MOLTEN SALT THERMAL ENERGY STORAGE SYSTEMS: SALT SELECTION

Project 8981 Topical Report

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ABSTRACT

A research program aimed at the development of a molten salt thermal energy storage system commenced in June 1976. This topical report describes work performed under Task I: Salt Selection. A total of 31 inorganic salts and salt mixtures, including 9 alkali and alkaline earth carbonate mixtures, were evaluated for their suitability as heat-of-fusion thermal energy storage materials at temperatures of 850°F to 1000°F. Thermophysical properties, safety hazards, corrosion, and cost of these salts were compared on a common basis. We concluded that because alkali carbonate mixtures show high thermal conductivity, low volumetric expansion on melting, low corrosivity and good stability, they are attractive as heat-of-fusion storage materials in this temperature range. A 35 weight percent Li_2CO_3 -65 weight percent K_2CO_3 (50 mole percent Li_2CO_3 - 50 mole percent K_2CO_3) mixture was selected as a model system for further experimental work. This is a eutectoid mixture having a heat of fusion of 148 Btu/lb (82 cal/g) that forms an equimolar compound, LiKCO_3 . The Li_2CO_3 - K_2CO_3 mixture is intended to serve as a model system to define heat transfer characteristics, potential problems, and to provide "first-cut" engineering data required for the prototype system.

The cost of a thermal energy storage system containing this mixture cannot be predicted until system characteristics are better defined. However, our comparison of different salts indicated that alkali and alkaline earth chlorides may be more attractive from a salt cost point of view. The long-term corrosion characteristics and the effects of volume change on melting for the chlorides should be investigated to determine their overall suitability as a heat-of-fusion storage medium.

OBJECTIVE AND SCOPE OF WORK

The objective of this work is to determine the feasibility of using a mixture of carbonate salts to store thermal energy by utilizing, primarily, the enthalpy change (heat-of-fusion) occurring at the melting point of the mixture in the temperature range of 850°F to 1000°F.

The work will include —

- The selection of a carbonate mixture
- The formulation of the heat exchange and storage equations governing the thermal fluxes, and parametric analysis using these equations to determine the effects of using inert supports to contain the carbonates and conductivity enhancers to improve the thermal conductivity of the carbonates
- Design and operation of laboratory-sized thermal energy storage systems (TES) to —
 - a. Verify the model analytical thermal equations derived and validate the use of inert supports and conductivity promoters
 - b. Provide "first-cut" engineering data required for the design of prototype thermal energy storage hardware
- Evaluation and analysis of the data generated.
- Recommendations for further work.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Introduction

The storage of energy available when demand is low for later use when demand is high is an important aspect of an efficient and economical energy system. The daily and seasonal variation in energy use combined with the increasing demand for energy has provided a greater incentive for the development of energy storage systems. The increasing demand, resulting from our growth in population and technology, causes concern in light of the diminishing availability of our energy resources, which are composed primarily of fossil fuels: coal, oil, and natural gas. Because they are fuels, supplying energy for conversion to more usable forms, they represent our current primary energy storage media. These resources are in demand because they have been readily available, easily transported from the source to the point of demand, and are easily converted to other forms of energy. However, our demand for energy has now surpassed the supply of these prime energy sources, so we must develop the methodology needed to increase the efficiency in the extraction and conversion of energy from these fuels, and to utilize other energy resources such as solar and nuclear energies. The development of storage systems to meet these requirements has therefore become essential.

Energy Storage Systems

Energy is stored several times during the course of extraction to end use, as shown in Figure 1.

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Figure 1. ENERGY FLOW AND STORAGE AT VARIOUS STAGES¹⁴

At present storage is primarily in the form of fossil fuels; however, advanced storage methods would be applicable if viable storage means were developed. They involve storage of energy as electrical, chemical, mechanical, and thermal energy in systems such as batteries, flywheels, "pumped hydro", compressed air, sensible heat, heats of reaction, heats of fusion, and superconducting electromagnets. Unfortunately, geographical, economical, environmental, and material specifications impose severe limitations on the practicality of many of these storage methods in their current and near-projected states of development.¹⁶ These limitations and the applications of the total energy system in which the storage system will be incorporated, make it difficult to predict which advanced method is the most suitable. Conceivably, more than one advanced storage method may be developed to fulfill the variety of end use applications. In the present study, we are concentrating our efforts on thermal energy storage for several reasons:

1. Thermal energy storage is readily adaptable to a number of applications, such as
 - Utility load leveling
 - Space heating
 - Solar applications
 - Industrial waste heat recovery
 - Vehicular transportation
 - Energy transportation.
2. It is conceptually simple.
3. Several other methods require conversion of thermal energy to electrical energy before storage. The electrical energy is then converted to chemical energy in a battery or is converted to potential or kinetic energy through pumps or motors. Inefficiencies in the thermal-to-electrical energy conversion are compounded by inefficiencies that may exist in the conversion of stored energy to usable energy.
4. A large number of low-cost materials are applicable to thermal energy storage systems.
5. Thermal energy is available over a wide range of temperatures, and there are possible thermal energy storage methods applicable to these ranges.
6. Supportive methodology, such as heat exchanger design, is relatively well developed.

7. High storage capacities in small volumes are obtainable at elevated temperatures.
8. Thermal energy is available from a variety of sources: from geothermal, solar, and combustion sources, nuclear reactors, and from industrial process or waste heat.
9. Most of our present power generation systems are based on the conversion of thermal energy.

Thermal Energy Storage Systems

Thermal energy may be stored as the heat required to induce a temperature change, a phase change, or a chemical change in a storage material. The first method utilizes heat capacities of thermal capacity materials (TCM); the second utilizes heats of fusion of phase change materials (PCM); the third utilizes heats of reaction of chemical change materials (CCM). Each method can be adapted for use over a wide temperature range by selection of the appropriate storage medium. The temperature range over which a particular storage method is best suited will, however, depend upon the end use of the stored energy and the ease of storage material optimization for that use. The broad temperature spectrum over which thermal energy storage systems may be applied can, therefore, be divided into four general ranges according to the end use of the stored energy:

<u>Temperature Range</u>	<u>Use</u>
Subambient	Cooling
Ambient to 200°F	Heating and Cooling
200°F to 600°F	Commercial/Industrial Application
600°F and above	Power Generation and High Temperature Processing

The applicability of a storage method for a particular use may then be evaluated by the system performance within the corresponding temperature range. Conversely, the use for which a particular storage method is best suited may be determined by the temperature range over which performance is optimum. For example, shaft power from a heat engine can be produced by heat exchange with a storage system (Figure 2) and can be considered the highest quality use of the stored thermal energy. However, the heat engine efficiency is a function of the temperature of input energy (Figure 3). Therefore, a storage method displaying optimum performance above 600°F, such as molten salt

heat of fusion, would be best suited for this application. The following are discussions of different thermal energy storage methods, their basis of operation, and performance limitations.

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Figure 2. THERMAL STORAGE SYSTEM FOR SHAFT POWER APPLICATION^{1a}

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Figure 3. WORK EFFICIENCY USING HEAT AVAILABLE AT TEMPERATURE T AND REJECTING HEAT AT 100°F
(Adapted from Reference 11)

Sensible Heat Thermal Energy Storage

Sensible heat is the simplest method of thermal energy storage and the most widely used today. Its primary application is in space heating, and to a lesser degree, in industrial waste heat recovery. Heat is stored by passing a heat transfer medium, frequently hot air or combustion products, through the thermal storage medium (TCM). Heat is absorbed by the TCM, causing

a temperature change proportionate to the TCM heat capacity and amount of material. The operating temperature range is limited by the melting point of the TCM or the entering temperature of the transfer medium. Porous beds of stone pebbles, refractory brick checkerwork, and water are the most commonly used materials for sensible heat storage. Heat capacities are generally low (< 4 Btu/lb $^{\circ}$ F, or often less than 1 Btu/lb $^{\circ}$ F), requiring large masses and volumes of a TCM relative to the storage capacity. The volumes and weights of MgO and steam, both TCM's, required to store one million Btu are compared to those of a PCM, molten salts, in Table 1.

Table 1. WEIGHT AND VOLUME OF MEDIUM REQUIRED FOR STORAGE OF 10^6 Btu THERMAL ENERGY IN TCM AND PCM (Storage Medium Operating Between 800 $^{\circ}$ F and 1000 $^{\circ}$ F)¹⁸

Medium	Pressure	Weight, lb/ 10^6 Btu	Volume cu ft/ 10^6 Btu
Molten Salts (Carbonates)	Atmospheric	4,500	39
Steam	100 psia	10,000	80,000
MgO	Atmospheric	22,000	100

The large volume and weight requirements of TCM's may be tolerable for small-scale applications, but they are not practical for large-scale applications.

Heat-of-Fusion and Heat-of-Reaction Thermal Energy Storage

Heat of fusion and heat of reaction thermal energy storage become most attractive when a large capacity is required. This is due to high storage capacities resulting from the large enthalpy changes accompanying fusion or reaction of storage materials. Both of these methods can also take advantage of sensible heat storage in heating the storage materials to their fusion or reaction temperatures. Both of these methods store energy in the breaking of interatomic bonds, but differ in the types of bonding and the energies associated with each. The stored energy is recovered by the re-forming of these bonds. Each method also has drawbacks. Thermal energy stored as heat of fusion in a PCM must be stored at or above the fusion temperature. This will result in lowered efficiency due to heat losses to ambient surroundings, or cause higher system costs to provide sufficient

insulation to minimize these losses. Fusion is also accompanied by substantial volume increases that can complicate containment designs or lead to only partial system utilization. Volume changes can be partially controlled by the addition of an inert supporting material to the PCM, but some storage capacity would be sacrificed.

