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Advanced High-Temperature Molten-Salt Storage Research

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ADVANCED HIGH-TEMPERATURE MOLTEN-SALT STORAGE RESEARCH

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ABSTRACT

We are researching advanced high-temperature molten-salt thermal storage for use in direct absorption receiver and thermal storage (DARTS) solar thermal systems. A molten salt at 900°C or higher is both the receiver heat transfer medium and the storage medium; a unique insulated platform (raft) separates the hot and cold medium in the thermocline thermal storage. We have measured raft performance experimentally, and it performs equally or better than a natural thermocline. Containment materials for the molten salts are being experimentally screened. NaOH has a very high corrosion rate on ceramics and metals. Both carbonates and chlorides can be contained at 900°C with relatively little corrosion. Based on the measured corrosion rates, the economic potential of molten-salt thermal storage was analyzed. Both the chlorides and carbonates have potential (i.e., cost less than value) at the capacity of storage expected for commercial-scale solar thermal systems.

INTRODUCTION

Future applications of solar thermal energy will require temperatures of 1100°C or higher. Advanced high-temperature molten-salt solar thermal systems can supply heat at these high temperatures (Copeland, Leach, and Stern 1982). Several salts have melting points, transport

properties, vapor pressures, and associated costs that make them attractive. Analyses show that hydrogen production costs and solar-thermal electric power costs can be reduced (Copeland, Leach, and Stern 1982; Copeland 1982) through the use of a high-temperature molten-salt system. The salts currently being studied include sodium-, potassium-, and other alkali or alkali-earth metal-compounds of carbonates, chlorides, hydroxides, and silicates. One of these salts would be used as the working fluid in both the receiver and the sensible-heat storage.

Figure 1 illustrates the thermal storage concept. The nature of the internal insulation and users' demands for high-temperature energy from storage make thermocline energy storage necessary. Mixed-tank thermal storage produces unacceptably low temperatures during discharge, and the nature of the side internal insulation does not allow the use of two tank thermal storage. The concept shown in Figure 1 includes a raft that separates the hot and cold fluid regimes and provides thermal insulation between the hot and cold regions of the liquid.

The system includes a direct absorption receiver and thermal storage (DARTS). During FY 1983, we received funding from the solar thermal program, and work on the direct absorption of concentrated solar radiation in a molten salt is proceeding. In FY 1982, we evaluated the raft thermocline concept, screened containment materials, and reevaluated the economic potential based on the latest information.

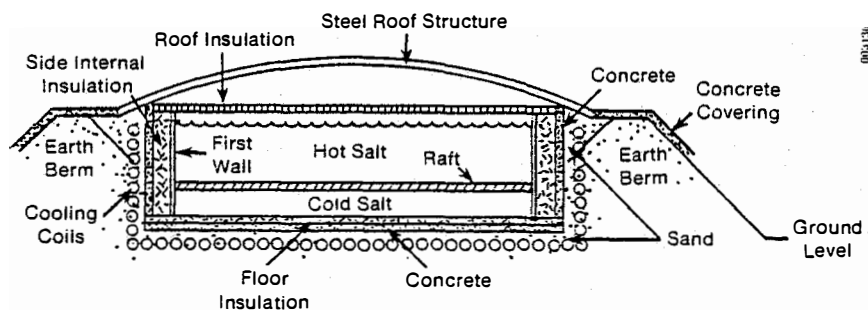


Figure 1. 950°C Molten Salt Thermal Storage

RAFT THERMOCLINE EXPERIMENTS

We checked the performance of a raft thermocline in water at low temperatures to compare the stability of raft thermoclines with that of natural thermoclines. The stratification index *S* given by Cole and Bellinger (1981) can be used to measure performance. Values of *S* range from 0 for a completely mixed tank to 1 for a perfectly stratified tank.

The Richardson number *R* strongly influences the performance of natural thermoclines and by implication should also influence raft thermoclines. The Richardson number for the tank is

$$R = \frac{g \beta \Delta T L}{v^2} \quad (1)$$

The nondimensional Richardson number provides a means of extrapolating data taken with one fluid to another fluid and other geometric conditions. We used water for the fluid for the experiments because of its cost, safety, and overall experimental convenience.

