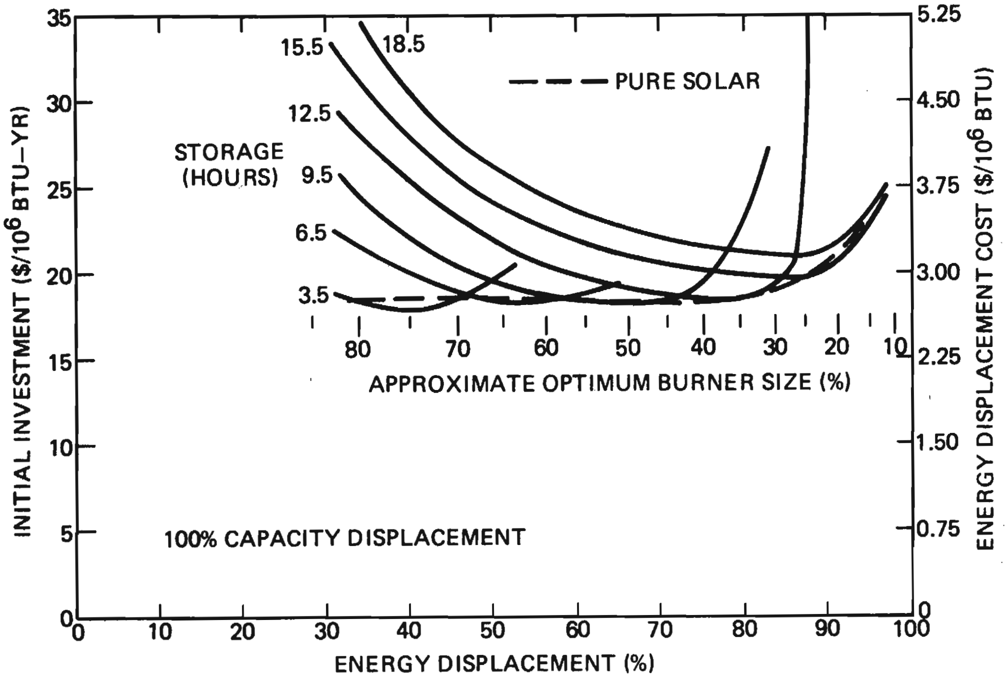

Figure 6.12 Initial Investment and Energy Displacement Costs for Hybrid Base Load Plant With Variable Burner Size

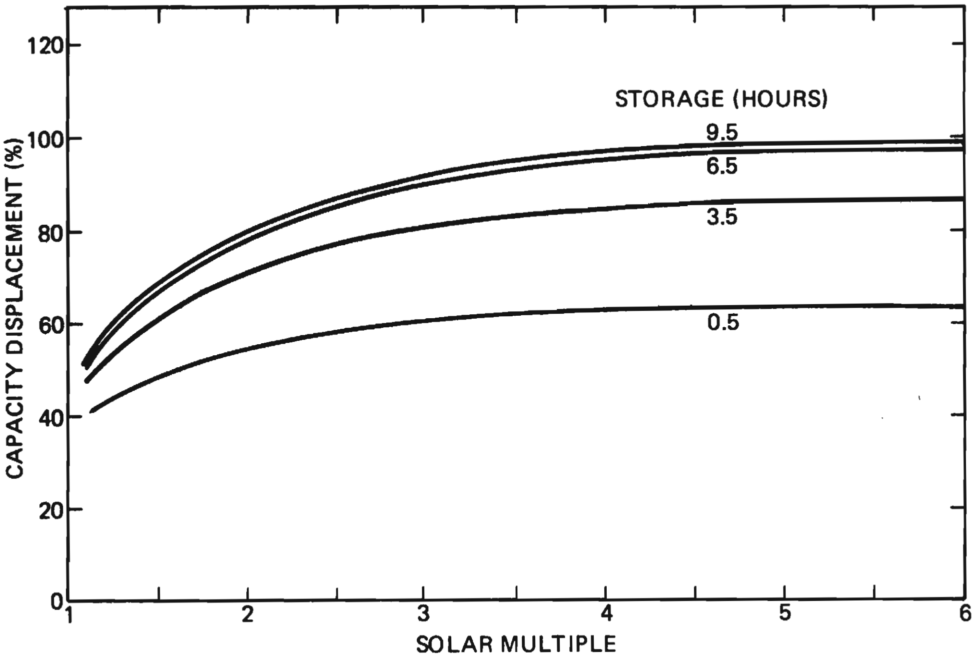

Figure 6.13 Intermediate Load Capacity Displacement

Figure 6.14 is a plot of the busbar energy cost for an intermediate load plant. The energy displacement of a plant exactly meeting an intermediate load would be 55%. Notice that the energy displacement is higher than 55% because excess electrical energy generated outside the demand window was assumed not to contribute to the capacity displacement. Figure 6.15 is a plot of the initial investment for intermediate load plants. The optimum designs for intermediate plants displace significantly less fossil energy than optimum base load plants with the same amount of storage.

6.2.4 Intermediate Load Hybrid Plants

Intermediate load hybrid plants are assumed to have 100% capacity displacement with 100% backup burners. For these systems, only small amounts of storage are economical. Figure 6.16 is a plot of the initial investment cost for a hybrid intermediate plant. Comparing this plot with Figure 6.9, it is apparent that there is no significant economic advantage for a hybrid intermediate plant compared to a hybrid base load plant.

6.3 Summary

The results presented in this section have illustrated some of the factors to be considered when assessing the impact of a storage subsystem on the overall solar conversion system performance. The general conclusions are summarized below. First, for both pure solar and hybrid power plants there is a direct relationship between the amount of storage which can be utilized effectively and the collection area of the solar system; this storage capacity depends upon the electrical demand which the plant is attempting to meet. Second, the cost of storage can have a significant impact on the capital investment required to construct a solar electric power plant. Unless the storage is extremely inexpensive, capacity and energy displacement can be increased more effectively by increasing the collection area than by incorporating large amounts of storage. Third, for a hybrid solar-fossil fuel plant, the incorporation of storage into the system can reduce capital costs to a level comparable to those for a pure solar plant; such a reduction is possible through the use of smaller backup equipment.

These results are for a system utilizing a particular collection fluid (HITEC), storage system (sensible heat), and conversion cycle (steam Rankine) and the cost estimates which apply to these particular elements. For systems with significantly different performance and cost characteristics, the conclusions might be considerably different. While certain aspects will tend to be generally applicable, thermal storage implications will have to be considered within the framework of specific system characteristics.

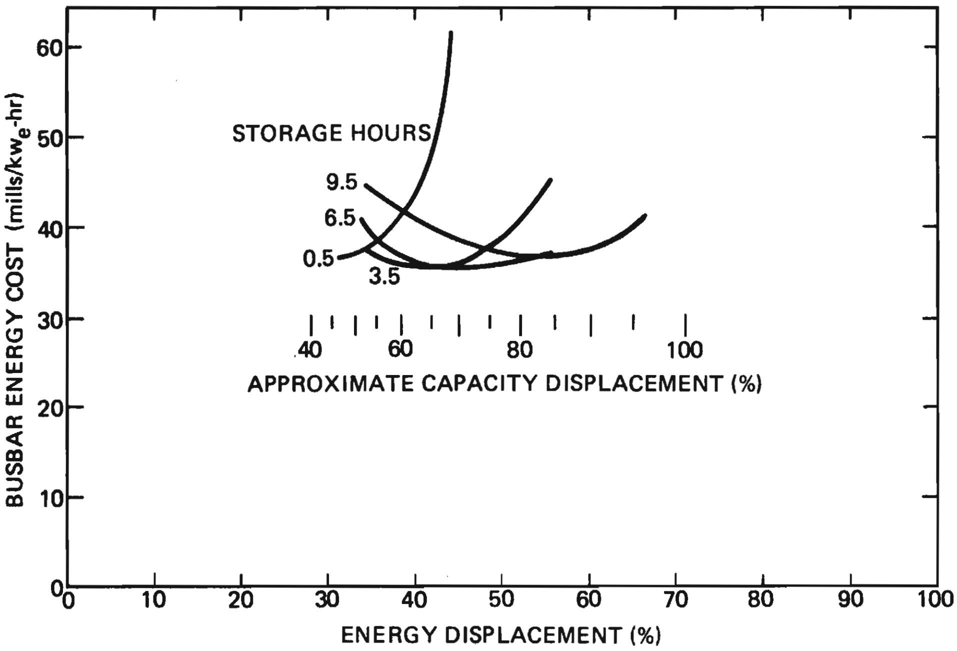

Figure 6.14 Intermediate Load Busbar Energy Cost for a Pure Solar Plant

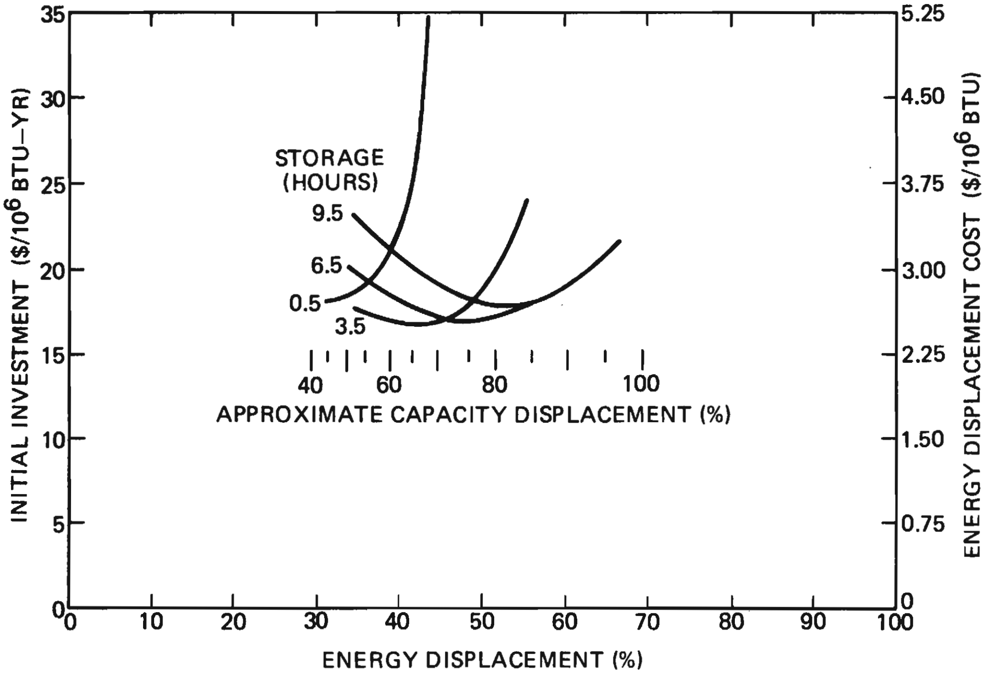

Figure 6.15 Initial Investment and Displacement Costs for Pure Solar Intermediate Load Plants