Thermal energy stored as the heat of reaction in a CCM requires the reaction products to be separated if storage (or transportation) at ambient temperatures to prevent heat loss is desired. This creates problems in both separation and storage of the products. The problem of separating reaction products has been eliminated by considering systems that yield a solid or liquid along with a gas that may be removed by pressure control. This requires pressure control systems as well as additional containment facilities, both of which increase the overall system complexity and capital cost. Storage of the gaseous products can also be accomplished by using reaction pairs in which the gas is a common reactant, such as in metal hydrides,¹⁰ ammoniated salts,¹² or hydrates and hydroxides⁸. The gas produced by the primary reaction is separated and reacted with the secondary storage material. This method results in high density gas storage without compression; however, some storage capacity is also sacrificed.

A total thermal energy storage system may incorporate both of these storage methods. Heat-of-reaction storage has a somewhat higher specific capacity, energy can be delivered over a range of temperatures and can be stored efficiently for longer periods of time, but system costs will be higher. Heat of fusion storage delivers energy at a constant temperature, utilizes sensible heat storage more fully, is simpler conceptually, and may have lower costs associated with system construction and maintenance. Several pertinent questions relative to both methods have yet to be answered. They refer primarily to cyclability and life of the storage materials, and system design. The purpose of Task I of the program is to select a model salt composition for use as a PCM in studying these questions as they pertain to heat-of-fusion thermal energy storage. Inorganic salts have been selected as the PCM because of the many low cost, heat-of-fusion systems with compositions whose melting points are compatible with temperatures at which heat for storage is, or will be, produced. The information gained using the selected salt will then be applicable to other candidate salt systems.

Considerations for Heat-of-Fusion Thermal Energy Storage

The storage of thermal energy at high temperatures is desirable for several reasons. The quality of stored heat is measured by its temperature, especially when used as "fuel" for heat engines. Higher temperatures represent higher quality heat and result in higher efficiencies in power production using heat engines (Figure 3). Storage of thermal energy at temperatures above 600°F is required for a number of applications:

- a. Storage of thermal energy from solar concentrators
- b. Storage of thermal energy from several types of base-load power plants
- c. Storage of thermal energy from cyclic- or batch-type industrial processes
- d. Storage of thermal energy for vehicular propulsion using heat engines.

In application b, base-load thermal generation may be increased (higher plant factors) and surplus thermal energy stored to meet peaking demand. In this application, the stored energy would have to be extracted over a short period of time (4 to 6 hours), requiring high heat fluxes. Heat flux is directly proportional to the temperature gradient existing between storage and heat transfer materials. Thermal energy stored at higher temperatures would, therefore, facilitate the generation of the heat fluxes demanded, without the addition of a heat transfer area, as may be required if lower temperature storage were implemented.

In the present study, we are concentrating our efforts on the viability of heat-of-fusion thermal energy storage for applications a and b because the potential near-term benefits are greatest in these applications. The desired useful temperature range of the storage media for these applications is expected to be 850°F to 1000°F. Accordingly, storage materials whose fusion temperatures (melting points) are between 850°F and 1000°F will be considered.

In selecting an appropriate storage material, several factors must be considered:

- Heat of fusion
- Thermal conductivity (solid and liquid)
- Heat capacity (solid and liquid)

- Volumetric thermal expansion
- Volume change on fusion
- Cost and availability
- Containment Materials
- Stability (solid and liquid)
- Safety.

The relevance of each of these factors to performance and life of a storage system becomes evident when the mode of operation of a heat-of-fusion thermal energy storage system is examined.

The energy storage is accomplished by the transfer of heat from a source (solar concentrator, reactor, blast furnace, boiler, etc.) to the storage medium (PCM) by some transfer medium (possibly air or steam) in appropriate heat exchange devices. The energy is stored as sensible heat while the PCM is heated to the fusion temperature, and as heat of fusion at the fusion temperature. In many practical applications requiring high quality heat, the storage temperature would be cycled around the PCM melting point, storing energy during fusion and recovering the energy during solidification. Thus the stored heat is available at an almost constant temperature, and the quality of heat is not degraded. Thus a majority of the sensible heat would not be recovered, but would be available as a reserve. The importance of storage material properties (PCM) in this mode of operation will be discussed.

Thermal Properties

The important thermal properties of storage materials include the heat of fusion, thermal conductivity, and heat capacity. These factors determine the suitability of a material to heat-of-fusion thermal energy storage from the point of storage capacity and heat-transfer characteristics. The heat of fusion (Btu/lb) determines the storage capacity of a material, and the thermal conductivity (Btu/hr-ft²F) of the liquid and solid phases will determine charging and discharging rates obtainable, and affect the complexity (and cost) of heat exchanger design. Materials with high heats of fusion and thermal conductivities will be desirable as they represent high-capacity systems which can be charged and discharged rapidly without the need for complex and costly heat exchange systems. High heat capacities, although

of secondary importance, are also desirable because they are indicative of storage capacity above the heat of fusion and reserve capacity.

Physical Properties

Storage material physical properties of interest are density, volume change with temperature (volumetric expansion), volume change on fusion, viscosity of the liquid phase, and vapor pressure. The density (lb/cu ft) and heat of fusion (Btu/lb) determine the specific capacity, or stored energy density (Btu/cu ft). This can have a strong effect on system design. If the specific capacity is low, large volumes of storage material will be required to meet storage requirements, or capacity will be limited by space availability. Configuration of heat exchange surfaces that may be satisfactory for a high specific capacity material may not be able to meet heat-flux requirements, because of increased thermal diffusion distances, to melt or solidify a low specific capacity material, leading to more costly heat-exchange systems. Volumetric thermal expansion must be considered in container design to compensate for the storage material volume change while heating from ambient temperature to the operating temperature range. Most materials exhibit an increase in volume upon fusion. The continuous thermal cycling through the melting temperature of a storage material will be accompanied by cyclic volume changes. If these volume changes are large, difficulties in containment may arise or voids may form in the storage material during solidification that will have detrimental effects on the conducting properties, causing losses in efficiency, charging rates, and possibly capacity. Viscosity of the liquid phase near the melting temperature, and of the liquid-solid slurry that may develop at the melting temperature, is important because of its effect on convective currents that may develop while the PCM is in these states. These currents, brought about by temperature variations in the PCM, aid in heat transfer and in homogenization of the storage material. The vapor pressure of either the storage material or a decomposition product at the operating temperature is a minor consideration, but it does reflect the stability of the storage material and the losses that might result from a leak in containment vessels. The storage system design may be affected by the vapor pressures of the PCM at operating conditions. Ideally, a heat-of-fusion storage material will have a high specific capacity, little volumetric thermal expansion or volume change

on fusion, and low viscosity and vapor pressure in the working temperature range.

Cost, Containment, Safety, and Stability

The storage material cost, although only a small part of the overall system cost, must be considered because of its effect on the economic feasibility of a system, and because it reflects the availability of the storage material. The toxicity and compatibility of the storage material with the heat-transfer medium must also be considered because possible system failures cannot be disregarded⁹ that may release storage materials into surrounding areas, or bring storage and heat transfer materials into contact. Toxic fumes or violent chemical reactions resulting from such system failures can produce harmful effects on life and environment. Containment of storage materials becomes problematical because of -

- a. The corrosive activity of molten storage materials
- b. Volume changes accompanying temperature changes in the storage material
- c. Volume changes accompanying fusion of storage materials.

If any of these storage material characteristics becomes excessive, complex containment designs or specialty containment materials may be required, challenging the feasibility of the overall system. Storage materials that show low corrosion of low-cost containment materials are desirable in maximizing the life of a storage system. Lifetimes of 20 to 30 years will be required if storage systems are to function dependably in commercial systems. This lifetime requirement necessitates good stability of thermal and physical properties in a storage material. Variations in these properties will lead to unpredictable performance over a storage system's lifetime that may or may not be compensated by other total system characteristics.

Inorganic Salts as Phase Change Materials

Inorganic salts and salt mixtures show great potential as phase change materials (PCM) for use in high temperature heat-of-fusion thermal energy storage systems because -

- a. The melting points are in the proper temperature range (850°F to 1000°F). This means that the relatively high latent heats of melting (>100 Btu/lb) can be utilized, leading to compact system sizes, and that the heat is available at a constant temperature (at the melting point), providing good quality input into a thermal engine.

- b. They have good heat-transfer coefficients, resulting in efficient heat transfer and thermal management.
- c. They have low vapor pressures, resulting in simple low-pressure design and potentially long usable lifetimes.

