

HIGH-TEMPERATURE MOLTEN SALT THERMAL ENERGY STORAGE SYSTEMS
FOR SOLAR APPLICATIONS

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PROJECT OUTLINE

Project Title: High Temperature, Molten Salt-Latent Heat, Thermal Energy Storage Development for Solar Applications

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Project Goals: Determine feasibility of using carbonate salts as storage media for high temperature applications (700°C - 870°C).

Review carbonate salt properties and select six salts as candidate media.

Investigate methods to enhance heat transfer through solid salt.

Conduct carbonate salt-containment material compatibility studies that include 3000 hour screening tests.

Measure thermophysical and transport properties of two most promising salts.

Project Status: Review of properties complete with the following six salts selected for compatibility studies: three (3) pure carbonates, K_2CO_3 , Li_2CO_3 and Na_2CO_3 ; two (2) eutectic mixtures, $BaCO_3/Na_2CO_3$ and $K_2CO_3/NaCO_3$, and one (1) off-eutectic mixture of Na_2CO_3/K_2CO_3 .

Compatibility studies scheduled to be completed by mid-1980.

Contract Number: DEN3-156

Contract Period: August 1979 to August 1980

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PROGRAM SUMMARY

The objective of this program is to select, test and develop alkali and alkaline earth carbonate latent-heat storage salts, metallic containment materials, and thermal conductivity enhancement (TCE) materials to satisfy the high-temperature (704° to 871°C; 1300° to 1600°F) thermal energy storage (TES) requirements of advanced solar-thermal power generation concepts. This will be accomplished by experimental screening of candidate salt/containment/TCE materials combinations in capsule compatibility tests employing both reagent-grade and low-cost technical-grade salts. The results of these compatibility tests will lead to the selection of the materials combinations that best meet the anticipated solar power system requirements. Needs for more reliable salt thermophysical and thermodynamic property data will be identified, and selected measurements will then be performed to support the future development and scale-up of solar-thermal TES subsystems.

MATERIALS COMPATIBILITY TESTING

Salt Selection

Alkali and alkaline earth carbonate salts are being developed as latent-heat thermal energy storage materials for high temperature (704° to 871°C) applications, on the basis of their desirable thermophysical properties, good thermal charge/discharge performances and endurance-stability exhibited by these materials in previous experimental programs at the Institute of Gas Technology.^{1,2} Table 1 is a list of the carbonate salts originally identified and studied under Contract No. NAS3-20806² as candidate storage media for Brayton or Stirling solar power TES applications. Table 1 includes pertinent thermophysical salt property data and thermal discharge characteristics determined experimentally in 12.7 cm (5 in.) high X 7.6 cm (3 in.) diameter laboratory-scale TES modules having a 1.3 cm (0.5 in.) diameter heat exchanger tube. These modules were fabricated from AISI 304 and 316 stainless steels. The six salts identified by asterisks in this table have been selected as candidate salts for the compatibility screening tests to be conducted under the current program. Considerations in selecting these carbonate salt storage media included —

- Energy density
- Cost
- Melting/solidification temperatures

- Thermal cycling performance and endurance in laboratory-scale TES modules
- Vapor pressure and high-temperature stability
- Impurity levels in commercial-grade salts
- Toxicity, safety, hygroscopicity, and handling considerations
- Volumetric expansion on melting
- Heat capacity

The economic feasibility of latent-heat TES concepts requires the use of low-cost salt materials. Therefore, the potential corrosion problems, salt instabilities, and other limitations associated with using commercially available (technical-grade) carbonates will be investigated in the capsule screening tests. Table 2 is a list of technical-grade alkali and alkaline earth carbonates along with recent costs of each salt in bulk quantities. A number of companies have been identified and contacted as prospective suppliers of technical-grade carbonates. Chemical and physical property specifications and cost information on these carbonates are being obtained from chemical companies supplying these materials. Selection of the technical grade salts to be included in screening tests will be based on types of impurities present, impurity levels, and cost.

Containment Materials Selection

The work completed under Contract No. NAS3-20806 demonstrated the need to improve the long-term resistance to corrosion and thermal aging effects of containment materials in the elevated temperature regime of 704° to 871°C. The materials selected as candidate containment materials are generally required to possess superior resistance to —

- Hot corrosion, oxidation, and carburization on the salt side
- Intermetallic-phase precipitation, embrittlement, or other long-term aging effects caused by high-temperature (704° to 871°C) exposure
- Thermal cycling effects on corrosion and strength
- Interactions with working fluids (air, helium, and sodium) or their impurities.