We tested the system shown in Figure 2 (Copeland and Green 1983) and obtained results for natural thermoclines as well as for three rafts with greatly

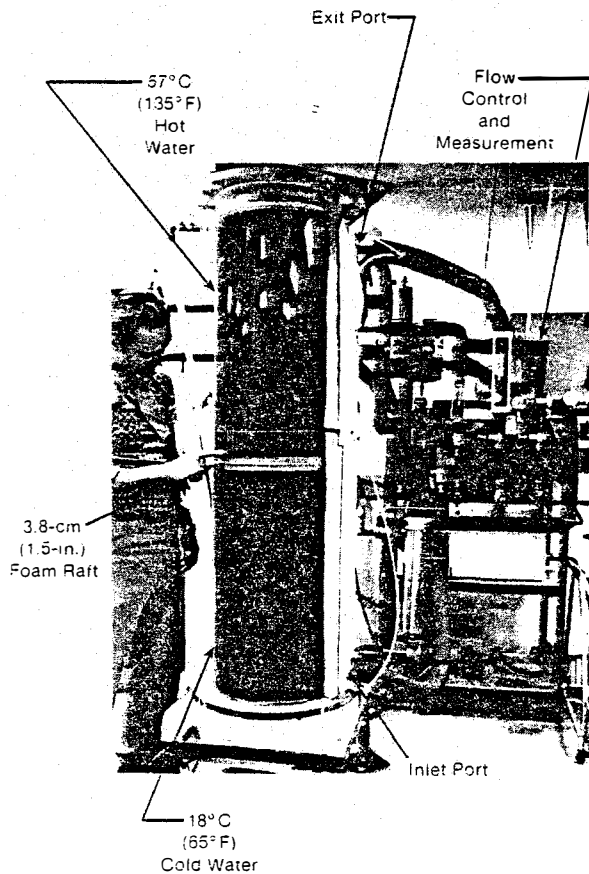
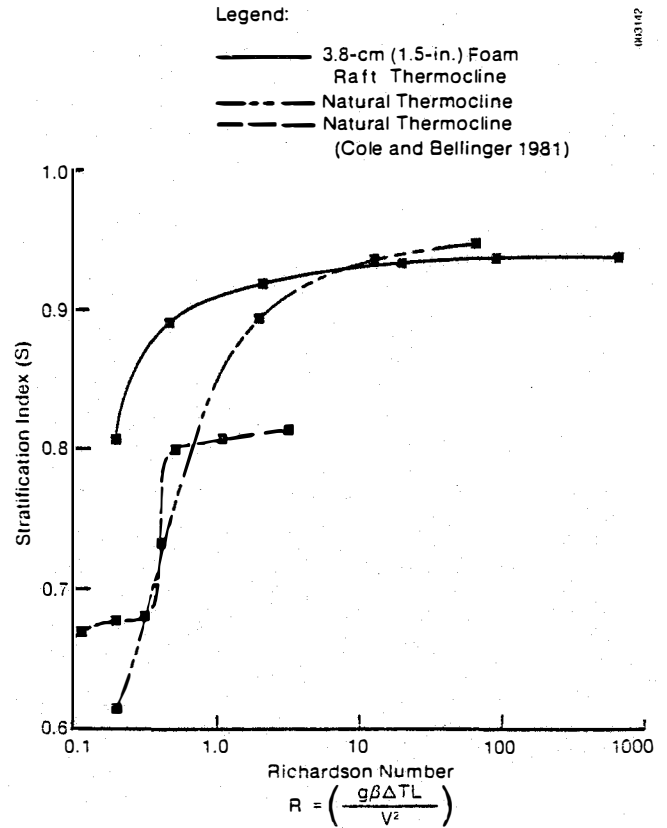


Figure 2. Experimental Apparatus for Testing a Raft Thermocline

varying thermal resistance. Figure 3 presents performance results for natural and raft thermoclines. The stratification index *S* is plotted as a function of the Richardson number *R*. Note the log scale for this figure. Cole and Bellinger's (1981) work is included. Their data show that a sharp drop in stratification occurs at the critical Richardson number of 0.25.



Note: All data are for side inlets and outlets.

Figure 3. Performance Results for Natural and Raft Thermoclines

Figure 4 shows the effect of insulation in the raft on the thermal performance. The data are for three different rafts with substantially different insulating factors. The insulating value of the rafts varies by as much as a factor of 50 (R-value of the 3.0-in. foam raft to the aluminum raft). There is no substantial difference in the performance of the three rafts; all three raft thermoclines are equally stratified at all flow conditions.