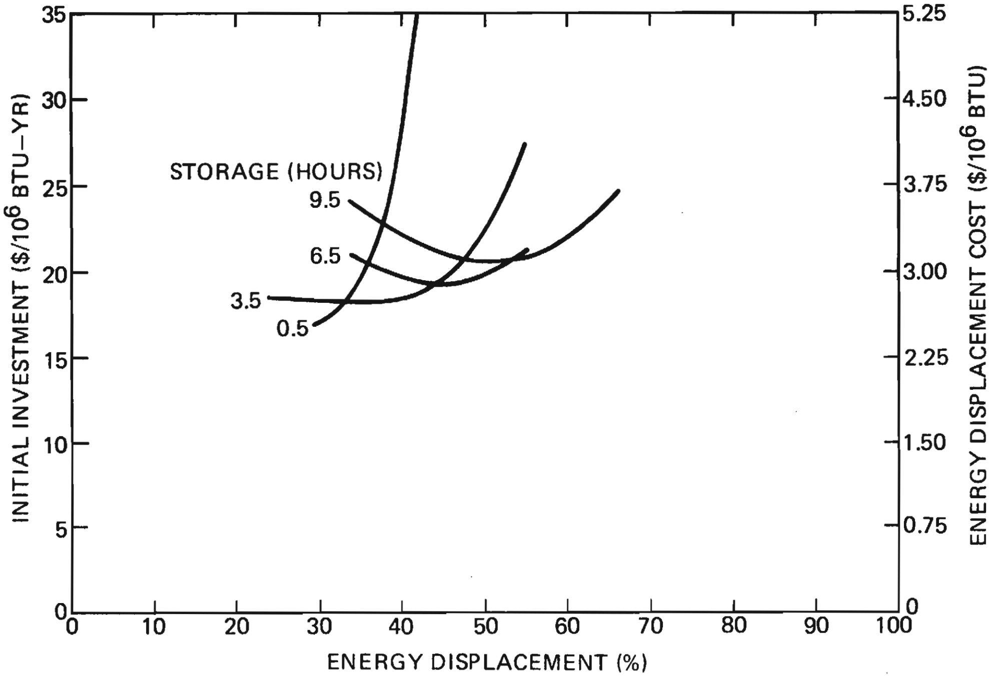

Figure 6.16 Initial Investment and Displacement Costs for Solar Intermediate Load Plant

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SECTION 7. CONCLUSIONS AND RECOMMENDATIONS

In this section the principal conclusions and recommendations of the study are summarized. Throughout the report the emphasis has been on identifying the technical problems associated with thermal energy storage at temperatures greater than 200°C. Specific recommendations concerning required research were made as each storage concept was discussed. In determining where future emphasis should be placed, one must consider the potential impact--in terms of energy conservation--that a given storage technique and application offer. In view of the large number of storage techniques and possible applications, such an assessment clearly is beyond the scope of the present study. Accordingly, two sets of conclusions and recommendations are given in this section. The first set is general in nature, and basically summarizes the findings of this study. The second set is more specific and attempts to identify those areas of research necessary to develope storage systems for use in solar electric power plants.

7.1 General Considerations

During the course of this study it has become clear that there is a general scarcity of the design-related information needed for the implementation of economical thermal energy storage. Specifically, there is a noticeable lack of experience in design, construction and operation of large (0.5 MW_t-hr or greater) thermal energy storage systems. In addition, much of the material property data needed in design calculations is not available, and there does not exist a very good understanding of the various material stability and compatibility problems.

The selection of a thermal storage concept for a specific application is going to depend on two primary criteria: whether the thermal characteristics of the storage system meet the requirements of the application, and whether the effective cost of utilization of the storage system is economically acceptable. In determining whether the first of these criteria is met, it will be necessary to predict the performance characteristics of the storage system. The analysis capability required is not, for the most part, very complex; many of the techniques which are required are readily available, but have not been brought together to form the needed prediction analysis. Note that the second criterion is the effective cost of utilization of storage, not simply storage cost. The implication here is that the cost of using storage depends not only upon how much it costs to build the storage subsystem, but also on the impact of storage upon the overall performance and cost of the total system. Thus in order to determine this "cost impact," it will be necessary to perform detailed systems analyses which consider the specific characteristics of energy supply, storage and conversion subsystems.

A final point concerning the choice of thermal storage system deals with the question of optimization. A storage system should be matched to the thermal characteristics of the supply and conversion systems in such a way that the availability loss from passing the energy through storage is minimized. In some systems sensible heat storage will be most appropriate, while in others latent heat or heat-of-reaction type storage will be better suited. This process of characteristic matching and availability-loss minimization also may result in the use of a combined-type or hybrid storage system. It is important that this system optimization consideration be made.

The specific recommendations relating to general system considerations include:

1. The difficulties encountered during this study in evaluating and making comparisons between the various storage systems have pointed out the need for a uniform procedure or common basis by which simple, generalized comparisons can be made between storage systems. Certainly this is not intended for engineering design purposes; it is mainly needed for preliminary system screening or design analysis to identify the best suited class of storage concepts.

2. The process of selecting a storage system for a specific application should begin with a system synthesis based strictly upon thermodynamic considerations in order to determine the optimum configuration (i.e., to minimize availability loss). In this way the advantages of various hybrid storage system configurations can be identified if they exist.

3. The final selection of a thermal storage system should be based on a detailed total system analysis which includes consideration of the performance characteristics of not only the storage subsystem but also the energy supply and conversion subsystems. Cost/benefit determination should be the primary emphasis of the analysis.

7.2 Sensible Heat Storage Systems

The concept of sensible heat storage represents the current state of thermal energy storage technology. This type of storage system can be designed and engineered using available technology and materials at a relatively low risk. Systems using water as the storage medium are limited in maximum temperature by the high vapor pressure with the costs of these systems being inflated by the need for high pressure containment. A significant decrease in storage cost is projected through the use of underground tanks or acquifers, although the latter is restricted to relatively low temperatures due to limited artesian pressure head. The vapor pressure problem can be alleviated by the use of heat transfer oils or molten salts. Although the reduction in containment cost is offset by higher material costs, these materials offer the possibility of higher temperature operation. If significant reductions in material costs can be realized, the oil or salt systems will become much more attractive. The use of a solid storage material has the advantages of high temperature operation, direct contact heat exchange and very low material costs. Hybrid systems consisting of a packed bed of solid particles through which a heat transfer oil or molten salt is flowing have been shown to reduce significantly the cost of an all-liquid system. The high temperature underground solid storage concept appears quite attractive, however reliable cost estimates are needed.

Specific recommendations relating to sensible heat storage systems include:

1. The physical phenomena affecting the formation and maintenance of a thermocline (i.e., thermal stratification of the hot and cold portions of a fluid) within a vessel containing a liquid thermal storage medium require more detailed understanding. Specifically, the effects of storage vessel geometric configuration, fluid input/output diffuser design, and container wall conduction have been shown to influence the system and thus require a detailed theoretical treatment along with comprehensive experimental verification.

2. The concept of an underground steam accumulator deserves investigation. Problems involving available overburden, heat losses, steam injection techniques and control must be evaluated.

3. The development of the concept utilizing an acquifer for the storage of moderate temperature thermal energy should be continued. Experimental verification of the current prediction techniques should be carried out and the techniques refined, if necessary. Ultimately a proof-of-concept experiment (or demonstration) should be performed.

4. The projected low cost of storing moderate to high temperature thermal energy in underground rock is a prime motivation for suggesting continued investigation. Initially, performance estimates and refined cost projections should be made and evaluated. These results can then be used as a basis for a decision to continue work on this concept.

5. Although a great deal of research has been carried out on packed bed solid particle/liquid heat transfer systems, there are a number of questions that should be addressed in order that designs of packed bed thermal storage systems can be optimized with respect to cost and performance. The effects of axial conduction, particle size and size distribution, fluid inlet distributor configuration and fluid channeling should be investigated both theoretically and experimentally and evaluated in terms of system performance.

6. The prospect of high heat transfer rates with small heat exchangers makes the application of a fluidized solid heat exchanger to a thermal storage system appear very attractive. Preliminary performance and cost estimates should be made to determine whether or not the advantage of a high heat transfer rate is offset by the increased pumping costs. Additional investigations should be guided by the results of this preliminary study.

7.3 Heat-of-Fusion Storage Systems

Thermal storage systems using the heat-of-fusion of the storage medium represent the next generation of storage technology. These systems offer the advantages of high temperature operation and high specific storage capacity, but may suffer from high costs of materials. Small heat-of-fusion systems using passive heat exchangers have been developed and can be constructed at costs comparable to an all-liquid sensible heat storage system. Direct cost comparisons between systems should be made carefully; the capability of higher temperature operation by one storage system relative to the other may result in overall system cost reductions which are not reflected in the storage cost. There is evidence that the use of active heat exchange processes in very large heat-of-fusion storage system can result in a reduction in size of the required heat exchanger surface; if the complexity of the active system is not offsetting, a reduction in storage costs may be realized. The continued development of heat-of-fusion storage system currently needs the identification of new, low cost, high temperature storage materials, the development of high flux active heat exchangers, and the design and construction of experimental storage systems for verification.

Specific recommendations relating to heat-of-fusion systems include:

1. "Active" heat exchanger concepts are needed in heat-of-fusion storage systems. The currently known concepts, as well as new ideas, should be evaluated through both performance and cost analysis along with small scale experimental verification.

2. Operational experience with large (1.0 MW-hr or greater) heat-of-fusion storage systems is needed. If possible, active heat exchangers should be used. The effects of cyclic operation should be evaluated along with the problems of system control.

3. Consideration should be given to advanced heat transfer techniques such as heat pipes.

7.4 Reversible Chemical Reaction Storage Systems

The storage of thermal energy as the heat of reaction of a reversible chemical reaction is a concept whose application is probably sometime into the future. The prospect of high specific storage capacity with isothermal, high temperature energy recovery and long-term storage at ambient conditions makes this storage concept very attractive. Thus far, cost estimates for these systems are based on material cost only. As the designs progress beyond the conceptual stage and specific containment and heat exchanger configurations are identified, improved cost estimates should be made in order to project more reliably the potential of this type of system. The future application of heat-of-reaction storage systems will depend upon the identification of reactions--involving inexpensive materials that are quantitatively conserved over many cycles--which occur at the proper temperatures, and the development of heat transfer processes which will efficiently operate in the presence of the reaction. System implications must be carefully evaluated. Two important considerations are (1) degradation of availability and (2) apportionment of energy stored versus energy which must be used in functioning the system.

Specific recommendations relating to heat-of-reaction systems include:

1. New concepts of heat-of-reaction thermal storage systems are needed. Conceptual designs should be made and preliminary performance and cost estimates carried out. Lab-scale experiments should be conducted for initial verification of concepts.

2. Advanced heat exchanger concepts (such as the use of heat pipes) for use in heat-of-reaction systems should be investigated in order to identify those capable of accommodating high heat fluxes at low cost. The promising concepts should be evaluated through both theoretical and experimental analysis which includes the various effects of the chemical reaction on the heat transfer process.