In addition, mechanical property data are being compiled and evaluated to assure structural compatibility for the proposed high-temperature TES applications, including —

- Stress-to-rupture at elevated temperatures
- Thermal cycling fatigue behavior
- Strain and thermal aging effects
- Thermal expansion coefficients

Candidate containment materials are being selected primarily from among iron- and nickel-based stainless steels and high-temperature alloys. Most of these alloys contain a significant amount of chromium and thus form Cr₂O₃-rich

oxidation product scales. Chromia scales are protective under air oxidation conditions, but Al_2O_3 -containing protective films are generally superior under molten carbonate conditions. Commercially available iron-nickel-chromium alloys, some containing approximately 2 to 5 wt % aluminum additions, are being considered. Application of a protective coating to iron-nickel-chromium alloy base materials by aluminizing techniques is also being evaluated. Various steel producers have been contacted as potential suppliers of these alloys, and available property data are being received.

Thermal Conductivity Enhancement Materials Selection

The incentive for TCE materials/configurations development arises from the fact that the thermal discharge performance of a TES subsystem is controlled largely by the rate at which the latent heat-of-fusion released at the solid/liquid interface is transported to the heat exchanger surface through the growing layer of solid salt. TCE selection criteria will thus include material thermal conductivity, expected chemical compatibility with the carbonate environment, cost, availability, and ease of fabrication into a desirable TCE configuration.

A preliminary list of candidate TCE materials is provided in Table 3. Aluminum is very attractive as a TCE material because of its high thermal conductivity of 220 W/m-K (127 Btu/hr-ft-°F) (~100X that of solid carbonates and 10X that of austenitic stainless steels). Under Contract No. NAS3-20806, a 95% porous reticulated aluminum structure increased the discharge heat flux through the ternary eutectic $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ salt (m.p. 397°C) by approximately 45%. However, aluminum cannot be used for the 704° to 871°C solar thermal TES applications because of its 660°C (1220°F) melting point. While iron and nickel-based materials are more compatible at these temperatures, they are more costly and have much lower thermal conductivities than aluminum and copper, greatly reducing their attractiveness as TCE materials. Copper also has a very high thermal conductivity of 308 W/m-K (178 Btu/hr-ft-°F) and a reasonably high melting point of 1083°C (1981°F). Pyrolytic graphite, while still a high-cost developmental material, is also reported to have a high thermal conductivity (208 W/m-K; 120 Btu/hr-ft-°F) and has a good thermal stability in non-oxidizing environments. Both copper and graphite would be severely oxidized in a high-temperature molten carbonate environment having access to the air environment. However, if gaseous oxidants are excluded by use of sealed containment or an inert cover gas, oxidation of copper and graphite TCE materials should be acceptably low. Candidate TCE materials will be corrosion tested in bulk form, or if available, as porous reticulated structures.

Screening Tests

Compatibility screening tests of the candidate salt/containment/TCE materials combinations will be conducted in welded containment capsules (2.54 cm diameter by 10.2 cm long) containing the salt and TCE material. The compatibility of 5 containment and 2 TCE materials will be evaluated with both reagent- and technical-grades of 6 candidate salt compositions. The first phase will be a 1000 hour test of the salt/containment/TCE matrix (minimum of 70 capsules).

Based on the post-test examination results of the 1000 hour test, the 30 most promising materials combinations will then be evaluated in a 3000 hour compatibility test. Compatibility evaluations will be based on —

- Depth and nature of salt-side corrosion of containment and TCE materials
- Air-side containment oxidation
- SEM/EDAX analysis of selected areas
- Containment alloy thermal aging effects
- Weld integrity in salt environment
- Gravimetric analyses of containment alloy and TCE coupons
- Chemical and physical analyses of salt

PROPERTY MEASUREMENTS

The design and scale-up of a latent-heat TES subsystem require accurate salt property data, such as melting/solidification temperatures, heat of fusion, volumetric expansion upon phase change, heat capacity and thermal stability. However, many of these salt property data for salts in the 704° to 871°C temperature range are either unavailable or subject to large error and inconsistency. Based on the results from previous experimental testing in laboratory scale TES modules and the 1000 and 3000 hour compatibility tests, at least two carbonate salt compositions most suitable for anticipated solar thermal energy storage applications will be identified. Available thermodynamic and thermo-physical property data for these salts will be critically reviewed and critical gaps will be identified. The required property measurements will then be performed on a maximum of six salt composition-purity level combinations. The results from this property measurement activity will subsequently be utilized in future carbonate TES development efforts.

REFERENCES

1. Maru, H. C., Dullea, J. F., and Huang, V. S., "Molten Salt Thermal Energy Storage Systems: Salt Selection", COO-2888-1, Institute of Gas Technology, Chicago, August 1976.
2. Maru, H. C. et al., "Molten Salt Thermal Energy Storage Systems: System Design," COO-2888-2, Institute of Gas Technology, Chicago, February 1977.
3. Petri, R. J., Claar, T. D., and Marianowski, L. G., "Evaluation of Molten Carbonates as Latent Heat Thermal Energy Storage Materials," 14th Inter-society Energy Conversion Engineering Conference, Boston, August 5-10, 1979.
4. Petri, R. J., Claar, T. D. and Tison, R. R., "High Temperature Molten Salt Thermal Energy Storage Systems", Contract No. NAS3-20806 Final Report, Institute of Gas Technology, Chicago, to be published.