These initial tests were performed with an L/D (column height of liquid to diameter) ratio of about 4. This ratio was selected to verify raft performance under conditions where good data for natural thermoclines are available from other researchers. Our results correlate within the experimental accuracy of the data with previous work with natural thermoclines. However, commercial application of raft thermoclines will require tanks of about 40 ft in height and 80 ft in diameter. The conditions are imposed by soil-bearing-strength limitations; L/D is 0.5,

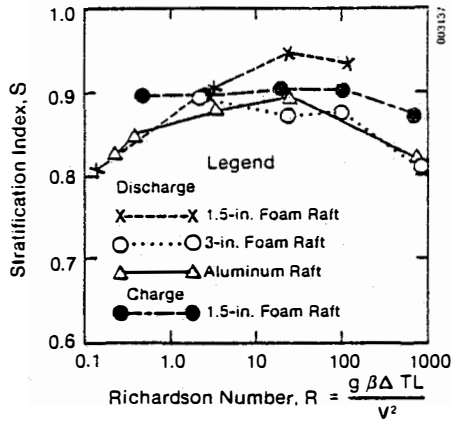


Figure 4. Effect of Raft Insulation

which is a ratio at which natural thermoclines do not perform well. Additional data are needed for raft thermoclines with a range of L/D ratios and to verify the nondimensional predictions in a molten salt.

SCREENING OF CONTAINMENT MATERIALS

For the thermal storage concept shown in Figure 1, there must be a first wall material that can contain the molten salt. The first applications for DARTS are anticipated to be in the 850^o-950^oC maximum salt temperature range. Experiments are being conducted at 900^oC (Coyle, Copeland, Burrows, and Goggin 1983) to screen candidate first wall materials.

Tests with molten sodium hydroxide showed very high corrosion rates on both metal alloys and ceramics. The rates were sufficiently high that many samples disintegrated and others broke into pieces under their own weight. Some specimens did survive, although at unacceptably high corrosion rates.

Tests with metal alloys in a molten chloride salt also showed high corrosion rates. However, previous work by

the Jet Propulsion Laboratories with chlorides and flourides did not show the high rates we observed. We believe water was present in our salt, causing HCl to form and attack the metals. Better control of the salt chemistry should lower corrosion rates of metal alloys by the molten chlorides, and additional work will be needed before definitive conclusions can be reached.

Molten chlorides showed negative corrosion rates on the ceramics tested (see Table 1). This indicates a slight weight gain during testing, which may be caused by the deposition of MgO on the ceramics from the MgCl₂ in the salt reacting with moisture.

Tables 2 and 3 present the corrosion rate data for molten carbonates on metals and ceramics. Although longer exposure durations and better analysis of the specimens are needed, the rates appear low enough to be usable with 30-year life.

ECONOMIC ASSESSMENT

The initial economic assessment was based on the use of sodium hydroxide as the molten medium. The corrosion rates of NaOH on metals and ceramics are very high. Our studies were not exhaustive, and it is possible that either other materials or the control of salt chemistry may make NaOH usable. At the currently anticipated corrosion rates, the use of NaOH is not practical at this time.

Recognizing these factors we reassessed the economic potential employing carbonates and chlorides. With the design of the system shown in Figure 1, we used the measured corrosion rates for materials and the Stearns-Roger (Dubberly et al. 19) costing data base and methodology. The insulation was salt packed with magnesium oxide pellets to prevent convection and sized for a 2% heat loss/day. A special technique was used with the carbonates to reduce the salt cost in the insulation. Figure 5 shows the unit capital cost of the thermal storage as a function of the storage capacity. For small-scale applications, the cost exceeds the value. For a commercial solar thermal central receiver system, the cost is less than or equal to the value. In these data, the value is given as a range and represents the expected

Table 1. Corrosion Rates of Ceramics in Molten Chloride at 900^oC after 2, 6, and 18 Days

Material	Composition	Corrosion Rate (m/day)*			Comments
		2 Days	6 Days	18 Days	
Fused-Cast	99.3 Al ₂ O ₃	-6	-3	-1	
Fused-Cast	93.9 Al ₂ O ₃ /5.6 Na ₂ O	-32	-19	-8	
Fused-Cast	78 Cr ₂ O ₃ /8.7 MgO/7.9 Fe ₂ O ₃ /4 Al ₂ O ₃ /1.6 SiO ₂	9	0.04	-0.2	Broke at 2 and 18 days
Fused-Cast	60 Al ₂ O ₃ /27 Cr ₂ O ₃ /6 MgO/4 Fe ₂ O ₃ /2 SiO ₂	-20	-12	-5	
Fused-Cast	50 Al ₂ O ₃ /36 ZrO ₂ /12 SiO ₂	-1	-1	-0.7	
Dense Al ₂ O ₃	99.8%	-0.3	-0.4	-0.3	
Porous ZrO ₂	Y ₂ O ₃ stabilized	13	1	--	Broke at 2 and 6 days