3. Proof-of-concept experiments are needed to ensure that all aspects of the concept have been adequately evaluated. Specifically, the critical area of system control requires special attention.

7.5 Storage Materials

To date, water has received a great deal of attention as a storage medium for sensible heat thermal energy storage systems because of its very low cost and its chemical and environmental neutrality. Water, however, is limited to temperatures below 300°C by vapor pressure restrictions. For somewhat higher temperatures heat transfer oils can be used as a storage material; however, these fluids can be quite expensive and will chemically break down if their high temperature limits are exceeded. The costs can be reduced somewhat if inert solid materials are employed in addition to the fluids as in a packed bed configuration. For higher temperature applications molten salts such as HITEC can be considered. The corrosion and stability characteristics of these materials must be evaluated, however.

For applications involving the combined sensible and heat-of-fusion of the storage materials, a number of inorganic salts appear attractive in terms of capacity and cost. Chemically, the fluoride salts have excellent thermal storage characteristics. Unfortunately, most fluoride systems melting at temperatures below 500°C contain Be or Li, and these salts can be quite expensive. At somewhat higher temperatures (up to 800°C) eutectics composed of the more common alkali and alkaline earth fluorides may be competitive with other classes of fused salts on the basis of storage capacity but are generally less attractive in terms of cost and materials compatibility. Considering the large available data base of characteristics of fluoride salt eutectics, it does not seem necessary that additional studies be conducted in search of new fluoride eutectics.

The thermophysical properties of many chloride systems nicely fit the requirements of thermal storage applications. In addition, they have a long-term chemical stability, moderately low corrosiveness toward structural materials at high temperatures, and are very inexpensive. Several chloride eutectics were identified in this study as being especially attractive, however, many large gaps exist in the thermophysical and chemical properties of these systems while some of the available information has never been experimentally verified. In order to utilize lower cost commercial grade materials, the effects of impurities on the system characteristics need to be evaluated. In addition, the compatibility of these salts with structural materials needs more extensive definition.

The hydroxides of sodium and potassium and their eutectic mixture possess favorable characteristics for thermal storage applications. These materials are moderately low in price and have a substantial storage capacity on both a weight and cost basis. Most studies of hydroxides for storage purposes have dealt with temperatures less than 500°C, and data should be obtained to extend the temperature range upward. The material compatibility and chemical stability of these systems at high temperatures may depend upon impurities present in the melt and the composition of the surrounding atmosphere and these questions must be adequately understood.

Carbonate and carbonate-containing systems appear especially attractive as storage media in view of their low cost and excellent materials compatibility characteristics. The thermophysical and transport properties of these systems need extensive characterization, as do the effects of impurities, blanketing atmosphere and passivity conferred to structural materials. The thermophysical properties of nitrates and nitrites are generally well known up to 500°C at which point the rate of decomposition generally becomes unacceptable. The use of these systems at the high end of their temperature range will depend upon the development of an adequate understanding of the various mechanisms of decomposition and the means to counteract or compensate for them. Salt eutectics containing, as major components, anions other than those discussed above appear less desirable for use in thermal storage systems due to unacceptably high melting points, chemical instability, material incompatibility, or cost limitations. In view of the large gaps in the data base pertaining to the more attractive material systems, work on the less desirable storage materials should be limited.

The extremely high storage capacities offered by heat-of-reaction storage systems is more than sufficient rationale for recommending materials-related research for this concept. New reactions should be identified for thermal storage applications which involve inexpensive and abundant materials. As in the case of sensible and heat-of-fusion systems, the transport properties and compatibility characteristics of the materials require definition, however in addition, the chemical characteristics (kinetic and equilibrium) are also needed.

Specific recommendations relative to thermal energy storage material include:

1. The investigation of the chemical interactions between heat transfer fluids and solid storage materials is needed. The variation in composition of the solid materials and the possible degradation of the fluids are the areas of prime concern.

2. Research studies are needed which deal with the problems of high temperature stability, material compatibility and corrosiveness characteristics of molten salt compounds.

3. Consideration should be given to the development of techniques for the in-situ monitoring of material condition, corrosion status and material depletion in thermal storage systems.

7.6 Thermal Energy Storage for Solar Electric Applications

A solar electric power generation system may require a thermal energy storage subsystem capable of from one-half hour storage for insolation transients to as much as fifteen hours for night-time operation. Currently, three different thermal storage system concepts are under consideration for the first generation of solar electric power systems. Two of these concepts utilize a form of sensible heat storage (fluids and packed solids) while the third utilizes heat-of-fusion storage. These systems represent the current state-of-the-art, and the related research areas recommended below should be emphasized in near term programs in order to support (in a timely manner) the engineering development of these systems.

Sensible Heat Systems - Fluids (Heat Transfer Oils and Molten Salts)

1. The high temperature stability of the storage materials requires thorough characterization.

2. The response of the storage materials to thermal cycling should be carefully evaluated.

3. The compatibility of the storage medium with the container and heat exchanger surfaces requires detailed examination.

4. The thermophysical properties of storage materials require complete identification.

Sensible Heat Systems - Packed Solids With Heat Transfer Oil

1. In addition to the material considerations listed above, the compatibility between the heat transfer oil and solid storage medium must also be examined.

2. The effects of axial conduction in the bed should be studied.

3. The effects of particle size and size distribution on pressure drop, solid/fluid heat transfer coefficient and such phenomena as channeling and wall effects must be evaluated.

4. The effects of input and output fluid distributers on the performance of the bed should be understood.

Heat-of-Fusion Systems

1. The areas of high temperature stability, thermal cycling and compatibility with containment materials are important in heat-of-fusion systems and should be well understood.

2. Detailed mathematical models of the heat transfer processes (both transient and steady) during heat addition and removal are necessary for accurate performance predictions, and thus should be available.

The storage systems which will be required in the next generation solar electric power systems may be refined versions of the three concepts being presently considered or perhaps a new concept such as one based on a reversible chemical reaction. The research recommendations considered necessary to support the development of these advanced systems are listed below.

1. Fluids and fused salts, for use as storage media as well as heat transfer agents, which are capable of operation at temperatures in excess of 500°C should be developed and characterized.

2. "Active" heat exchangers for use in heat-of-fusion storage systems should be developed.

3. Reversible chemical reactions which could be employed in a thermal energy storage system should be identified.

4. Heat exchange processes for use in reversible chemical reaction storage systems need to be developed along with related performance prediction models.

5. Various candidate storage system concepts should be carried through engineering development in order to determine actual system performance and cost characteristics.

APPENDIX A--THERMODYNAMIC CONSIDERATIONS

Energy Availability Analysis

The available energy of a system can be defined as the maximum portion of energy which can be converted to useful work by processes which reduce the system to a "dead state" (i.e., in equilibrium with its surroundings). Since the maximum work obtainable from a system has a single value, the energy availability is a property of the system. The processes by which the energy is converted to work must necessarily be ideal in order that the maximum work can be obtained. The energy of a system can be in various forms; thus one must consider various ideal processes in converting the energy to work. For example, a system which is at a pressure and temperature different from its surroundings could produce work from both an expansion process and a heat engine. For the present situation only thermal energy is considered and thus the ideal process needed to convert heat to useful work is a reversible, external heat engine (i.e., a Carnot engine). It can be shown (Equation A-1) that the fraction, dR, of the energy, dQ, which is available, is $(1 - T_0/T)$ or

$$dR = \left(1 - \frac{T_0}{T}\right) dQ \qquad \text{(A-1)}$$

where

dR = availability

T_0 = sink temperature

T = temperature of energy dQ

If one recalls that the efficiency of a Carnot cycle operating between the temperatures T_H and T_L is

$$\eta_{Carnot} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H} \quad , \qquad \text{(A-2)}$$

it is clear that in Equation (A-1) the available energy is simply that portion of dQ that can be converted to work by a Carnot cycle operating between the temperatures T and T_0.

Consider a system containing energy in the form of sensible heat stored between the temperatures T_L and T_H as indicated in the T - h diagram in Figure A-1(a). The availability of the energy in this system can be determined from Equation (A-1) and the fact that sensible energy content is related to the temperature by the specific heat. For a constant specific heat,

$$dQ = mcdT \tag{A-3a}$$

where

m = mass

c = specific heat

and

$$dR = \left(1 - \frac{T_0}{T}\right) mcdT \tag{A-3b}$$

To determine the total availability of the energy contained between T_L and T_H, Equation (A-3b) must be integrated between these limits. Performance of the integration and division by the mass, m, results in the following expression,

$$r = c(T_H - T_L) - cT_0 \ln\left(\frac{T_H}{T_L}\right) , \tag{A-4}$$

which specifies the specific availability, r (availability per unit mass), of energy.

In Figure A-1b the temperature-enthalpy curve for a phase transformation system is shown. Note that in this case the heat is stored or released isothermally, so that

$$Q = m\Delta h_{pc} \tag{A-5}$$

where Δh_{pc} is the latent heat of the phase transformation. Upon multiplying Equation (A-5) by the Carnot efficiency at the phase change temperature and dividing by m, one obtains the following equation for the specific availability of energy in the form of latent heat:

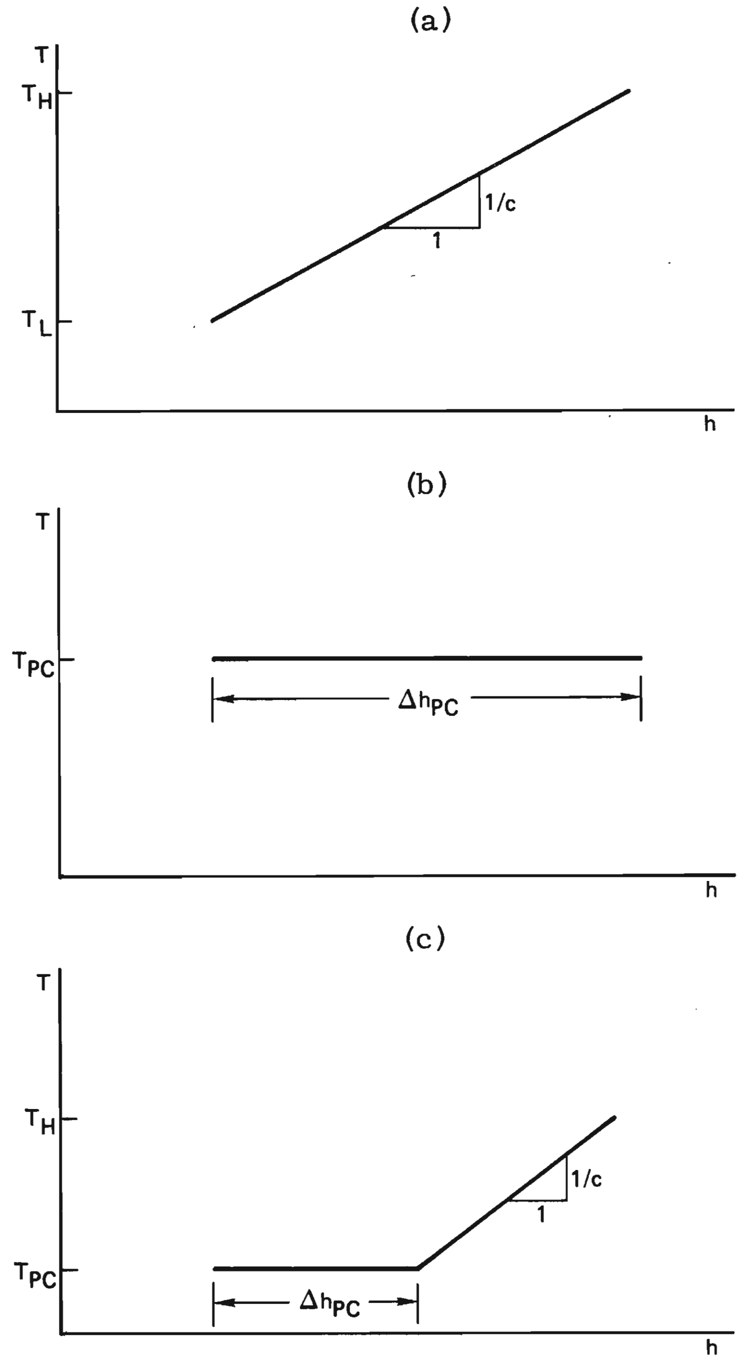


Figure A-1 Temperature-Enthalpy Diagrams for Energy in the Form of (a) Sensible Heat, (b) Latent Heat, and (c) A Combination of Latent and Sensible Heats