In using salt mixtures, other material considerations must also be made. The first of these is whether a eutectic or a noneutectic composition will best satisfy the property requirements. Noneutectic compositions melt incongruently, that is, the solid forms a liquid and another solid of different composition. This effect may be advantageous in that the second solid phase formed in the liquid could act as a nucleating agent during solidification of the liquid, preventing supercooling effects. However, the different compositions of the solid and liquid will also have different densities, which may result in separation by settling of the solid, producing a wide composition variation throughout the storage medium. This problem could be alleviated by some type of agitation, but that would only lead to increased system costs. Eutectic compositions melt congruently, so this problem would not be encountered if one were used.

The change in melting temperature of a salt mixture as a function of composition within a system is also of primary importance. Composition variations within a storage material system may occur as a result of corrosion reactions or vapor losses if any leaks develop in the storage system. Changes in the melting temperature (generally increases) can result in longer charging times and heat recovery at varying temperatures. If the melting temperature increases sufficiently, fusion may not even be obtainable with the heat source for which the storage system was designed to operate. In this extreme case, storage capacity could be decreased significantly and the system would actually be converted to a sensible-heat storage system.

Thermal conductivities and volume changes occurring during operation are important considerations in determining the practicality of a salt as a PCM. Although these properties are characteristic of the salts, they may be modified in the storage system by the addition of inert materials to the salts. Metals have relatively high thermal conductivities. The addition of metallic screens, wires, rods, or tubes to the salt would enhance the overall heat transfer properties, although some capacity would be lost. The volume change on fusion of the total storage system can also be controlled by the

addition of ceramic supporting material to the salt. The weight percent of support material required to eliminate this volume change may, however, result in a significant loss of capacity. In selecting materials as additives for these purposes, heat capacities and thermal conductivities should be maximized. Compatibility of the PCM with such additives should also be considered when selecting the heat-of-fusion storage materials.

Some work has already been carried out in developing heat-of-fusion thermal energy storage systems using salts as the storage material. The results of this work are discussed in the following section.

Status of Latent Heat Thermal Energy Storage at Temperatures Above 600°F Utilizing Salts as Storage Materials

Although scores of thermal energy storage programs are now underway worldwide, only a handful are studying the use of high temperature molten salt systems. Some laboratory work has been carried out in connection with space-vehicle solar energy storage^{5, 20, 21, 23} wherein lithium hydride (mp 1256°F) was used as a storage system. Another system was developed for underwater propulsion for the Navy⁷ utilizing LiF/LiOH eutectic mixture as a storage medium. This eutectic mixture was selected because of the very small volume change at the melting point. No data, however, has been reported for either of the above systems under actual operating conditions.

Two of the more advanced studies for application of high temperature molten salt storage systems are for 1) vehicular applications (Philips Research Laboratory^{22, 27, 28, 30} in West Germany) and for 2) space heating and industrial hot water systems (Comstock and Wescott^{6, 24} in Cambridge, Mass.).

Most of the work done by Philips has been performed with fluoride mixtures having melting points between 1100°F and 1450°F for the purpose of supplying thermal energy to a Stirling engine for vehicular applications. High melting points are desirable because the efficiency of the thermal engine improves with the supply temperature; the attainment of the higher temperature is possible because the thermal input is supplied by fuel combustion. The high latent heats provided by the fluorides combined with their high melting points have resulted in some very compact and efficient vehicular power plant designs (Figure 4).

HM-18

Figure 4. PHILIPS RESEARCH LABORATORIES THERMAL ENERGY STORAGE SYSTEM²²

HM-15

Figure 5. COMSTOCK AND WESCOTT THERMAL ENERGY STORAGE SYSTEM⁶

Philips states that the fluorides exhibit good thermophysical characteristics, no supercooling is observed, and there is very little tendency for phase separation due to sedimentation, etc. In addition, when a small amount of aluminum is added to the fluoride melt as a corrosion inhibitor, no corrosion of 18/8 stainless steel is observed at 1560°F for long periods of time. Obtaining a cost-effective thermal insulation, improving the thermal conductivity of the salt mixtures, and eliminating the need for argon pressurization of the salt-containing module to prevent collapse of the module due to contraction of the salt during solidification (~ 20% to 30%) appear to be some of the problems facing the Philips researchers.

Comstock and Wescott,^{6, 24} in cooperation with Edison Electric Institute, designed and tested a number of electrically heated thermal storage units using sodium hydroxide during the early 1960's. The purpose of the program was to determine the feasibility of storing off-peak electricity via thermal energy storage for use in supplying heat pumps. The storage units (Figure 5) operated between approximately 265°F and 900°F and supplied a total of 420,000 Btu at a heat rate of approximately 20,000 to 30,000 Btu/hr. Some of these units were later supplied to Philadelphia Electric Co. Results of the testing of these units were reported by Philadelphia Electric Co. in a recent survey study,¹ and indicated that a number of component and design problems were discovered that caused the program to be terminated on the basis that "it [thermal storage] was found to be costly and impractical." Mr. Rice,²⁵ the program manager for Comstock and Wescott, recently indicated that these storage problems were not as severe as reported and that economics and the state of technical development of the heat pump were the primary causes for program termination. Mr. Rice further indicated that the thermal storage program since 1965 has been sponsored by Hooker Chemical Co., and that sufficient progress has been made so that cost-effective operation for operating times of 20 years is presently being projected.

More recently, Honeywell Corporation in Minneapolis has initiated a study,^{17, 29} "The Use of Thermal Energy Storage for Solar Power Plant." They have selected salts with melting points between 400°F and 550°F, primarily nitrates or their mixtures with chlorides, hydroxides, or sulfates. Researchers at Honeywell feel that because of possible passivation by nitrates, a mild steel material may be suitable for containment³². Both eutectic and noneutectic mixtures are being considered and also the use of an external

"homogenizer" to even out any phase separation. Mechanical scrapers may be used to improve the heat transfer coefficient during the heat-removal cycle.

Other recently proposed systems include a) NaF-FeF₂ (mp 1260°F) by General Electric,^{4, 10} and b) a germanium sulfide compound,³¹ Ge_{0.4}S_{0.6}. Both of the systems are in conceptual stages only; the technoeconomic feasibility of these systems has not yet been established.

Based on the present status of high-temperature latent-heat thermal-energy storage, it appears that no system in the temperature range of 850°F to 1000°F has been, or is being, developed, and that studies to define heat-transfer characteristics, cycle life, etc., in this temperature range are expected to be valuable.

Evaluation of Candidate Storage Materials

The compositions of 31 candidate salts are presented in Table 2 with the experimental or estimated* values of properties relevant to their applicability as heat-of-fusion thermal energy storage materials. The salts listed were selected for consideration in this study because their melting points fall in or near the temperature range of interest (850°F to 1000°F), and they do not display any particular difficulties in handling, containment, stability, or availability. Some salts that are applicable to thermal energy storage at temperatures either well below or above the temperature range of primary interest have been included for comparative purposes. The materials under consideration include single salts and binary and ternary salt mixtures of both eutectic and noneutectic compositions, with and without an ionic species common to each component. Quarternary systems were not investigated due to the lack of pertinent thermal behavior data and suitable procedures for the estimation of properties needed for evaluation.

The purpose of this task is to -

- a) Identify salts or salt mixtures having desirable thermophysical characteristics for heat-of-fusion thermal energy storage and,
- b) To select a salt for experimental study in Task III of this program, wherein we plan to develop the methodology and technology for studying the feasibility of heat-of-fusion thermal energy storage systems at high temperatures.

* Refer to Appendix for estimation procedures.