*Exposure time in hours is in parentheses; d indicates the coupon disintegrated. Corrosion rates with superscript l are determined by thickness change; the rest is determined by weight. Negative corrosion rates indicate a weight gain.

Table 2. Corrosion Rate of Alloys in Molten Carbonate at 900°C After 2 Days and 6 Days

Material	Composition	Corrosion Rate (m/day)*		Comments
		2 Days	6 Days	
Alloy 600	72 Ni/15.5 Cr/8 Fe	5	-2	**
Alloy 600**	72 Ni/15.5 Cr/8 Fe	5	3	**
Alloy 800	42 Fe/32.5 Ni/21 Cr	13	-2	**
Alloy 800H***	42 Fe/32.5 Ni/21 Cr	10	3	**
Alloy X750	70 Ni/15.5 Cr/7 Fe/2.5 Ti	1	-1	**
Stainless 304	68 Fe/19 Cr/10 Ni/2 Mn	15	14	**
Stainless 316	65.5 Fe/17 Cr/12 Ni/2.5 Mo/2 Mn	10	11	**
Nickel	99.99+ Ni	10	85	Faceted surface, **
Alloy 230	99.5 Ni	-10	12	Cracked, **
Alloy 556	27 Fe/22 Cr/20 Ni/20 Co/3 Mo/3 W	5	6	**
Alloy 214	37 Co/22 Cr/22 Ni/14.5 W/3 Fe	11	6	**
Alloy 188	39 Co/22 Ni/22 Cr/14 W/3 Fe	14	5	**
Alloy R-41	52 Ni/19 Cr/11 Co/10 Mo/5 Fe/1.5 Al/3 Ti	3	20	**
Alloy S	63 Ni/16 Cr/16 Mo/3 Fe/2 Co	8	-9	Cracked, **
Alloy N	71 Ni/17 Mo/7 Cr/5 Fe	10	2	**
Alloy X	48 Ni/22 Cr/18.5 Fe/9 Mo/1.5 Co	-2	-1	**

*Exposure time in hours is in parentheses; d indicates the coupon disintegrated. Corrosion rates with superscript 1 are determined by thickness change; the rest is determined by weight. Negative corrosion rates indicate a weight gain.

**Showed flaking of the corrosion product.

***Differs from Alloy 800 by having less carbon because of a solution heat treatment.

Table 3. Corrosion Rates of Ceramics in Molten Carbonate at 900°C after 2 Days and 18 Days

Material	Composition	Corrosion Rate (m/day)*	
		2 Days	18 Days
Fused-C ast	99.3 Al ₂ O ₃	40	8
Fused-C ast	94.5 Al ₂ O ₃ /3.9 Na ₂ O/1 SiO ₂	-12	-4
Fused-C ast	93.9 Al ₂ O ₃ /5.6 Na ₂ O	-10	-12
Fused-C ast	78 Cr ₂ O ₃ /8.7 MgO/7.9 Fe ₂ O ₃ /4 Al ₂ O ₃ /1.6 SiO ₂	110	38
Fused-C ast	60 Al ₂ O ₃ /27 Cr ₂ O ₃ /6 MgO/4 Fe ₂ O ₃ /2 SiO ₂	20	23
Fused-C ast	50 Al ₂ O ₃ /36 ZrO ₂ /12 SiO ₂	30	13
Dense Al ₂ O ₃	99.8%	1	0.7
Porous ZrO ₂	Y ₂ O ₃ stabilized	-18	-6

*Exposure time in hours is in parentheses; d indicates the coupon disintegrated. Corrosion rates with superscript 1 are determined by thickness change; the rest is determined by weight. Negative corrosion rates indicate a weight gain.

difference in value for different applications (e.g., electric power plants, industrial process heat). The range is from \$20 to \$30/kWh_t, nominally \$25/kWh_t.