$$r = \left(1 - \frac{T_0}{T_{pc}}\right) \Delta h_{pc} \qquad \text{(A-6)}$$

For the more general case where the energy is in the form of both sensible and latent heat such as shown in Figure A-1c, the results given in Equations (A-4) and (A-6) can be combined to give the following expression;

$$r = c\left[(T_H - T_{pc}) - T_0 \ln\left(\frac{T_H}{T_{pc}}\right)\right] + \left(1 - \frac{T_0}{T_{pc}}\right) \Delta h_{pc} \qquad \text{(A-7)}$$

The discussion presented in the preceding paragraphs has developed the concept of energy availability and the means for its determination for the various forms of thermal energy. The next step is to apply these concepts to the processes associated with thermal energy storage in order to illustrate the "energy penalties" that must be dealt with and the system considerations which affect them.

The processes which affect the availability of stored thermal energy are the transfer and losses of energy from the system. The heat transfer processes are the transfer of heat into the storage medium from a heat transfer fluid which carries the heat from the energy source; or, the transfer from the storage medium to a heat transfer fluid carrying energy to the load. In the situations where the storage medium is also one or both of the heat transfer fluids, the transfer processes are not needed. The transport of heat will always result in a reduction in energy availability due to the "Second Law" requirement of a finite temperature difference for heat transfer. The impact of a loss of energy from a storage system depends upon the type of system under consideration. In a sensible heat system, energy losses will always result in a drop in storage temperature and consequently a loss in specific availability. On the other hand the loss of energy from a latent heat storage system does not affect the phase change temperature and thus the specific availability is unaffected. However, in both systems, since the total amount of heat is reduced due to energy loss, the total availability must necessarily decrease.

The impact of a transfer of heat on the availability of the energy transferred can be formulated on the basis of the development presented earlier in this section. Consider first the transfer of energy from one sensible heat system to another, where the specific heat capacities are constant for both systems. This process is illustrated in the T-$\dot{m}$h diagram shown in Figure A-2. The product of the mass flow rate $\dot{m}$ and the specific enthalpy h is sometimes called a duty function and is used as the abscissa coordinate in order to allow a direct comparison of the energy change with temperature for the two fluids. The minimum temperature difference ΔT_{min} that can be realized will depend upon the nature of the heat exchanger configuration and the convective heat transfer characteristics of the fluids. The availability of the energy in fluid 1 is given as a function of the temperature swing by Equation (A-4). If the temperature swing of fluid 2 is expressed in terms of the temperature swing of fluid 1 and ΔT_{min}, the availability of the energy in fluid 2 can be determined also from Equation (A-4). By multiplying Equation (A-4) by $\dot{m}$ to be consistant with Figure (A-2) an availability rate, $\dot{r}$, is obtained. For fluid 1

$$\dot{r}_1 = \dot{m}_1 c_1 (T_H - T_L) - \dot{m}_1 c_1 T_0 \ell n \left(\frac{T_H}{T_L} \right) , \qquad \text{(A-8)}$$

and for fluid 2 with $\dot{m}_1 c_1 / \dot{m}_2 c_2 < 1$

$$\dot{r}_2 = \dot{m}_1 c_1 (T_H - T_L) - \dot{m}_2 c_2 T_0 \ell n \left[1 + \frac{(T_H - T_L)}{(T_L - \Delta T_{min})} \frac{\dot{m}_1 c_1}{\dot{m}_2 c_2} \right] \qquad \text{(A-9a)}$$

or with $\dot{m}_1 c_1 / \dot{m}_2 c_2 > 1$

$$\dot{r}_2 = \dot{m}_1 c_1 (T_H - T_L) - \dot{m}_2 c_2 T_0 \ell n \left[\frac{1}{1 - \frac{\dot{m}_1 c_1}{\dot{m}_2 c_2} \frac{(T_H - T_L)}{(T_H - \Delta T_{min})}} \right] \qquad \text{(A-9b)}$$

Equations (A-8) and (A-9) describe how the energy availability is affected by the heat transfer process. In Figure A-3, Equations (A-8) and (A-9) have been plotted to illustrate the variation of the availability rate with temperature swing ratio, T_L / T_H, both before and after the transfer of energy from fluid 1 to fluid 2.

Consider next the transfer of energy from a sensible heat system to a latent heat system as illustrated in Figure A-4. The availability of the energy before transfer is given by Equation (A-8), while that of the latent heat system after transfer may be determined in a manner similar to that used in the previous case. By expressing the phase change temperature in terms of T_L and ΔT_{min}, and substituting this into Equation (A-6), it can be shown that the energy availability after transfer is given by:

$$\dot{r} = \dot{m}_1 c_1 (T_H - T_L) - \frac{\dot{m}_1 c_1 T_0 (T_H - T_L)}{T_L - \Delta T_{min}} \qquad \text{(A-10)}$$

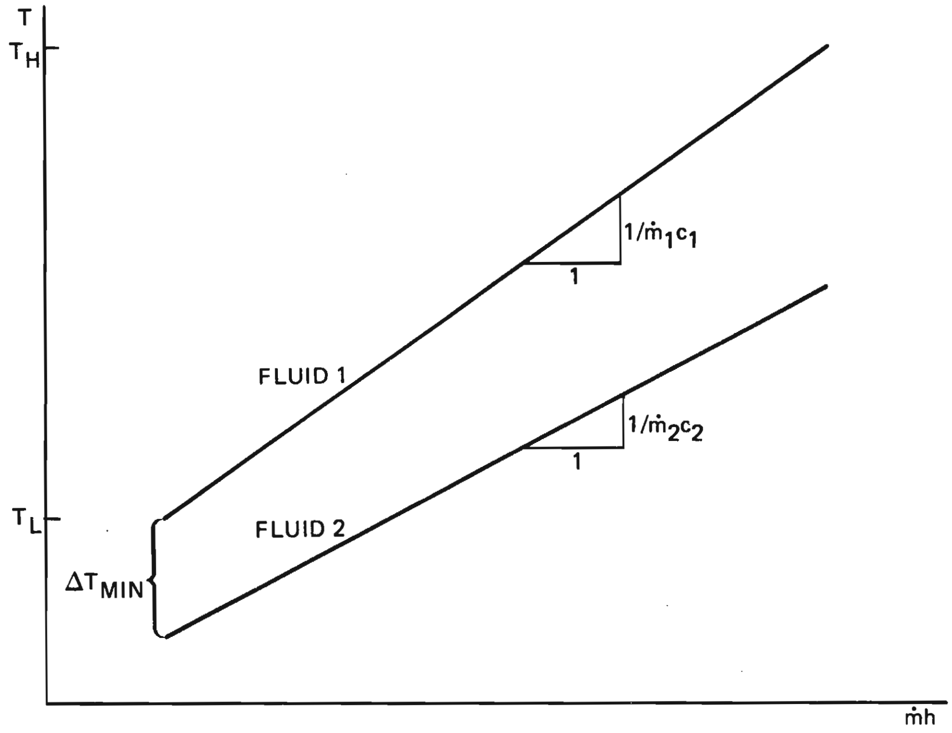


Figure A-2 Temperature-Duty Function Diagram Describing the Transfer of Energy from Sensible Heat System 1 to Sensible Heat System 2

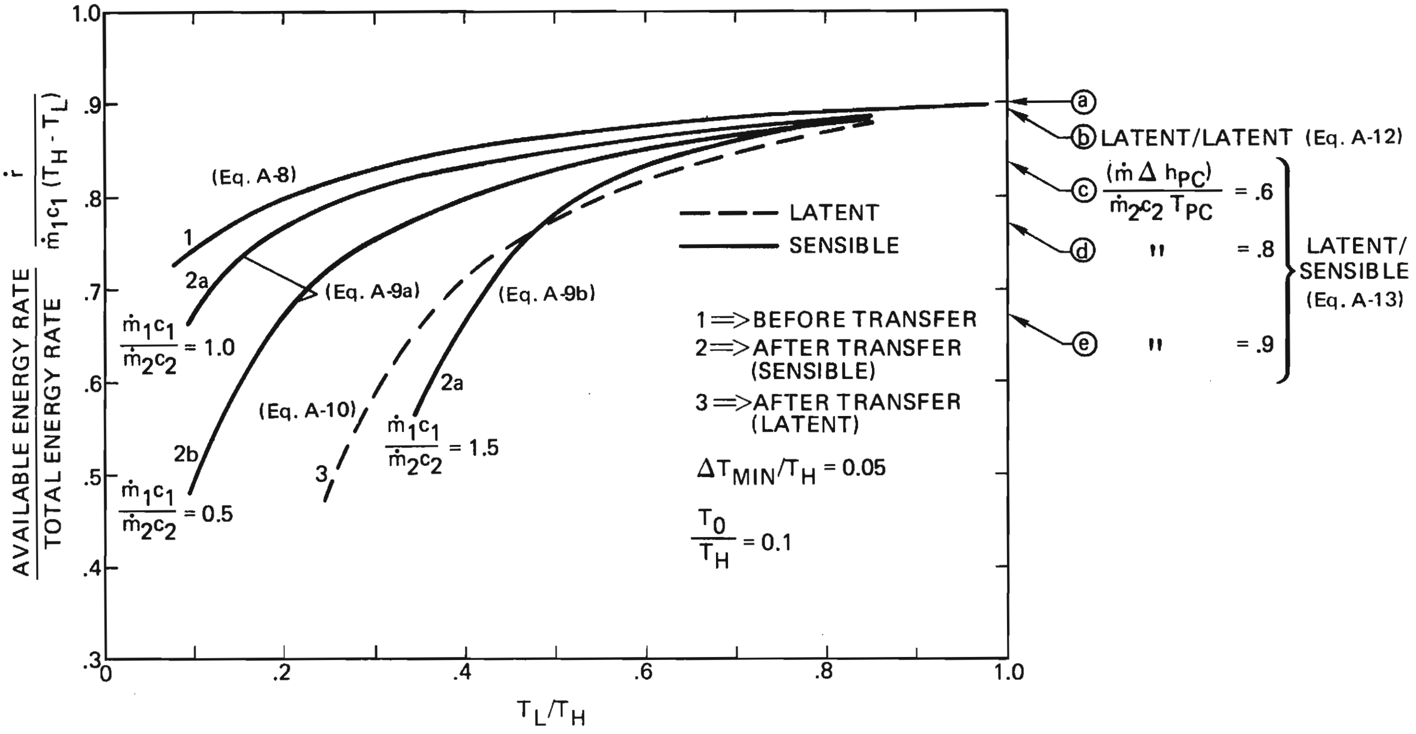


Figure A-3 Comparison of the Effects of Heat Transfer on Availability for Various Types of Energy Systems

Equation (A-10) has been plotted in Figure A-3 (dotted line) and illustrates how the availability after transfer to a latent heat system compares with that after transfer to a sensible heat system.