Table 2. PROPERTIES OF SELECTED SALTS

Composition	Salt ^b	Melting Point, °F	ΔH_f , Btu/lb	Heat Capacity at Melting Point		Thermal Conductivity at Melting Point		Viscosity, cP		Density at 25°C lb/cu ft	Volume Change On Fusion at mp, %	Safety Hazard ^d (Inhalation)	Containment Material	Salt Cost, \$/lb	Capacity Cost, \$/10 ⁶ Btu	Specific Capacity ^h (based on ρ at 25°C) Btu/cu ft	Comments	Composition
				$C_p(s)$	$C_p(l)$	$k(s)$	$k(l)$	At Melt- ing Point	Melting Point + 50°F									
1	LiOH	864	376	0.59	0.94					91.1		2	Mild Steel ^g	1.97	5,265	34,265		1
2	LiBr	1017	88	0.26	0.18		0.23	1.8	1.7	216.0		2 ^e	SS	3.00	33,335	19,010		2
3	NaOH	606	69	0.48	0.51		0.53	4.8	4.0	133.0		2 ^f	Mild Steel ^g	0.12	1,740	9,110	- Comstock Wescott System ⁶⁻²⁴	3
4	B ₂ O ₃	842	142	0.41	0.44	0.90	0.58			115.5		1	SS	0.19	1,755	16,400		4
5	54KCl-46ZnCl ₂	810	94	0.16	0.21		0.48	406	208	150.5	17.5 ^c	2 ^e	SS	0.27	1,820	14,100		5
6	61KCl-39MgCl ₂	815	151	0.19	0.23		0.47			131.7	23.6 ^c	2 ^e	SS	0.06	395	19,915		6
7	98NaCl-52MgCl ₂	842	185	0.22	0.24		0.55			139.1	27.6 ^c	2	SS	0.08	430	25,685		7
8	36KCl-64MgCl ₂	878	167	0.20	0.23		0.48			137.3	26.2 ^c	2 ^g	SS	0.09	540	22,860		8
9	33NaCl-67CaCl ₂	932	121	0.20	0.24		0.59	30	14	134.8	14.5 ^c	1	SS	0.03	281	16,350		9
10	37MgCl ₂ -63SrCl ₂	995	103	0.16	0.19		0.61			173.6	16.3 ^c	2	SS	0.33	3,225	17,880		10
11	47Li ₂ CO ₃ -53K ₂ CO ₃	910	147	0.26	0.32		1.15	21	17	137.3	8.5	2	SS	0.47	3,225	22,860		11
12	44Li ₂ CO ₃ -56Na ₂ CO ₃	925	159	0.43	0.50		1.21	23	19	144.8	13.5	2	SS	0.35	2,229	22,980		12
13	28Li ₂ CO ₃ -72K ₂ CO ₃	928	113	0.35	0.43		1.07	17	15	139.8	9.3	2	SS	0.36	3,175	15,770		13
14	51K ₂ CO ₃ -49Na ₂ CO ₃	1310	70	0.40	0.37		1.00	5.4	5.2	149.8		2	Protected SS	0.11	1,597	14,230		14
15	33LiF-67KF	918	266	0.32	0.39	2.4-4.8	2.30			157.9		3 ^g	316 SS ^g	1.21	4,545	42,065		15
16	67NaF-33MgF ₂	1530	265	0.34	0.33	2.4-4.8	2.69			133.6	22.8	3 ^g	316 SS ^g	0.57	2,150	35,405	Phillips System ^{22, 27}	16
17	45NaBr-55MgBr	808	91	0.12	0.14		0.52			217.9		2 ^g	316 SS	1.62	18,180	19,765		17
18	20LiF-80LiOH	799	374	0.21	0.24					99.9		3	300 Series SS	2.06	5,555	37,395		18
19	25KCl-27CaCl ₂ -48MgCl ₂	909	147	0.19	0.22		0.51			157.9	20.5 ^c	2 ^g	SS	0.08	539	23,245		19
20	5KCl-29NaCl-66CaCl ₂	939	120	0.28	0.24		0.58	17	13	134.2	12.2 ^c	2 ^g	SS	0.03	283	16,070		20
21	13KCl-19NaCl-68SrCl ₂	939	96	0.16	0.20		0.61	198	22	171.7	12.9 ^c	2 ^g	SS	1.37	14,285	16,485		21
22	28KCl-19NaCl-53BaCl ₂	1008	95	0.15	0.19		0.50	107	71	189.2		2 ^g	SS	0.09	945	18,050		22
23	24KCl-47BaCl ₂ -29CaCl ₂	1024	94	0.16	0.20		0.55	96	68	182.9		2 ^g	SS	0.09	985	17,140		23
24	32Li ₂ CO ₃ -35K ₂ CO ₃ -33Na ₂ CO ₃	747	119	0.40	0.39		1.17	171	60	143.6		2	SS	0.33	2,741	17,835		24
25	12NaF-59KF-29LiF	849	257	0.32	0.38	2.4-4.8	2.60			157.9		3 ^g	316 SS ^g	1.11	4,350	40,630		25
26	40KCl-23KF-37K ₂ CO ₃	982	122	0.24	0.30		0.69			142.5		3 ^g	SS	0.23	1,885	17,395		26
27	17NaF-21KCl-62K ₂ CO ₃	968	118	0.28	0.33		0.87			148.9		3 ^g	SS	0.18	1,525	17,600		27
28	35Li ₂ CO ₃ -65K ₂ CO ₃	941	148	0.32	0.42		1.09	18	15	141.5	9.6	2	SS	0.40	3,175	17,875	Eutectoid	28
29	20Li ₂ CO ₃ -60Na ₂ CO ₃ -20K ₂ CO ₃	1022	122	0.38	0.45		1.05	4.1	3.7	148.6		2	SS	0.21	1,705	18,460	Non-Eutectic	29
30	22Li ₂ CO ₃ -16Na ₂ CO ₃ -62K ₂ CO ₃	1022	124	0.43	0.50		1.13	3.9	3.5	146.3		2	SS	0.30	2,410	17,770	Non-Eutectic	30
31	68K ₂ CO ₃ -32MgCO ₃	860	--	--	--	--	--	--	--	--	--	--	--	--	--	--	Phase diagram determined at high pressure only.	31

^a Values underscored are experimental. Other values are estimates.^b Mixture composition on weight basis.^c Estimated from experimental values of single salts.^d Toxic hazard rating code: 0: None, 1: slight, 2: moderate, 3: high, U: unknown (see Appendix.)^e When strongly heated, they emit highly toxic fumes.^f Will react with water or steam to produce heat and will attack living tissue.^g Suggested material if suitable corrosion inhibitors are used.^h Based on ΔH_f value only.

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For the latter purpose, the salt compositions whose thermophysical properties are most conducive to accurate heat flux measurements and maximum system sensitivity, and for which first-hand knowledge on the variation of time and temperature dependent behavioral characteristics is readily available, will be heavily favored. However, every reasonable attempt will be made to ensure the practicality of the salt composition selected, and to select a salt most representative of all of the compositions considered, so that results obtained will be readily adaptable to other heat-of-fusion thermal energy storage materials. Our rationalization for salt selection is presented below.

Cost, Specific Capacity, and Safety

Cost, specific capacity, and safety become primary considerations when evaluating the practicality of salts for thermal energy storage on a large-scale industrial or commercial basis. The capacity cost ($\$/10^6$ Btu) as a function of volume (cu ft/ 10^6 Btu) of those salts presented in Table 2 are shown graphically in Figure 6. The practicality of very high capacity-cost salts for large-scale applications is questionable due to the importance of salt cost in determining the degree to which a thermal energy storage system can be economically competitive with alternative energy storage systems. The highest capacity-cost salts are composed of bromides, fluorides, and hydroxides (compositions 1, 2, 15, 17, 18, 21, and 25). The lowest capacity-cost salts are composed entirely of mixtures of alkali and alkaline earth chloride salts (compositions 6, 7, 8, 19, and 22), whereas moderate to high capacity-cost salts are composed of carbonate salt mixtures (compositions 11, 12, 13, 14, 24, 28, 29, 30) and mixtures of carbonate and some chloride and fluoride salts (compositions 5, 9, 10, 20, 23, 26, and 27). However, several of these low to moderate capacity-cost salts emit highly toxic fumes when heated (compositions 5, 6, 8, 19, 20, 22, 23, 26, and 27), presenting potential safety hazards that would place further restrictions on their use and increase the cost of containment to prevent any leakage.

Thermal Properties

The latent heat of fusion and heat capacities of a storage material define the material's storage capacity and are critical parameters. The higher

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the values of these parameters, the greater the storage capacity. The thermal conductivities of both the solid and liquid phases of the storage material are also critical because they determine the heat-transfer areas required to meet charging and discharging rates required for optimum performance. For a given rate, a low thermal conductivity material will require greater heat-transfer areas, and consequently more elaborate and costly heat-exchange systems, than a higher thermal conductivity material.

Fluoride salts (compositions 15, 16, and 25) and lithium hydroxide (compositions 1 and 18) exhibit the highest heats of fusion, and thermal conductivities, and moderate to high heat capacities. These salts appear ideally suited for thermal energy storage, but their high costs and toxicity make them questionable. Chloride and carbonate salt compositions have nearly equal heats of fusion although they are much lower than those of the fluorides. The heat capacity of the solid phase, reflective of sensible heat storage capacity, and the thermal conductivity of the liquid phase, indicative of heat transfer rates, are plotted in Figure 7 for chloride and carbonate salt compositions. Carbonate salt mixtures are superior to chlorides with respect to both of these properties by a factor of two in each case. These properties will play an important role in determining the accuracy of heat flux measurements.

Physical Properties, Containment, and Stability

Reliable experimental values of the physical properties (vapor pressure, viscosity, and volume change on fusion) for salt mixtures are scarce and often inconsistent. Values of these properties for some single salts contained in salt mixtures under consideration are available,¹³ and give some indication of the properties of the mixtures. Volume changes on fusion ($\Delta V/V_{\text{solid}}$) for chlorides range from less than 1% (CaCl_2 , 0.1%) to approximately 30% (MgCl_2 , 30.5%). The chloride mixtures that look most attractive from a cost standpoint (compositions 6, 7, and 8) contain magnesium chloride, potassium chloride, and sodium chloride, which have $\Delta V/V_{\text{solid}}$ values of 30.5%, 20.2%, and 25.6%, respectively. Large volume changes on fusion of the mixtures would be expected ($>20\%$) from the large volume changes of the single salts. However, carbonates show smaller total volume changes on heating from room temperature (77°F) to well above their melting points

Figure 7. THERMAL CONDUCTIVITY VS. HEAT CAPACITY FOR CHLORIDE AND CARBONATE SALT MIXTURES

(Li_2CO_3 , 15.6%; K_2CO_3 , 21.0%). Aside from the smaller volume changes observed in carbonates, inert support material that can be added to the salts to further decrease the volume change has already been developed at the Institute of Gas Technology (IGT) for use with carbonate mixtures. Binary carbonate mixtures also show lower melt viscosities than chloride mixtures, particularly near the melting points. In addition, vapor pressures of single chloride salts appear relatively high,* and some salts emit highly toxic vapors. These same characteristics might be expected for mixtures containing those salts.