**Table 1. CANDIDATE CARBONATE COMPOSITIONS TESTED UNDER
CONTRACT NAS3-20806**

No.	Salt System	Composition		Literature Melting Point		ΔH_f J/kg	Thermal Conductivity W/m-K
		Wt %	Mol %	°C	°F		
1	Li ₂ CO ₃ -CaCO ₃	44.3-55.7	37-63	662	1224	274,468	-
*2	Na ₂ CO ₃ -BaCO ₃	52.2-41.8	37-63	686	1267	172,124	-
*3	K ₂ CO ₃ -Na ₂ CO ₃ - Li ₂ CO ₃	48.8-50.0- 1.2	44-55-1	706	1303	162,820	1.73
*4	K ₂ CO ₃ -Na ₂ CO ₃	50-50	44-56	710	1310	162,820	1.73
*5	Li ₂ CO ₃	100	100	726	1333	607,086	1.96
*6	Na ₂ CO ₃ -K ₂ CO ₃	81-3-18.7	85-15	790- 737	1454- 1360	253,534	-
*7	Na ₂ CO ₃	100	100	858	1576	265,164	1.83
*8	K ₂ CO ₃	100	100	891	1636	200,036	1.73

No.	Heat Capacity at Melting Point J/kg-K		Density at 25°C kg/m ³	Discharge Solidification Range		\bar{Q} mp + 50°C (90°F) mp - 50°C (90°F) W/m ²	No. of Cycles	Hours at Operational Temperature
	Cp (s)	Cp (k)		°C	°C			
1	-	-	-	662	- 657	40,420	25	312
*2	-	-	-	717	- 712	41,680	36	984
*3	1674.7	1549.1	2399.6	706	- 695	44,420	22	528
*4	1674.7	1549.1	2399.6	708	- 700	36,950	13	336
*5	2637.7	2512.1	2108.0	734	- 730	76,660	22	672
*6	-	-	2513.3	790	- 738	46,120	38	1032
*7	1004.8	1004.8	2527.7	868	- 862	45,650	21	288
*8	1507.2	1507.2	2428.4	916	- 912	72,510	2	96

* Selected as candidate salt for compatibility screening tests.

Table 2. ESTIMATED COSTS OF TECHNICAL GRADE ALKALI
AND ALKALINE EARTH CARBONATES*

Salt	Description	Cost,	
		\$/kg	\$/lb
1. Li_2CO_3	Powder, bags	2.06	1.03
2. Na_2CO_3	Powder	0.07	0.03
3. K_2CO_3	Granulated, purified	0.44	0.20
	Calcined 99 to 100% K_2CO_3	0.42	0.19
4. MgCO_3	Powder, bags	0.22	0.10
5. CaCO_3	Ultrafine, USP bags	0.20	0.09
	Natural dry-ground air-floated, -325 mesh, bags	0.02	0.01
6. SrCO_3	Glass ground, bags	0.62	0.28
7. BaCO_3	Precipitated, bags	0.46	0.21
	Photo grade, bags	0.37	0.17
	Electronics grade, bags	0.37	0.17

* Chemical Marketing Reporter, September 19, 1979.

Table 3. POTENTIAL HEAT CONDUCTION ENHANCEMENT MATERIALS

Material	Melting Pt., °C (°F)		Thermal Conductivity at 500°C (932°F),		Heat Capacity Room Temp.		Materials Cost			
			W/m-K	Btu/hr- ft-°F	J/kg-K	Btu/lb- °F	\$/kg	\$/lb	\$/m ³	\$/ft ³ *
Aluminum	660	(1220)	220	127	921	0.22	1.74	0.79	4,732	134
Copper	1083	(1981)	308	178	385	0.09	1.65	0.75	14,726	417
Iron	1536	(2797)	38	22	461	0.11	3.02	1.37	23,766	673
Molybdenum	2610	(4730)	116	67	255	0.06	9.70	4.40	99,128	2,807
Nickel	1453	(2647)	57	33	502	0.12	4.76	2.16	42,448	1,202
316 Stainless Steel	1370	(2478)	21	12	502	0.12	2.80	1.27	22,531	638
ATJ Graphite	sublimes		78	45	837	0.20	9.85	4.47	22,107	626
Pyrolytic Graphite	sublimes		208	120 [†]	837	0.20	---	---	---	---
Silicon Carbide	2700	(4892)	87	50	836	0.20	---	---	---	---
CS Graphite	sublimes		76	44	837	0.20	1.10	0.50	2,401	68

* Costs based on 100% of theoretical density.

† a -b plane.