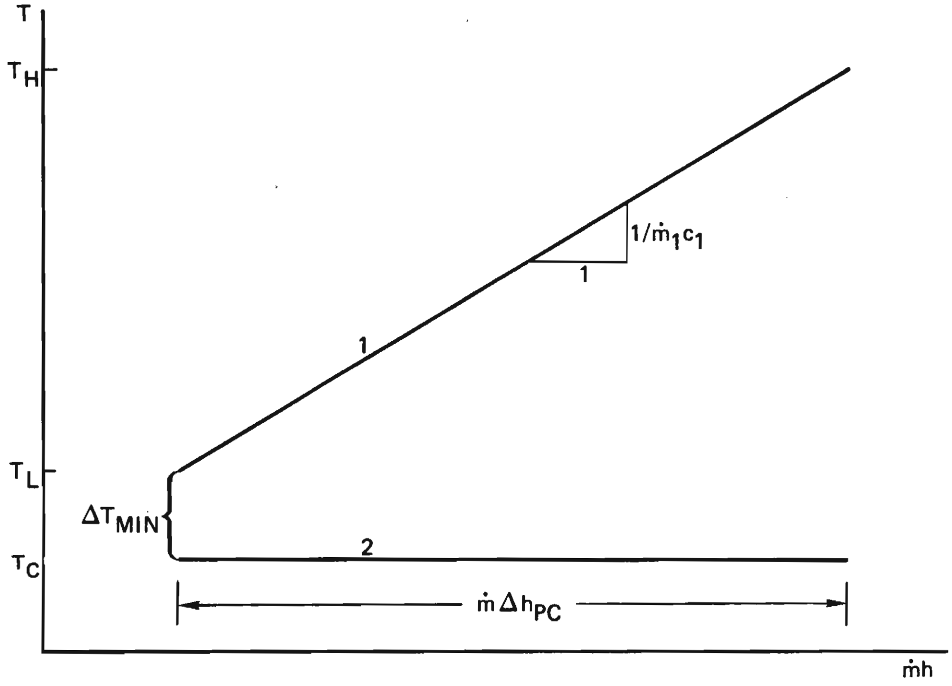


Figure A-4 Temperature-Duty Function Diagram Describing the Transfer of Energy from Sensible Heat System 1 to Latent Heat System 2

The next case to be considered is the transfer of energy from a latent heat system to another latent heat system, as shown in Figure A-5. Before transfer the availability is given by Equation (A-6); after transfer the availability can be computed in terms of ΔT_{min}. The following relations express the availability before and after transfer for this case:

$$\dot{r} = (\dot{m}\Delta h_{pc})_1 \left(1 - \frac{T_0}{T_{pc}}\right) \qquad \text{(A-11)}$$

where T_{pc} is the phase transformation temperature,

$$\dot{r} = (\dot{m}\Delta h_{pc})_1 \left[1 - \frac{(T/T_{pc})}{1 - \frac{\Delta T_{min}}{T_{pc}}}\right] \qquad \text{(A-12)}$$

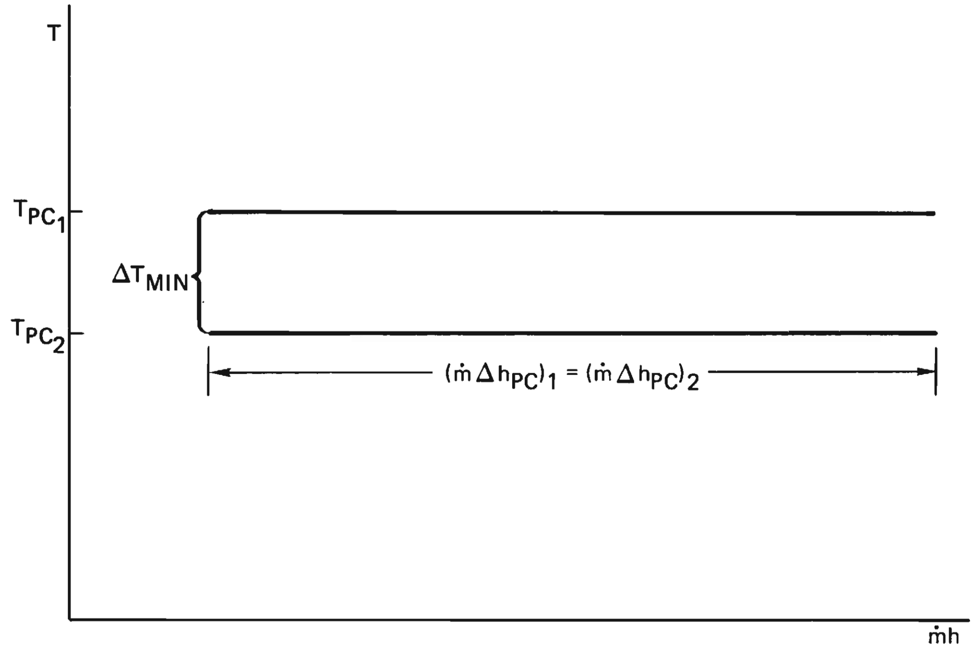


Figure A-5 Temperature-Duty Function Diagram Describing the Energy Transfer Process Between Two Latent Heat Systems

Since there is no temperature swing associated with latent heat storage, the above two equations are plotted as single points in Figure A-3 at $T_L/T_H = 1$, or $T_L = T_H$ (see right-hand margin of the figure for identication of these points).

The last case to be considered here it that of energy transfer from a latent heat system to a sensible heat system as illustrated in Figure A-6. Before transfer the availability is given by Equation (A-11). The expression for the energy availability after transfer can be determined by specifying the temperature swing of the sensible heat system in terms of $(\dot{m}\Delta h_{pc})_1$, $\dot{m}_2c_2$, T_{pc}, and ΔT_{min} and substituting this into Equation (A-4). The resulting expression for the availability after transfer is

$$\dot{r} = (\dot{m}\Delta h_{pc})_1 - \dot{m}_2 c_2 T_0 \ell n \left[\frac{1}{1 - \dfrac{\dfrac{(\dot{m}\Delta h_{pc})_1}{\dot{m}_2 c_2 T_{pc}}}{\left(1 - \dfrac{\Delta T_{min}}{T_{pc}}\right)}} \right] \qquad \text{(A-13)}$$

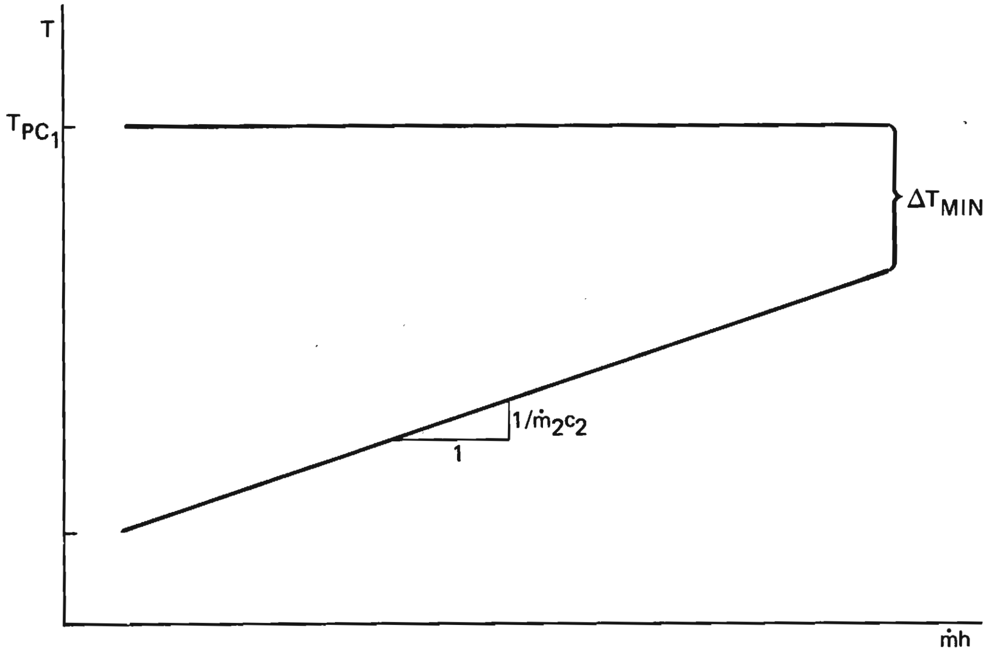


Figure A-6 Temperature-Duty Function Diagram Describing the Transfer of Energy From a Latent Heat System 1 to a Sensible Heat System 2

Again the availability is independent of the temperature swing and thus may be plotted as individual points on Figure A-3 at $T_L/T_H = 1$ for various values of the parameter $(\dot{m}\Delta h_{pc})_1/(\dot{m}_2 c_2 T_{pc})$.