Long-term studies of the corrosivity and stability of molten salts have not been undertaken for most of the candidate salt mixtures. Short-term (<1000 hours) tests have shown adequate passivation of stainless steels in the presence of molten chlorides. No information is available on the long-term stability of molten chlorides at high temperatures or with repetitive thermal cycling through the melting point. On the other hand, extensive research carried out at IGT and elsewhere† has shown that the 300 series stainless steels are compatible with alkali carbonate mixtures for periods of over 5 years, and the corrosive properties of these carbonate salts have been well characterized. Thermal cycling of these same carbonate mixtures has shown that no significant variation in composition occurs even after several cycles.

* See Appendix for vapor pressure estimation.

† See Appendix for a discussion of corrosion characteristics of carbonates.

CONCLUSIONS

Considering the cost and safety requirements for suitable heat-of-fusion thermal energy storage salts, mixtures of lithium, potassium, and sodium carbonates or sodium, calcium, and magnesium chlorides are the most practical of the salts studied for this application. However, the thermal properties of mixtures of carbonate salts, particularly their superior thermal conductivities and smaller volume changes on fusion, make them best suited as model storage materials in the 850°F to 1000°F temperature range. To prevent complications due to sedimentation or phase separation, a congruently melting composition should be studied, and in light of the extensive research already carried out at IGT^{15, 19} with respect to the stability, corrosivity, and volume change control of salts in the lithium carbonate-potassium carbonate system, a salt composition in this system would be most appropriate for modeling studies.

The phase diagram for the lithium carbonate-potassium carbonate system is shown in Figure 8. Three candidate storage material compositions are in this system: two eutectic compositions (numbers 11 and 13) and one eutectoid composition (number 28), all of which melt congruently. Composition 13, 28 weight percent lithium carbonate - 72 weight percent potassium carbonate, shows the lowest heat of fusion, thermal conductivity, and specific capacity of the three compositions, and so may be eliminated from further consideration. The thermal and physical properties of compositions 11 and 28 are nearly identical. However, several of these properties (heat of fusion and liquid and solid heat capacities) have been experimentally determined for composition 28, whereas those for composition 11 have only been estimated and may not be as accurate. Composition 11 shows a higher specific capacity, but also is more expensive. A 2.5 weight percent increase in the lithium carbonate content in composition 11 is sufficient to move the liquidus temperature out of the working range. In comparison, almost an 8 weight percent variation in either component of composition 28 would be required to increase the liquidus temperature above the working range. Aside from these observations, composition 28 is an intermediate compound (LiKCO_3) in this carbonate system, and may show greater stability as a result. In light of these considerations, composition 28, 35 weight percent lithium carbonate - 65 weight percent potassium carbonate (equimolar mixture), will be used as a model storage material in this study.

Figure 8. PHASE DIAGRAM FOR THE Li_2CO_3 - K_2CO_3 SYSTEM

Recommendations for Further Research

The thermal and physical properties of many single salts, particularly when molten, have been studied, but sufficient work has not been carried out to determine these properties for salt mixtures. This is especially true for higher fusion point mixtures that may be applicable to heat-of-fusion thermal energy storage in the temperature range under investigation in the present study (850°F to 1000°F). Standard procedures have already been developed to measure many of these properties, such as heat of fusion, melting point, heat capacity, thermal conductivity, and viscosity, but design work will be required to more accurately determine some properties, such as volume changes on fusion, which are primary system design considerations. Work should be carried out to measure these properties and design more advanced equipment to obtain more accurate values. Furthermore, work should be carried out to determine interfacial phenomena occurring between storage and containment materials, and to characterize their effects on system performance.

Various sources^{3, 26} have indicated that storage systems must have a capital cost between \$20 and \$30/kW_e-hr at current fuel prices to be economically competitive with other energy generating processes currently in use. This would require thermal energy storage system costs between \$7 and \$10/kW_{th}-hr (assuming 33% efficiency in thermal-to-electrical energy conversion). If salt costs are assumed to be one third of the total system cost, a suitable salt would have to cost between \$2.50/kW_{th}-hr and \$3.50/kW_{th}-hr to be competitive. This is equivalent to capacity costs between \$725/10⁶ Btu and \$1025/10⁶ Btu. Only two of the thirty-one salt compositions could meet this cost requirement and safety requirements:

48 weight percent NaCl - 52 weight percent MgCl₂

33 weight percent NaCl - 67 weight percent CaCl₂.

However, the low thermal conductivities and large volume changes on fusion are less acceptable properties of these salts. Research should be carried out with these materials to develop conductivity enhancers and volume change control materials that are low in cost and compatible. If carbonate salt mixtures are to be useful under these cost requirements, lower cost systems,

such as the potassium-magnesium carbonate system (the phase diagram for this system has only been studied under a 15,000 psi CO₂ pressure), must be investigated more thoroughly; also, quaternary mixtures of low cost salts must be studied where phase equilibrium characteristics have not yet been determined. With the growing needs for energy storage systems, and the adaptability and practicality of high temperature heat-of-fusion thermal energy storage, extensive research efforts should be instigated in these areas to determine the feasibility of these systems quantitatively.

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APPENDIX. Estimation Procedures and Assumptions

1. Estimation of Heats of Fusion of Salt Mixtures

Heat of fusion is one of the most important characteristics to be considered in the evaluation of salt materials having melting points in the range 850°F to 1000°F. Although the composition of a salt mixture and its eutectic temperature can be ascertained using phase diagrams²⁹ and molten salt characteristics,¹⁵ the experimental values of heats of fusion are not available for most salt mixtures. A procedure to estimate these data is therefore required.

Several estimation methods were considered, and sample estimates using these methods were compared with available experimental data. The methods and some examples are discussed below.

Method 1. Molar Additivity

The mole fraction additivity rule can be stated as —

$$\Delta H_{f,m} = \sum x_i \Delta H_{f,i} \quad (A-1)$$

where

$\Delta H_{f,m}$ = heat of fusion for the salt mixture at its melting point

x_i = mole fraction composition of the single salt i in the mixture

$\Delta H_{f,i}$ = heat of fusion for the single salt i at its melting point.

Method 2. Kirchhoff's Method

The estimation of $\Delta H_{f,m}$ based on molar additivity ($\sum x_i \Delta H_{f,i}$) can lead to significant errors where the melting temperatures of the mixtures are significantly different from those of the pure components. Kirchhoff's formula²⁸ adjusts for the differing liquid and solid heat capacities of the pure components between the melting point of the mixture, $T_{f,m}$, and that of each component, $T_{f,i}$. Therefore —

$$\Delta H_{f,m} = \sum x_i \Delta H_{f,i} + \sum x_i \int_{T_{f,m}}^{T_{f,i}} [C_{p_i}(s) - C_{p_i}(l)] dT \quad (A-2)$$

where

$\Delta H_{f,m}$ = heat of fusion for the mixture at its melting temperature, $T_{f,m}$

x_i = mole fraction of component i in the mixture

$\Delta H_{f,i}$ = heat of fusion for component i at its melting temperature, $T_{f,i}$

$C_{p_i}(s)$ = heat capacity for the solid phase of component i

$C_{p_i}(l)$ = heat capacity for the liquid phase of component i

Equation A-2 can also be written in terms of standard state enthalpies -

$$\Delta H_{f,m} = \sum x_i \Delta H_{f,i} + \sum x_i [(H^0_{T_{f,i}} - H^0_{T_{f,m}})_s - (H^0_{T_{f,i}} - H^0_{T_{f,m}})_l] \quad (A-3)$$

where

$H^0_{T_{f,i}}$ = enthalpy of component i at temperature $T_{f,i}$

$H^0_{T_{f,m}}$ = enthalpy of component i at temperature $T_{f,m}$

Subscripts s and l refer to solid and liquid states of the single compounds.

The term $(H^0_{T_{f,i}} - H^0_{T_{f,m}})$ can be expressed as $(H^0_{T_{f,i}} - H^0_{298})$

$- (H^0_{T_{f,m}} - H^0_{298})$ where H^0_{298} is the standard enthalpy.

Example:

Predict the heat of fusion for 43.5 mole percent Li_2CO_3 - 31.5 mole percent Na_2CO_3 - 25.0 mole percent K_2CO_3 ; the mixture melts at 670°K ($T_{f,m}$).

From data given in the JANAF tables⁴² -

	$T_{f,i}, ^\circ K$	$\Delta H_{f,i}$	$\frac{(H^0_{T_{f,i}} - H^0_{T_{f,m}})_s}{\text{kcal/mole}}$	$\frac{(H^0_{T_{f,i}} - H^0_{T_{f,m}})_l}{\text{kcal/mole}}$	A - B
Li_2CO_3	996	10.7	$(H^0_{996} - H^0_{670})_s$ 13.193	$(H^0_{996} - H^0_{670})_l$ 14.331	-1.138
Na_2CO_3	1127	6.7	$(H^0_{1127} - H^0_{670})_s$ 18.861	$(H^0_{1127} - H^0_{670})_l$ 20.605	-1.744
K_2CO_3	1169	6.6	$(H^0_{1169} - H^0_{670})_s$ 21.623	$(H^0_{1169} - H^0_{670})_l$ 23.516	-1.893
$\Delta H_{f,m} = 0.435(10.7) + 0.315(6.7) + 0.250(6.6)$ $+ [0.435(-1.138) + 0.315(-1.744) + 0.250(-1.893)]$ $= 6.899 \text{ kcal/mole (124.183 Btu/lb)}$					

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Method 3. Estimation Method Based on Entropy-of-Fusion Rule

An empirical rule¹⁶ for estimating ΔH_f , the heat of fusion for inorganic materials, is -

$$\Delta H_f = T_f \Delta S_f \quad (\text{A-4})$$

where

T_f = melting temperature

ΔS_f = entropy of fusion.