For carbonates and chlorides, the cost of the internal insulation was the largest factor. For carbonates the medium cost was also a major factor. Recognizing these facts, SERI is currently trying to reduce the cost impacts by conducting a competitive procurement to find and research methods of improving the internal insulation. SERI

is also conducting in-house research to reduce the cost of the carbonates. The quantity of lithium present in the mixture is the reason for the high cost, but the lithium also provides a low melting point.

Adding quantities of barium carbonate will provide a low melting point with a lower cost than the ternary carbonate eutectic salt. Our research is directed toward finding the cost optimum mixture.

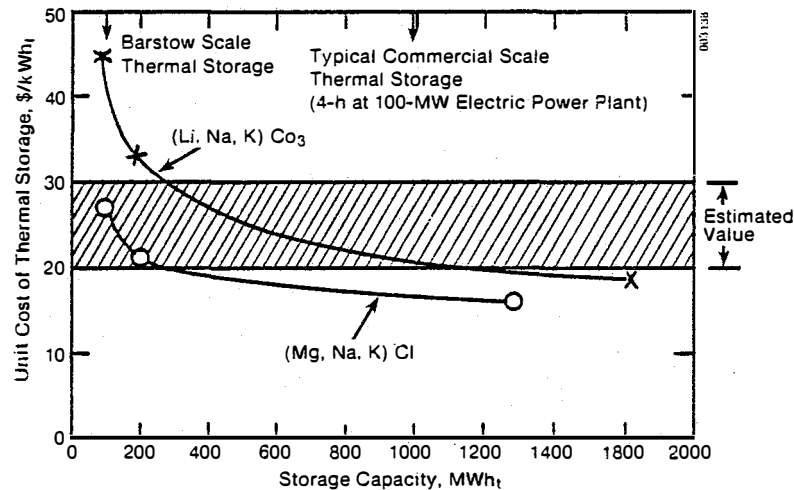


Figure 5. Projected Cost of Molten Salt Thermal Storage in Solar Thermal Applications

FUTURE PLANS

In FY 1984, we plan to test new rafts, research materials, and work on internal insulations. We also plan to evaluate raft performance in molten salts. Those experiments will be conducted in nitrate salts because there are better data on the physical properties, and known containment methods. These data will allow us to verify raft performance prediction methods. We will continue to evaluate corrosion rates for carbonates as a function of temperature and to investigate alternative salts (carbonates, chlorides, etc.). The work on internal insulation will be performed by subcontractors yet to be selected.

NOMENCLATURE

g	Acceleration caused by gravity
β	Coefficient of volume expansion
ΔT	Temperature difference
L	Length of the tank
R	Richardson number
v	Flow velocity

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PROJECT SUMMARY**Project Title:**

Advanced, High-Temperature Molten-Salt Storage

Performing Institution:

Solar Energy Research Institute
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Golden, Colorado 80401

Project Manager:

R. J. Copeland, (303) 231-1012 (FTS 327-1012)

Project Objectives:

The objective is to research key issues in advanced, high-temperature molten salt thermal storage. Applications have been identified for maximum temperatures of 900^oC and 1100^oC; the highest potential temperature is 1100^oC. A multiphase project is being conducted. Initially, the 900^oC case is being explored since it has lower risk; the 1100^oC case will be emphasized in the latter phases.

Project Status:

During FY 1983, research is being conducted on two of the key issues: an insulated floating platform (raft) and materials compatibility. The insulated raft floats between hot molten salt (900^o to 1100^oC) and cold molten salt in a thermocline thermal storage tank. Experiments have been conducted in a water thermocline to evaluate raft stabil-

ity and performance. Raft thermoclines are shown to be equally or more stable than natural thermoclines. Structural and insulating materials are in close contact with the molten salts (NaOH, carbonates, or chlorides). A literature survey and experiments on materials compatibility have shown that NaOH is very corrosive to both metals and ceramics. Chlorides are very corrosive on metals but not on ceramics. Carbonates are overall the least corrosive and currently are the primary molten salt medium.

Plans and Objectives for FY 1984:

Research into specific internal insulations will be pursued through subcontracting. Experiments on materials corrosion rates as a function of temperature will be performed, and alternative carbonate salts compositions will be evaluated. Tests of raft thermoclines in molten salts are planned to be part of a new task.

Contract Number:

EG-77-C-01-4042

Contract Period:

October 1982-September 1983

Funding Source:

Department of Energy

FY 1983 Funding:

\$209K