The four energy transfer processes described above have by no means exhausted all possible cases (for example, transfer to and from combined sensible and latent systems were not included); they do, however, adequately illustrate the effect of heat transfer on energy availability for these simple systems. Figure A-3 summarizes these effects for the four systems based on the specific conditions of

$$\frac{T_0}{T_H} \quad \text{or} \quad \frac{T_0}{T_{pc}} = 0.1$$

and

$$\frac{\Delta T_{min}}{T_H} \quad \text{or} \quad \frac{\Delta T_{min}}{T_{pc}} = 0.05.$$

A very important point that should be recognized in Figure A-3 is the difference in the availability between energy in the form of sensible heat (curve 1) and energy in the form of latent heat (point a). For the sensible heat system the larger the temperature swing, the lower the availability. In the case of latent heat, the availability of the energy is independent of any temperature swing, and is the upper limit of the sensible heat availability (in the limit as $T_L/T_H \to 1$. When heat is transferred from a sensible heat system, the loss in availability due to the transfer is a minimum when the parameter $\dot{m}_1c_1/\dot{m}_2c_2$ is unity (curve 2a). This is the situation which results in the smallest temperature drop over which the heat transfer occurs. When heat is transferred from a sensible heat system to a latent heat system (curve 3), a large loss in availability is realized; again, this is due to the large temperature difference over which the heat is transferred. The transfer of heat from one latent heat system to another (point a) results in the least drop in availability, since the temperature is constant in both systems and all the energy is transferred across only the minimum temperature difference ΔT_{min}. Finally, in the situations where the energy transferred from a latent heat system to a sensible heat system (points c, d, and e), the availability loss due to the transfer will increase with the parameter $(\dot{m}\Delta h_{pc})_1/\dot{m}_2c_2T_{pc}$, which can be shown to characterize the magnitude of the temperature difference over which the transfer occurs.

It was stated earlier in this section that energy availability could be reduced by system heat losses, in addition to heat transfer processes. This effect can be quantified using the availability analysis developed previously. Let X represent the fraction of the total stored energy which is lost during storage. For sensible heat storage, this heat loss will reduce T_H, the high end of the temperature swing; assume for this discussion that T_L, the lower end of the temperature swing, remains fixed. Under these conditions, the after-loss temperature of the storage medium, can be determined by an energy balance to be

$$T_H^1 = T_L + (1 - X)(T_H - T_L). \tag{A-14}$$

By substituting Equation (A-14) into Equation (A-4), the specific availability of the stored energy after the storage loss can be specified

$$r = c(1 - X)(T_H - T_L) - cT_0 \ell n \left[(1 - X)\left(\frac{T_H}{T_L} - 1\right) + 1\right] \tag{A-15}$$

For latent heat storage, the storage loss will reduce only the quantity of heat stored not the storage temperature. Thus, the specific availability after a storage loss can be determined by simply multiplying the right-hand side of Equation (A-6) by (1 - X) to obtain

$$r = \Delta h_{pc}(1 - X)\left(1 - \frac{T_0}{T_{pc}}\right) \qquad \text{(A-16)}$$

The effect of storage losses on energy availability is illustrated in Figure A-7 where Equations (A-15 and (A-16) have been plotted (actually, the fraction of the initially stored energy which is available after the loss has been plotted). Notice that the availability decrease due to a storage loss is greater for the sensible heat storage than for the latent heat storage. This is because a storage energy loss will produce a decrease in the storage temperature; the drop in temperature results in a decrease in availability which is in addition to the decrease due to the energy lost. Note also that the magnitude of the temperature swing will affect the availability loss; that is, the greater the temperature swing of the storage system, the greater the availability loss due to energy loss.

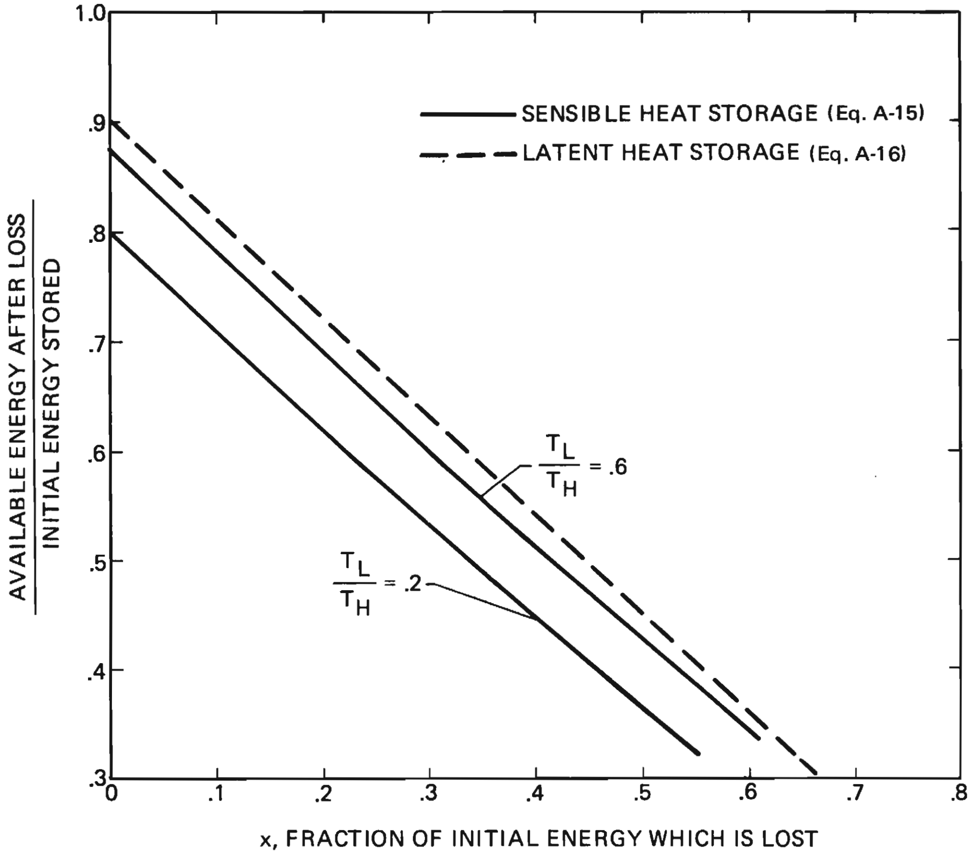


Figure A-7 The Loss of Available Energy Due to Storage Losses for Sensible and Latent Heat Storage Systems

In this Appendix the concept of energy availability has been applied to the various types of thermal energy storage systems as an attempt to illustrate a means for specifying the thermodynamic performance of the overall energy conversion system. The concept of energy availability, or quality, has significance when the energy is to be converted from heat to work.

Obviously, in systems where the energy is not converted, the availability has no significance with regard to the thermodynamic performance of the system.

Heat Transfer Processes in Heat-of-Fusion Systems

When a passive heat-of-fusion storage system is operated at a sufficiently high heat transfer fluid (HTF) flow rate that heat transfer occurs all along the length of the heat exchanger, the assumption of negligible axial heat flow makes the heat transfer process locally one-dimensional. The additional assumption that the sensible heat removed from the solid phase - when cooling it below the melting temperature - can be neglected allows the formulation of a simple analytical model of the discharging heat transfer process. Consider the problem illustrated in Figure A-8 where the liquid phase change material (PCM) and the HTF are assumed to be at the melting temperature T_F and at $T_\infty (T_\infty < T_F)$, respectively. If the thermal resistance of the wall separating the two materials is neglected, the heat flux from the PCM to the HTF can be related to the temperature difference between the liquid PCM and the HTF and the thermal resistance of the solid phase PCM,

$$\frac{q}{A} = \frac{T_F - T_\infty}{\frac{\epsilon}{k_s}} \qquad \text{(A-17)}$$

where

ϵ = thickness of solid phase,

k_s = thermal conductivity of solid phase.

The heat flux to the HTF can also be related to rate-of-increase of the thickness of the solid layer,

$$\frac{q}{A} = \rho h_f \frac{d\epsilon}{dt} \qquad \text{(A-18)}$$

where

ρ = density of the liquid phase

h_f = heat-of-fusion

t = time.

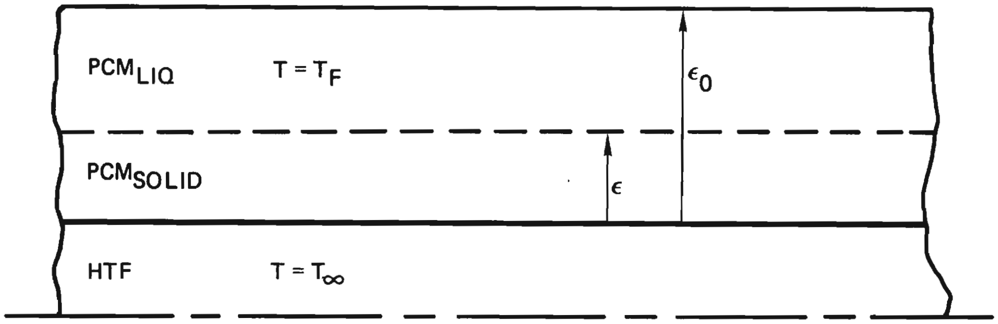


Figure A-8 Geometric Configuration of One-Dimensional Phase Change Heat Transfer Model

By equating Equations (A-17) and (A-18) and solving the resulting differential equation, an expression relating ϵ, the solid layer thickness, to time, t, is obtained,

$$\theta^* = \left(\frac{\epsilon^*}{2}\right)^2 \tag{A-19}$$

where

$$\theta^* = \text{dimensionless time} = \frac{k_s (T_F - T_\infty) t}{\epsilon_0^2 \rho h_f}$$

$$\epsilon^* = \frac{\epsilon}{\epsilon_0} \quad \left(\epsilon_0 = \text{final solid phase thickness used as characteristic length in dimension less parameters}\right)$$

By solving Equation (A-19) for ϵ^* and substituting the result into Equation (A-17) an expression of the heat flux is obtained,

$$\left(\frac{q}{A}\right) = (2\,\theta^*)^{-1/2} \tag{A-20}$$

where

$$\left(\frac{q}{A}\right) = \text{Dimension less heat flux} = \frac{q/A}{k_s (T_F - T_\infty)/\epsilon_0}$$

A similar analysis can be applied to the cylindrical configurations shown in Figure A-9a and A-9b to obtain the following:

Cylindrical Containment (Figure A-9a)

$$\theta^* = \frac{(1 - \epsilon^*)^2}{2} \ell n\,(1 - \epsilon^*) - \frac{(1 - \epsilon^*)^2 - 1}{4}$$

$$\left(\frac{q}{A}\right)^* = \frac{1}{\ell n \left(\frac{1}{1 - \epsilon^*}\right)} \qquad \text{(A-21)}$$