The value of ΔS_f is estimated as 3 cal/ g-atom- $^\circ K$ for most compounds.

Thus -

$$\Delta H_f = 3 \cdot n \cdot T_f \quad (\text{A-5})$$

where n is the number of gram atom equivalents in the compound or mixture.

Janz¹⁶ suggested the following procedures to calculate n for a single compound or for mixtures.

If the material is a compound of formula $M_a X_b$, then $n = (a + b)$

Example: NaCl , $n = 2$; MgCl_2 , $n = 3$; NaNO_3 , $n = 2$

For a mixture of three compounds, $A_l B_m C_o D_p$, and $E_q F_r$, then

$$n = x_1 (l+m) + x_2 (o+p) + x_3 (q+r)$$

where

x_1, x_2, x_3 are the mole fractions of the three compounds, respectively.

Example: For a 50 mole percent NaCl -50 mole percent MgCl_2 mixture,

$$n = 0.5 (1 + 1) + 0.5 (1 + 2) = 2.5$$

Method 4. Modified Entropy-of-Fusion Rule

Equation A-5 does not take into account the heat of mixing, ΔH_{mix} , of a salt mixture. The entropy-of-fusion rule can be modified¹⁶ to include ΔH_{mix} :

$$\Delta H_f = (3n) T_f + \Delta H_{\text{mix}} \quad (\text{A-6})$$

If the experimental value of ΔH_{mix} is not available, an empirical formula may be used for binary mixtures:

$$\Delta H_{\text{mix}} = -x_1 x_2 \left[140 \times 10^3 \left(\frac{d_1 - d_2}{d_1 + d_2} \right)^2 \right] \quad (\text{A-7})$$

where d_1 and d_2 are the distances of closest approach of atoms and can be obtained by summing the Pauling values of the ionic radii.

Comparison of Estimation Techniques for ΔH_f

Experimental values of ΔH_f were compared with estimated values for four salt mixtures, as shown in Table A.1.

Table A.1. COMPARISON OF HEAT OF FUSION VALUES OBTAINED BY DIFFERENT ESTIMATION METHODS WITH EXPERIMENTAL VALUES

Salt, mol %	Melting Point, °C	ΔH				
		Experimental Value	Molar Additivity, Method 1	Kirchhoff's Method, Method 2	Heat-of-Fusion Rule, Method 3	Modified Heat-of-Fusion Rule, Method 4
						kcal/mole
58LiCl - 42KCl	354	3.2	5.4	3.2	3.8	3.2
50Li ₂ CO ₃ - 50K ₂ CO ₃	505	8.7	8.9	7.4	7.0	6.7
56Na ₂ CO ₃ - 44K ₂ CO ₃	710	4.7	6.7	5.9	8.8	8.7
43.5Li ₂ CO ₃ - 31.5Na ₂ CO ₃ - 25.0K ₂ CO ₃	397	6.6	8.2	6.9	6.0	N.A.*

* Not available.

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The Kirchhoff's method appears to provide a reasonable estimate. This method was also used by Bremlette et al.⁴ for salt mixtures. Therefore, ΔH_f for most salt mixtures for which experimental values were not available were estimated using Kirchhoff's method. Some of the salts, such as ZnCl₂, SrCl₂, and BaCl₂, that are not listed in the JANAF tables⁴², were calculated by Method 3. ΔH_f for those single salts shown in Table 2 of the main text were taken directly from the Molten Salts Handbook¹⁵.

2. Estimation of Heat Capacity of Solid and Liquid Mixtures

The estimation of heat capacity for solid and liquid salt mixtures, C_{pm} , was based on the molar additivity rule:

$$C_{pm}(s) = \sum x_i C_{pi}(s) \quad (A-8)$$

and

$$C_{pm}(l) = \sum x_i C_{pi}(l) \quad (A-9)$$

where

x_i = mole fraction of single component i

C_{pi} = heat capacity of single component i at the melting point of the mixture

s and l denote solid and liquid phases.

To check the validity of this approximation, Equations A-8 and A-9 were applied to estimate $C_{pm}(s)$ and $C_{pm}(l)$ of binary and ternary carbonate mixtures and were compared with reported values, as shown in Table A.2.

Table A.2. COMPARISON OF EXPERIMENTAL AND ESTIMATED VALUES OF HEAT CAPACITY FOR THREE CARBONATE MIXTURES

Salt, mol %	Experimental Value		Refer- ence	Estimated Value	
	$C_p(s)$	$C_p(l)$		$C_p(s)$	$C_p(l)$
	cal/mol°C			cal/mol°C	
50Li ₂ CO ₃ - 50K ₂ CO ₃	33.82	44.65	23	38.59	46.79
56Na ₂ CO ₃ - 44K ₂ CO ₃	47.63	44.26	23	43.40	47.39
43.5 Li ₂ CO ₃ - 31.5Na ₂ CO ₃ - 25.0K ₂ CO ₃	40.02	39.51	22	37.89	44.26

A fair agreement is obtained between the experimental and the estimated values. This method was therefore employed for all the salt mixtures.

3. Estimation of Thermal Conductivities of Solid and Liquid Mixtures

An extensive survey of the literature revealed that adequate data on the thermal conductivities of molten salt mixtures were not available. Hence, estimation methods and empirical correlations had to be used.

Solids

The thermal conductivities of mixtures in the solid state are best correlated with Russell's equation³⁶:

$$\frac{k_{\text{comp}}}{k_{\text{cont}}} = \frac{\nu p^{2/3} + 1 - p^{2/3}}{\nu(p^{2/3} - p) + 1 - p^{2/3} + p} \quad (\text{A-10})$$

where k_{comp} = thermal conductivity of the composite mixture, Btu/hr-ft²F

k_{cont} = thermal conductivity of the continuous phase (or of the higher volume fraction component), Btu/hr-ft²F

ν = ratio of the conductivity of the lower volume fraction component to that of the higher volume fraction component

p = porosity (volume fraction of voids), that is, volume fraction of the lower volume fraction component.

With this method, thermal conductivities of the individual salts have to be known to calculate the thermal conductivity of the mixture. Thus, the thermal conductivities of many of the mixtures considered could not be calculated because the thermal conductivities of the single salts at the melting point of the mixture were not available.

Liquids

Several techniques are available for estimating the thermal conductivities of mixtures in the liquid phase. The following methods were considered:

- a. Method of Scheffy and Johnson³⁸
- b. Prediction Method of Gambill⁹, and
- c. Empirical Correlation of Vargaftik.⁴⁶

- a. Method of Scheffy and Johnson.³⁸ Although we originally believed this method would be useful, further study showed that it was not suitable because of its validity mainly for organic liquids.
- b. Prediction Method of Gambill.⁹ Gambill considers fused salts as an intermediate between the cases of 1) pure organic liquids, which are nonelectrolytes with conductivities due solely to atomic or molecular contributions; and 2) liquid metals, where the electron drift (corresponding to the ionic contribution for fused salts) is almost entirely dominant. Thus, in his correlation for fused salts, he accounts for each of these mechanisms. The atomic portion of the total thermal conductivity is -

$$(k_A)_m = 10.43 T_m^{1/2} \rho_m^{4/5} / M_{\text{avg}}^{9/5} \quad (\text{A-11})$$

where

$$\begin{aligned}(k_A)_m &= \text{atomic contribution to the total thermal conductivity} \\ &\quad \text{of the mixture, Btu/hr-ft. } ^\circ\text{F} \\ T_m &= \text{temperature of the mixture, } ^\circ\text{K} \\ \rho_m &= \text{density of mixture, g/cc} \\ M_{\text{avg}} &= \text{average molecular weight of the mixture} = \sum_i x_i M_i\end{aligned}$$

The remainder of the total conductivity, the ionic contribution, was correlated on the basis of existing auxiliary data by the relation -

$$A\% = 43.8 - 9.0 N_{\text{avg}} \quad (\text{A-12})$$

where

$$N_{\text{avg}} = \text{average ion number} = \sum_i x_i N_i$$

The total thermal conductivity of the fused salt, $(k_T)_m$, is -

$$(k_T)_m = \frac{(k_A)_m}{A\%} \quad (\text{A-13})$$

This method, as the author notes, is heavily dependent on the data for the fused fluoride mixtures on which his correlation is based. Its accuracy for other salt mixtures, such as chlorides and carbonates that we are interested in, may be questionable. Hence this method was used for fluoride mixtures only.

- c. Empirical Correlation of Vargaftik.⁴⁶ Vargaftik's empirical correlation for the thermal conductivities of liquids is -

$$k = 4.28 \times 10^{-3} C_p \rho^{4/3} / M \quad (\text{A-14})$$

$$\begin{aligned}\text{where } k &= \text{thermal conductivity of the salt, cal/sec-}^\circ\text{K-cm} \\ C_p &= \text{specific heat of the salt, cal/g-mol-}^\circ\text{K} \\ \rho &= \text{density of the salt, g/cc, and} \\ M &= \text{molecular weight, g/g-mol}\end{aligned}$$

In the case of mixtures, the above parameters are molar averaged.