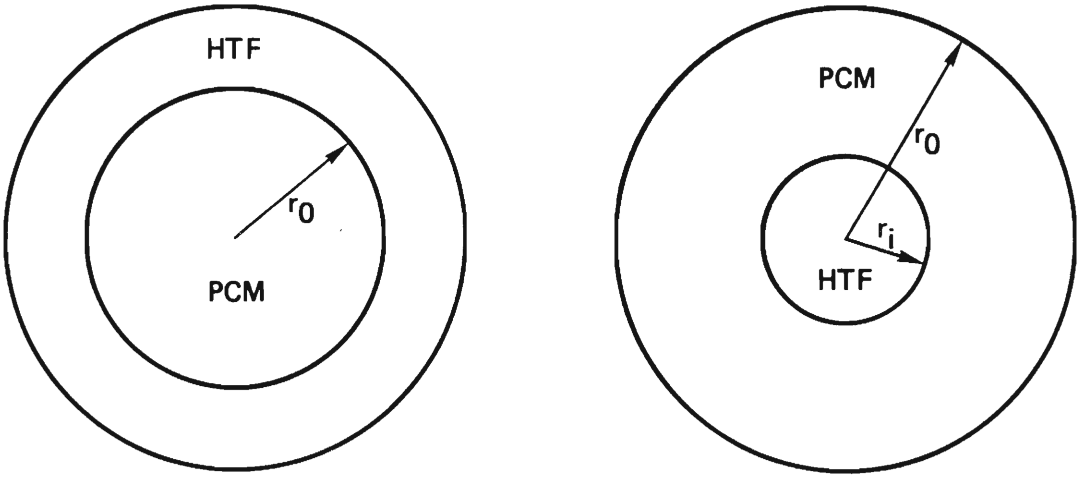
Annular Containment (Figure A-9b)

$$\theta^* = \frac{1}{2}(r^* + \epsilon^*)^2 \ell n \left(\frac{r^* + \epsilon^*}{r^*}\right) + \frac{1}{4}\left[r^{*2} - (r^* + \epsilon^*)^2\right]$$

$$\left(\frac{q}{A}\right)^* = \frac{1}{r^* \ell n \left(\frac{r^* + \epsilon^*}{r^*}\right)}$$

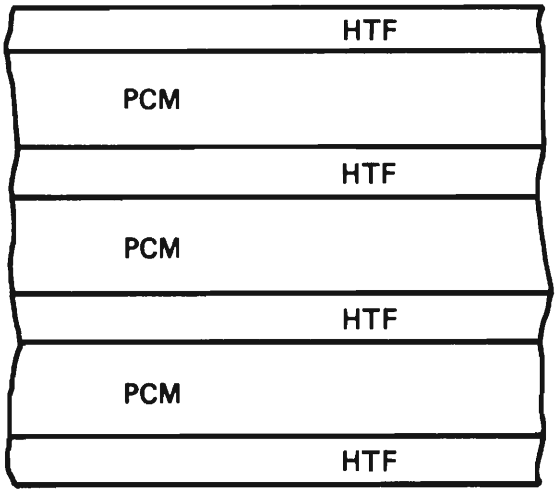
$$r^* = \frac{r_i}{r_0 - r_i} \qquad \text{(A-22)}$$

In Figure A-10, Equations (A-20), (A-21), and (A-22) have been plotted in order to illustrate the variation of the dimensionless heat flux, $(q/A)^*$, with the dimensionless time θ^* for the three passive heat-of-fusion configurations shown in Figure A-9. The curves shown in the figure indicate that the annular containment configuration yields the highest heat flux of the three. For this comparison, the annular geometry was based on a value of $r^* = 1$ ($r^* = \epsilon_0/r_0$), since this geometry corresponds most closely to the other two. For large values of r^* the curve for the annular configuration will tend to approach that of the planar geometry. For values of $r^* \ll 1$ the heat flux is quite high (increases inversely with r^*), but θ^*_{max} becomes very small (decreasing as r^{*2}), so that a fair comparison with the other configurations becomes impossible. The heat flux obtained with the planar and cylindrical containment configurations are both lower than that of the annular case with the cylindrical containment having the lowest of the three. There is a simple explanation for this result; the surface area of the plane containing the solidification front increases as the thickness of the solid phase increases for the annular geometry, whereas, it is constant for planar and decreases for cylindrical containment configurations. Thus for equal thicknesses of solid phase material there



(a) CYLINDRICAL CONTAINMENT
OF PCM

(b) ANNULAR CONTAINMENT
OF PCM



(c) PLANAR CONTAINMENT
OF PCM

Figure A-9 Common Configurations of Heat of Fusion Storage Systems will be different surface area of solidifying material. Another point which merits discussion involves the maximum value of dimensionless time, θ^*_{max}, for the cylindrical containment case. Due to the geometry of the model developed above for the cylindrical containment configuration, the point at which all of the PCM has frozen (i.e., $\epsilon^* = 1$) is a singularity of the solution, and thus has not been specified [see Equation (A-21)] on Figure A-10.

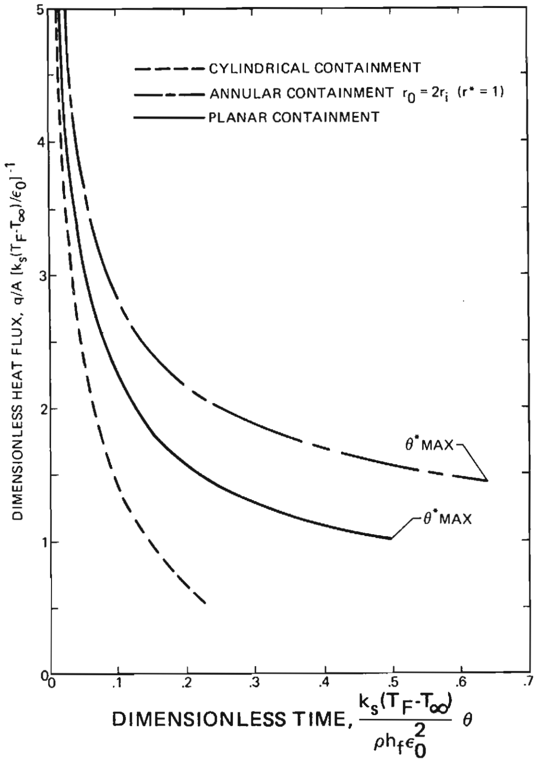


Figure A-10 Comparison of Temporal Variation of Dimensionless Heat Flux for Three Heat-of-Fusion Heat Exchange Configurations

The discussion of the previous paragraph has dealt only with the high HTF flowrate situation - that is the case where the heat transfer occurs in a nearly uniform manner along the length of the containment vessel. The low HTF flowrate case - the moving heat transfer zone or thermal stratification case - can also be included in the comparison presented above with only a simple extension of the analysis. If it is assumed that the solidification front can be approximated by a linear variation of solid-phase thickness with axial position with the width of this heat transfer zone being specified (i.e., see dashed lines in Figure A-11), then the expressions given in Equations (A-20) to (A-22) can be used to give the heat flux as a function of axial position which can in turn be integrated axially across the zone to yield the heat transfer rate for this manner of operation (recall that it is invarient with time). Carrying out this operation for the planar geometry case (noting that the limit of integration cannot be $\epsilon^* = 0$ or $\epsilon^* = 1$ due to singularities in the solution) with the limits of integration of $\epsilon^* = 0.05$ to 0.95, the following result is obtained;

$$\left(\frac{q}{A}\right)^{*}_{ZONE} = 2.94 \left(\frac{w_z}{\ell}\right) \qquad \text{(A-23)}$$

where

w_z = width of heat transfer zone

ℓ = length of the containment vessel

A = total heat exchange surface area

Notice that this result is indeed independent of time, depending only upon the width of the heat transfer zone and the length of the containment vessel. When using this mode of operation of the storage system, the ratio w_z/ℓ should be less than 1 in order that some period of steady operation of the system can be obtained. In fact, values for w_z/ℓ of about 0.2 have been recently proposed (see Reference A.3) and a value of 0.1 is probably not unreasonable. In Figure A-12, the results previously shown in Figure A-10 have been replotted along with curves representing Equation (A-23) for values of w_z/ℓ equal to 1.0, 0.5, 0.2, and 0.1. As would be expected, since w_z/ℓ is the ratio of heat exchanger area in use to total heat exchanger area, the dimensionless heat flux (based on total area) decreases with w_z/ℓ. For a constant heat removal rate, increasing the storage capacity will result in a decrease in w_z/ℓ; thus the lower values of w_z/ℓ are likely to be more typical. From Figure A-12 it is seen that the low values of w_z/ℓ result in values of heat flux below those of the unstratified heat exchanger case. Thus the advantage of constant heat extraction rate must be paid for by the necessity of using larger heat exchangers.

Consider next the case of a heat-of-fusion heat exchanger in a planar geometry (Figure A-9c), which can be used either in the passive mode or an active mode. In the passive mode with a final solid phase thickness of ϵ_0, the heat flux is specified as a function of time by Equation (A-20). This equation also applies to the active mode where the solid phase is removed after reaching a thickness t_0, if the dimensionless variables $(q/A)^*$ and θ^* are appropriately stretched by the ratio t_0/ϵ_0. In Figure A-13 the planar heat exchange process is compared for active and passive configurations. The curve for the passive case is identical to the curve for planar geometry presented in Figure A-10. The results for the active case are shown as straight lines representing a mean value of the dimensionless heat flux for various values of t_0/ϵ_0. This actual heat flux decreases in a manner similar to the passive case; however, the times required to reach maximum solid

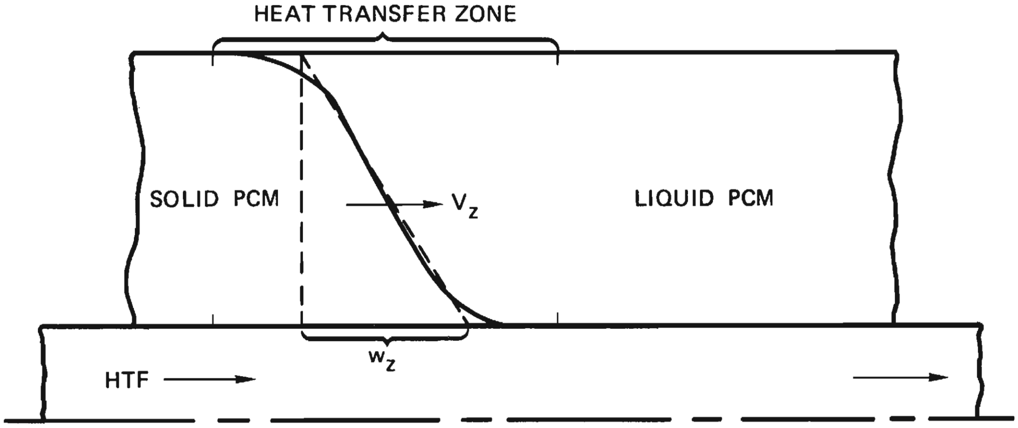


Figure A-11 Geometric Configuration of Heat Transfer Model for Low HTF Flow Rate Situation

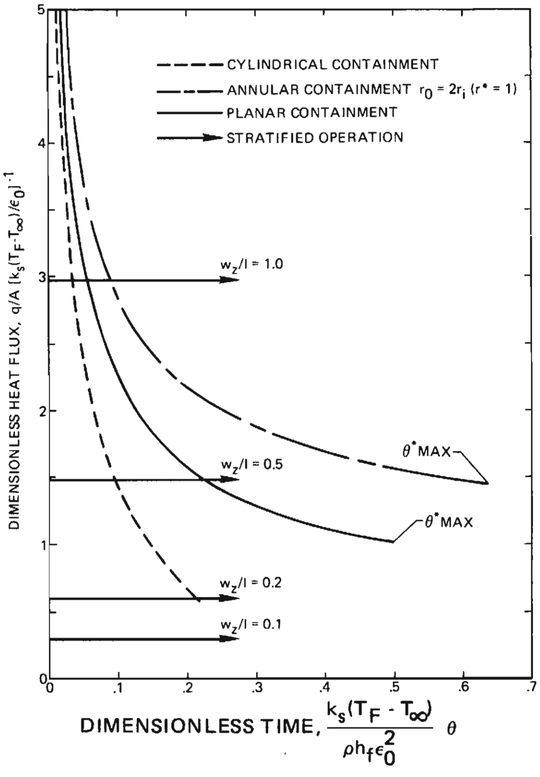


Figure A-12 Comparison of Temporal Variation of Non-Dimensional Heat Flux for the Cases of Stratified and Non-Stratified Operation of Heat-of-Fusion Heat Exchangers phase thickness are much shorter [θ^*_{max} for the active case is proportional to $(t_0/\epsilon_0)^2$], and the process is repeated after the removal of the solid phase. Thus the curves for the active case really have a "sawtooth" appearance which smears out very fast as t_0/ϵ_0 increases. The important thing to note in Figure A-13 is the large increase in heat flux obtained when operating an active heat exchanger. The true significance of this is the fact that with active heat exchange systems very large reductions in heat exchanger surface areas can be realized over the passive systems. Of course, it should be pointed out that the active system must necessarily be more complex, and thus some of the advantages of its use may well be neutralized.