The values obtained using this correlation agreed quite closely with the values reported in the literature especially with chlorides such as NaCl and KCl and carbonates such as Na_2CO_3 . Thus we concluded that this fair degree of accuracy may be expected for salt mixtures also.

The calculated values are compared with experimental values obtained from the literature,^{14,44} as shown in Table A.3.

Table A.3. COMPARISON OF ESTIMATED AND EXPERIMENTAL THERMAL CONDUCTIVITY VALUES FOR SEVERAL MOLTEN SALTS AND SALT MIXTURES

Salt	$k_{\text{experimental}}^{14}$	$k_{\text{estimated}}$	
		Gambill ⁹ Btu/hr-°F-ft	Vargaftik ⁴⁵
LiBr	0.23	0.79	--
NaOH	0.53	0.53	1.14
LiCl	0.26	1.97	0.63
KNO ₃	0.25	0.41	0.64
NaCl	0.58	--	0.51
KCl	0.39	--	0.38
Li ₂ CO ₃	1.14	--	1.27
Na ₂ CO ₃	1.06	0.81	1.04
ZnCl ₂	0.20	0.45	0.63
NaNO ₃	0.33-0.35	--	1.06
74NaNO ₃ -26KNO ₃ *	0.27	0.51	0.95
24NaCl-76ZnCl ₂ *	0.21	0.49	0.63
12NaF-59KF-29LiF *	2.6	2.24	1.06

* Composition on a weight basis.

4. Estimation of Viscosity of Liquid Mixtures

The temperature dependence of the viscosity, η , of single salts is usually expressed by the equation¹⁰ -

$$\eta = A_{\eta} \exp(E_{\eta}/RT) \quad (\text{A-15})$$

where

A_{η} = empirical constant

E_{η} = activation energy for viscous flow

R = molar gas constant

T = temperature.

For salt mixtures, it was found²⁴ that the simple mole fraction viscosity relationship, $\sum x_i \eta_i$, is very nearly obeyed by the AgNO_3 - TiNO_3 binary mixture in the temperature range above the melting point of single salts. The predicted viscosities for the AgNO_3 - TiNO_3 eutectic mixture at temperatures below the melting point of the single components are also very close to experimental values (Table A. 4), provided the values for single salts are extrapolated to the corresponding temperature.³⁰ Estimated viscosity for a CaCl_2 - NaCl mixture (composition 9) at the eutectic point is compared with an experimental value² as shown in Table A. 4.

Table A. 4. COMPARISON OF EXPERIMENTAL AND PREDICTED VISCOSITIES FOR A TiNO_3 - AgNO_3 MIXTURE AND AN NaCl - CaCl_2 MIXTURE

Salt, mol %	Temp., °C	Viscosity	
		Experimental	Predicted
		cP	
48 TiNO_3 -52 AgNO_3	160	7.4 (ref. 24)	7.0
48.3 NaCl -51.7 CaCl_2	600	5.5 (ref. 2)	7.6

Therefore molar additivity of extrapolated viscosities was assumed for our estimation.

Experimental values for molten carbonates are only available in the temperature range of 1290°F to 1650°F. The viscosity data listed in Table 2 (main text) are extrapolated from these experimental values.

5. Estimation of the Volume Change on Fusion of Salt Mixtures

The volume change on fusion for some single salts has been measured.^{3,15} Values obtained for salts that are components of some of the mixtures under consideration are presented in Table A. 5.

Table A. 5. VOLUME CHANGE ON FUSION FOR SOME SINGLE SALTS

Salt	Volume Change, %
NaCl	25.58
KCl	20.20
MgCl ₂	30.46
CaCl ₂	0.09
SrCl ₂	2.40
ZnCl ₂	11.64

The volume change on fusion, ΔV_f , of the salt mixtures containing these salts was estimated by molar additivity. For example, the volume change on fusion of salt composition 7 (Table 2) was calculated as -

$$\begin{aligned}
 & 48 \text{ weight percent NaCl} - 52 \text{ weight percent MgCl}_2 \\
 & = 60 \text{ mole percent NaCl} - 40 \text{ mole percent MgCl}_2 \\
 \frac{\Delta V_f}{V_s} & = (0.60) (25.58) + (0.40) (30.46) \\
 & = 27.55\%
 \end{aligned}$$

where V_s = volume of the solid phase salt at the melting point.

Volume changes for mixtures containing salts other than those listed in Table A. 5 were estimated on the assumptions that a) the magnitude of the volume change is independent of the temperature at which it occurs, and b) the density of the single molten salt can be extrapolated to the melting point of the mixture by assuming a temperature dependence similar to that of the solid salts. Therefore, density corrections can be made on the molten salts (values for which may be calculated from experimentally determined density-temperature equations) to compensate for density changes resulting from the difference in the melting temperatures of the single salts and the mixture. Changes in density with temperature of some salts have been characterized (primarily for those salts in Table A. 5). An average change in density with temperature was calculated from these salts to be $1.01 \times 10^{-4}/^\circ\text{C}$.

The densities, ρ_{fi} , of the solid salts at the melting point of the mixture, T_f , were then calculated by a correction on the room temperature density for those salts. The equation used was -

$$\rho_{fi}(s) = \rho_{25} [1 - (1.01 \times 10^{-4}/^{\circ}\text{C})(T_f - 25^{\circ}\text{C})] \quad (\text{A-16})$$

The liquid densities, ρ_{fi} , were determined similarly from -

$$\rho_{fi}(l) = \rho_T [1 + (1.01 \times 10^{-4}/^{\circ}\text{C})(T - T_f)] \quad (\text{A-17})$$

where

ρ_T is the liquid density at temperature T.

Densities of both the solid and liquid mixtures near the melting point were then estimated by simple molar additivity of these corrected densities. The volume change was then determined from the density differences between the solid and liquid:

$$\left(\frac{\Delta V_f}{V_s} \right) \% = \frac{\frac{1}{\rho_{fm}(l)} - \frac{1}{\rho_{fm}(s)}}{\frac{1}{\rho_{fm}(s)}} \times 100\% \quad (\text{A-18})$$

The volume change on fusion for composition 7 (Table 2) can be calculated by this method as follows:

$$\begin{aligned} \text{NaCl: Melting point} &= 776^{\circ}\text{C (Ref. 47)} \\ \rho_{25}(s) &= 2.165 \text{ g/cc} \\ \rho_{778}(l) &= 1.555 \text{ g/cc (Ref. 47)} \\ \rho_{450}(s) &= 2.165 [1 - (1.01 \times 10^{-4}/^{\circ}\text{C})(450^{\circ}\text{C} - 25^{\circ}\text{C})] \\ &= 2.072 \text{ g/cc} \\ \rho_{450}(l) &= 1.555 [1 + (1.01 \times 10^{-4}/^{\circ}\text{C})(778^{\circ}\text{C} - 450^{\circ}\text{C})] \\ &= 1.606 \text{ g/cc} \end{aligned}$$

$$\begin{aligned} \text{MgCl}_2: \text{Melting Point} &= 683^{\circ}\text{C (Ref. 47)} \\ \rho_{25}(s) &= 2.323 \text{ g/cc} \\ \rho_{702}(l) &= 1.674 \text{ g/cc (Ref. 47)} \\ \rho_{450}(s) &= 2.323 [1 - (1.01 \times 10^{-4}/^{\circ}\text{C})(450^{\circ}\text{C} - 25^{\circ}\text{C})] \\ &= 2.223 \text{ g/cc} \\ \rho_{450}(l) &= 1.674 [1 + (1.01 \times 10^{-4}/^{\circ}\text{C})(683^{\circ}\text{C} - 450^{\circ}\text{C})] \\ &= 1.713 \text{ g/cc} \end{aligned}$$

Mixture:

$$\rho_{fm}(s) = (0.6)(2.072) + (0.4)(2.223) = 2.133 \text{ g/cc}$$

$$\rho_{fm}(l) = (0.6)(1.606) + (0.4)(1.713) = 1.649 \text{ g/cc}$$

The volume change on fusion is, therefore -

$$\frac{\left(\frac{1}{1.649}\right) - \left(\frac{1}{2.133}\right)}{\left(\frac{1}{2.133}\right)} \times 100 = 29.3\%$$

This value agrees very well with the 27.6% calculated by molar additivity.

6. Vapor Pressures of Single Salts at The Melting Temperature

Sufficient data on vapor pressures of mixtures of salts were not available. As an indication of maximum vapor pressure, however, a list of vapor pressures of single salts appears in Table A.6.

Table A.6. VAPOR PRESSURE OF SEVERAL SALTS
AT THE MELTING POINT

Salt	Melting Point, °F	Vapor Pressure, mm Hg
LiF	1548	6.15×10^{-5}
NaF	1810	0.57
NaCl	1442	0.56
KCl	1429	0.70
CaCl ₂	1422	3.46×10^{-4}
MgCl ₂	1307	0.18
ZnCl ₂	541	1.05×10^{-2}
NaBr	1391	0.57
NaOH	604	4.92×10^{-5}
LiCl	1137	0.10
LiBr	1017	4.26×10^{-2}
Li ₂ CO ₃	1355	$11.6 (P_{CO_2})^\dagger$
(Li, K, Na) CO ₃ eutectic	1382	$10.5 (P_{CO_2})^\dagger$
Na ₂ CO ₃	1544	0 (P _{CO₂})

* From Reference 15.

† Equilibrium dissociation pressures from References 21 and 41.

Vapor pressures of carbonates were not available, but dissociation pressures ^{21,41} for the reaction -

are included in Table A. 6. Trachtenberg and Cole⁴⁵ have estimated a vapor pressure of 0.08 mm Hg for a LiNaCO₃ mixture (similar to composition 12 in Table 2) at 650°C, when sufficient CO₂ was present to prevent dissociation.

7. Safety Hazards

Molten salts may pose safety hazards upon skin contact, ingestion, or inhalation. The inhalation of vapors that may be released from a storage system into its surroundings if any leaks develop in containment materials would be a primary hazard when commercial, industrial, or utility applications are considered. Other safety hazards are present, but because they are associated with skin contact or ingestion, are more easily avoided. Therefore, we have evaluated the safety hazards associated with the use of the salts listed in Table 2 on the basis of the toxicity of any vapor species that they may emit, and have rated them by their effects upon inhalation. The rating code is explained in detail below.

Inhalation Hazard Rating Code³⁷

0	None	(a) No harm under any conditions
(b) Harmful only under unusual conditions or overwhelming dosage
1	Slight	Causes reversible changes that disappear after end of exposure
2	Moderate	May involve both irreversible and reversible changes, not severe enough to cause death or permanent injury
3	High	May cause death or permanent injury after very short exposure to small quantities

8. Corrosion by Storage Materials Under Consideration

Reliable information on long-range corrosion is not available for many of the salts under consideration. Our estimation of the probable containment materials as presented in Table 2 is based on general information available for various groups of mixtures or similar compounds. The following discussion presents some detailed information on corrosion by various salts.

Corrosion by Hydroxides

An excellent review of corrosion of various materials in fused NaOH is presented by Theus⁴³. Purity levels and gas atmosphere are critical parameters in the extent of corrosion by NaOH. Data by Peoples et al³⁵ indicate that a small amount of water in the atmosphere above the melt has little effect on the corrosion rate of nickel, but a greater amount of water vapor enhances corrosion. This data is contradicted by Craighead et al,⁷ who found corrosion rates reduced in a wet gas atmosphere. Both effects were found by Lux³¹ depending on the particular metal. Sodium carbonate is another likely impurity because NaOH reacts readily with carbon dioxide in the atmosphere. Various studies^{7, 27, 48} suggest that Na_2CO_3 has a very slight effect on corrosion rates by NaOH.

Extensive corrosion has been reported at 1000°F for Types 316 and 446 stainless steel by Craighead et al,⁶ but Comstock and Wescott⁵ used mild steel up to 900°F in their thermal energy storage system. The Comstock and Wescott system uses a proprietary "Thermokeep" material, which is a mixture of NaOH with a corrosion inhibitor, that allows the use of mild steel containment.

Shimotake and Hesson⁴⁰ note that corrosion rates of Armco iron, Type 300-series stainless steel, etc., by fused alkali salts increase in the order of increasing ionic radii, $\text{Li} < \text{Na} < \text{K}$. Thus it may be possible to contain LiOH in a mild steel, provided a suitable inhibitor is used.

Corrosion by Fluorides

Fluorides as nuclear fuel carriers have been studied extensively for the molten salt reactor program. Below 1240°F (670°C), the corrosion of Ni-Cr-Fe alloys by fluoride melts is reported to be small³³. No noticeable attack by NaF was noted on stainless steel type 316 in 3 hours under vacuum³². Glenn¹¹ has suggested containing NaF-MgF₂ and LiF-NaF-MgF₂ mixtures in a 300 series stainless steel. No detailed information however is available regarding the effect of gas atmosphere and moisture on corrosion.

For a hermetically sealed system, Schröder³⁹ reports that 18/8 stainless steel showed no significant long-term attack at 1560°F (850°C) by molten fluorides, if a small amount of aluminum was added as a corrosion inhibitor.

Corrosion by Chlorides

Kochergin²⁶ has studied the solution rate of iron in LiCl-KCl mixtures and also in eutectic mixtures of alkali and alkaline earth metals at 1300°F (700°C). The iron dissolved most rapidly in LiCl-KCl and least rapidly in a low melting mixture of BaCl₂-KCl; however, adding magnesium prevented the iron from dissolving almost completely. The iron corrosion rate in chloride mixtures increased in the order of MgCl₂-KCl (compositions 6 and 8), MgCl₂-NaCl (composition 7), MgCl₂-BaCl₂, MgCl₂-CaCl₂, ZnCl₂-KCl (composition 5), and ZnCl₂-NaCl at temperatures up to 1300°F (700°C).

Water content in chloride melts is especially harmful; it acts like hydrogen chloride and readily oxidizes most construction metals with the liberation of hydrogen. Therefore removal of moisture from the chloride melts would be desirable; however, it is usually very difficult.⁴⁰

The compilation by MacKenzie³² indicates that stainless steel may be acceptable as a container material for NaCl at 1830°F (1000°C) based on short-term experiments. Janz and co-workers¹⁷ made a similar observation for the KCl-LiCl eutectic mixture.

Glenn¹¹ has suggested 300-series stainless steels as container materials for chlorides as thermal energy storage media.

Long-term corrosion tests are recommended for the proposed containment metals in chloride salt mixtures at the operating conditions under consideration to obtain more reliable information.

Corrosion by Bromides

MacKenzie³² has noted Type 316 stainless steel as a suitable container material for NaBr at 1750°F (953°C). Judging from this information, it appears that the use of stainless steels at 850°F to 1000°F in bromide melts may be satisfactory. The moisture content in the mixture or in the atmosphere may enhance the corrosion by bromides.

Corrosion by Carbonates

Carbonates are less aggressive compared with the halides with respect to corrosion. No special treatment may be necessary to remove moisture from these salts because the moisture does not have a significant effect

on corrosion by carbonates. Molten carbonate fuel cells have been operated at the Institute of Gas Technology ^{28,34} and elsewhere for several thousand hours using conventional stainless-steel hardware.

Janz and co-workers studied the corrosion of the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary eutectic mixture (composition 24) under submerged conditions by a potentiostatic polarization technique ²⁰ and also by prolonged exposure.^{18,19} The authors concluded that both Types 304 and 347 stainless steel passivate under submerged conditions in an oxidizing environment.

Davis and Kinniburgh ⁸ studied corrosion by the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ eutectic mixture (composition 12) under fully and partially submerged conditions, and reported a greater corrosion attack under partially submerged conditions. However, they noted that ferro-aluminum alloys such as Kanthal A, Kanthal Al, and Hoskins 815 were more resistant than the 300-series stainless steels.

Atomics International has employed carbonates for sulfur removal and as reaction media for in situ combustion. Detailed studies of corrosion by carbonates under various conditions have been carried out at Atomics International. A 1-year test ¹ with the ternary eutectic mixture showed that corrosion of Type 347 stainless steel was only 0.2 mils/yr at 500°C. A 1500-hour test¹ at 600°C showed a corrosion rate of only 0.3 mils/yr. Examination of the outer film of the stainless steel showed that a dense, compact, protective layer of LiCrO_2 was formed, which is protective up to 700°C. Stress corrosion cracking and the effect of additions of chlorides, sulfides, sulfites, and sulfates under various conditions were also studied.¹² They reported that sulfur compounds enhance corrosion, but that chloride compounds do not alter the corrosion rate markedly.

Corrosion by Miscellaneous Salts

For the B_2O_3 melt, MacKenzie ³² noted that stainless-steel containment was acceptable and that no noticeable attack was observed at 800°C for several hours.

9. Current Single Salt Prices* Per Pound (June 1976)

LiOH	\$1.97	NaCl	\$0.022
LiBr	\$3.00	CaCl ₂	\$0.04
B ₂ O ₃	\$0.19	SrCl ₂	\$2.00 [†]
LiF	\$2.42	NaF	\$0.032
NaBr	\$1.65	BaCl ₂	\$0.16
MgBr ₂	\$1.60	Li ₂ CO ₃	\$0.78
KCl	\$0.024	K ₂ CO ₃	\$0.20
ZnCl ₂	\$0.34	Na ₂ CO ₃	\$0.02
MgCl ₂	\$0.13	NaOH	\$0.13
KF	\$0.62	MgF ₂	\$15.12 [†]

* Prices apply to large lot size technical or chemical grade salts.
Obtained from Chemical Marketing Report, May 24, 1976.

† Reagent Grade; price obtained through McKesson Chemical Company,
100 to 200 lb lots.

Prices of salt mixtures were calculated by summing the products of the weight fraction of a component and its single salt price:

$$\begin{aligned}
 & \text{36 weight percent KCl - 64 weight percent MgCl}_2 \\
 \text{Cost} &= (0.36)(\$0.024/\text{lb}) + (0.64)(\$0.13/\text{lb}) \\
 &= \$0.09/\text{lb.}
 \end{aligned}$$

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