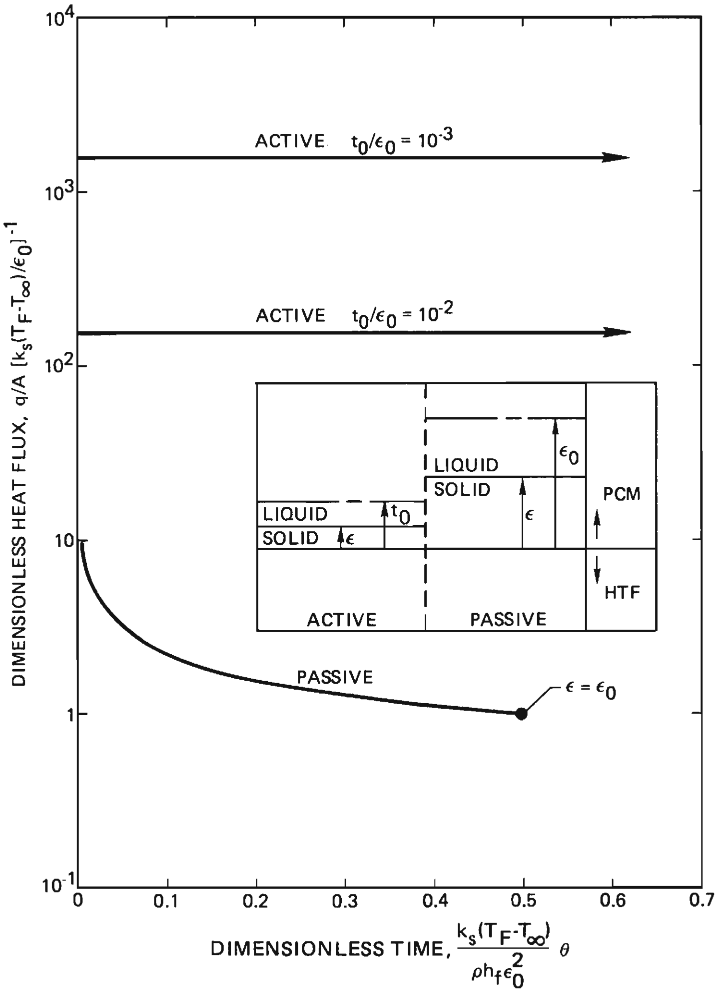


Figure A-13 Comparison of Temporal Heat Flux Variation for Active and Passive Heat-of-Fusion Heat Exchangers

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APPENDIX B--CALCULATION OF ΔH_f FOR EUTECTIC SALT MIXTURES USING KIRCHHOFF'S CORRECTION

Compilations of phase diagrams,$^{B.1}$ phase change,$^{B.2}$ and molten salt$^{B.3}$ characteristics permit the choice of suitable eutectics for a latent heat thermal storage system. Although the eutectic temperature and composition can be ascertained using sources mentioned above, the eutectic fusion enthalpy must be estimated.

An average eutectic fusion enthalpy $\Delta H_{f,e}$ is frequently calculated for binary (A-B) systems:

$$\Delta H_{f,e} = X_A \, \Delta H_{f,A} + X_B \, \Delta H_{f,B} \quad , \tag{B-1}$$

where X_A and X_B are the mole fraction compositions of A and B in the eutectic. Equation (B-1) can lead to significant errors in the estimation of $\Delta H_{f,e}$ where eutectic melting temperatures are significantly removed from those of the pure components. Kirchhoff's formula$^{B.4}$ can be applied which adjusts for the differing liquid and solid heat capacities of the pure components between the fusion point of the eutectic $T_{f,e}$ and that of components ($T_{f,A}$ $T_{f,B}$). Therefore:

$$\Delta H_{f,e} = X_A \, \Delta H_{f,A} + X_B \, \Delta H_{f,B} + \int_{T_{f,e}}^{T_{f,A}} \left(Cp_A(s) - Cp_A(\ell) \right) dT$$

$$+ \int_{T_{f,e}}^{T_{f,A}} \left(Cp_B(s) - Cp_A(\ell) \right) dT \tag{B-2}$$

in terms of enthalpies

$$\Delta H_{f,e} = X_A \, \Delta H_{f,A} + X_B \, \Delta H_{f,B} + \left[\underset{\text{solid}}{\left(H^\circ_{T_{f,A}} - H^\circ_{T_{f,e}} \right)} - \underset{\text{liquid}}{\left(H^\circ_{T_{f,A}} - H^\circ_{T_{f,e}} \right)} \right]$$

$$+ \left[\underset{\text{solid}}{H^\circ_{T_{f,B}} - H^\circ_{T_{f,e}}} - \underset{\text{liquid}}{\left(H^\circ_{T_{f,B}} - H^\circ_{T_{f,e}} \right)} \right] \qquad \text{(B-3)}$$

Although form (B-3) is complicated, tabulatized values[B.5] of $H^\circ_T - H^\circ_{298}$ allow rapid interpolation. An illustrative example follows:

LiCℓ - KCℓ eutectic (58 mole % LiCℓ, 42 mole % KCℓ).

melts at: 354.3°C = $T_{f,e}$.[B.6]

$$\Delta H_{f,e} = 0.58 \, (4.74 \text{ kcal mol}^{-1}) + 0.42 \, (6.282 \text{ kcal mol}^{-1})$$

$$\Delta H_{f,e} = 5.387 \text{ kcal mol}^{-1}$$

From data in Reference B.5

	T_f/K	ΔH_f/kcal mol^{-1}	solid	liquid	Net
KCℓ	1044	6.272	$\left(H^\circ_{1044} - H^\circ_{627}\right)$ -	$\left(H^\circ_{1044} - H^\circ_{627}\right)$	
LiCℓ	833	4.74	2.887	-7.335	-4.448
Eutectic	627		$\left(H^\circ_{833} - H^\circ_{627}\right)$ -	$\left(H^\circ_{833} - H^\circ_{627}\right)$	
			3.593	-4.058	-0.465

Using Equation (B-1)

$$\Delta H_{f,e} = 0.58 \, (4.74) + 0.42 \, (6.282) = 5.387 \text{ kcal mol}^{-1}$$

Using Equation (B-3)

$$\Delta H_{f,e} = 0.58 \, (4.74) + 0.42 \, (6.282) + \left\{ 0.42 \, (-4.448) + 0.58 \, (-0.465) \right.$$

$$\Delta H_{f,e} = 5.387 - 2.138 = 3.249 \text{ kcal mol}^{-1}.$$

The calculated $\Delta H_{f,e}$ obtained via the average method (Equation B-1) is 68 percent higher than that obtained using the Kirchhoff method. Experimentally,[B.7] this eutectic has a heat of fusion of 3.20 ± 0.06 kcal mol^{-1}; therefore, the Kirchhoff formula is within experimental error. The results of similar calculations for selected eutectics are presented in Table I.

TABLE B-I

ENERGY DENSITY COMPARISON OF SELECTED EUTECTIC SALTS MIXTURES

Eutectic		Melting Temperature °C			ΔHm/kcal/mol			ΔH $\frac{cal}{g}$
$X_a A$	$X_b B$	A	B	C	Avg.	Corr'n.	Net	
0.52 NaCl	0.48 $MgCl_2$	801	435	450	8.44	-2.62	5.82	76.4
0.52 $CaCl_2$	0.48 NaCl	772	801	500	6.74	-0.98	5.76	67.2
0.67 KCl	0.33 $MgCl_2$	771	435	470	7.69	-1.62	6.07	70.1
0.58 LiCl	0.42 KCl	560	771	354	5.39	-2.14	3.25	58.1
0.66 KCl	0.34 $CaCl_2$	771	772	600	6.47	-0.48	5.99	71.6
0.61 LiF	0.39 NaF	848	996	652	7.06	-1.45	5.61	174.2
0.50 KCl	0.50 NaCl	771	801	658	6.51	-0.43	6.08	91.4

Although the calculated ΔH_f for the $LiC\ell/KC\ell$ eutectic compares favorably with the experiment, the enthalpy of mixing and solution non-ideality effects are neglected in the Kirchhoff formula. The magnitude of these two effects varies depending upon the chemical interactions of the constituents.

The complexities of solute-solvent interactions in nonaqueous systems has been under study for years.[B.9] Attention has been directed to the simple alkali and alkaline earth halides, nitrates, sulfates and some of the oxides. A brief compilation of the ΔH_f calculated using the Kirchhoff formula, the experimental ΔH_f and the difference ΔH is provided in Table II. An accurate value of ΔH_f of a eutectic considered for latent-sensible thermal energy must be or have been experimentally determined to insure confidence.

TABLE B-II

COMPARISON OF CALCULATED AND EXPERIMENTAL HEATS OF FUSION (REF. 8)

Eutectic	T_f / k	$\Delta H_{f_{exp}}$ / kcal mol^{-1}	$\Delta H_{f_{calc}}$ / kcal mol^{-1}	$\Delta\Delta H$ / kcal mol^{-1}
$CdBr_2$(0.47) + NaBr (0.53)	643	6.2	6.7	-0.5
$CdBr_2$ (0.15) + $CdBr_2 \cdot KBr$ (0.85)	611	10.0	9.9	+0.1
$CdBr_2$ (0.18) + $CdBr_2 \cdot T\ell Br$ (0.82)	649	10.3	10.7	-0.4
$CdBr_2 \cdot KBr$	619	10.3	13.3	-3.0
$CdBr_2 \cdot RbBr$	609	10.1	12.8	-2.7
$CdBr_2 \cdot CsBr$	694	8.8	13.2	-4.4

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