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Sandia Laboratories Materials Task Group Review of the Advanced Central Receiver Preliminary Designs I. Molten Salt and Liquid Metal

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SANDIA LABORATORIES MATERIALS TASK
GROUP REVIEW OF THE ADVANCED
CENTRAL RECEIVER PRELIMINARY DESIGNS
- I. MOLTEN SALT AND LIQUID METAL

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ABSTRACT

Potential materials problems associated with the preliminary designs for liquid sodium and molten salt advanced central receivers are identified and recommendations suggested. Appendices which detail generic sodium materials issues and selected bibliographies on each fluid have been included.

Liquid sodium systems are well defined technically, and code certified materials exist. Large components for power plant applications have been developed and tested. Molten nitrate salt systems, while used frequently in process industries, do not have an extensive user history at typical power plant steam temperatures. Significant development and testing will be required to achieve a materials data base comparable to that for water-steam and sodium technologies.

At present, no unsolvable materials issues are apparent, however a wide variety of question need to be resolved before design can be committed to a power plant.

Introduction

The Charter of the Solar Materials Task Group states that potential materials problems be identified, their importance quantified, and possible solutions suggested. In this role, the task group is meant to complement current studies of materials--not to serve as a guiding or lead group for solar materials research. The task group independently evaluates potential materials problems within the solar central receiver designs using available documentation, without regard to unpublished current or planned R&D.

A previous report dealt with the 10-MW_e Barstow pilot plant (memorandum from J. J. Bartel to R. C. Wayne, RS 8313/206, dated May 10, 1978 and SAND79-8632 published July 79). The following reviews the molten salt and liquid metal advanced (alternate) central receiver designs.

TABLE I. SUMMARY OF MATERIALS CONCERNS FOR
MOLTEN SALT SOLAR LARGE POWER SYSTEMS

<u>Priority</u>	<u>Problem Area</u>	<u>Recommendations/Solutions</u>
1.	Corrosion of Containment Materials	Perform corrosion experiments under proposed operating conditions. Perform screening experiments in realistic environments. Determine the corrosion mechanisms.
2.	Salt Stability	Determine decomposition rate, mechanism, and extent as a function of various design environments. Determine the effects of anticipated impurities (chlorides, sulfates, water) on salt stability.
3.	Thermal Energy Storage Tank Insulation	Create list of candidate concepts and materials and perform screening experiments.
4.	Receiver Materials Mechanical Properties	Model and experimentally verify the structural materials response to the solar - thermal stress field; quantify the effects of high flux, single - side tube heating, large ΔT 's, and cycling frequency.
5.	Salt Purification	Develop an on-site reprocessing technique to remove impurities and decomposition products.
6.	Analytical Instrumentation	Develop analytical equipment to monitor cover gas and molten salt stability or chemical changes on a real time basis. Develop monitoring devices for the water side of steam/salt heat exchangers.
7.	Alternate Salt Systems	Seek non-nitrate based systems and determine their initial thermo-physical properties, including viscosity, heat capacity, and thermal conductivity as a function of temperature.
8.	Raw Material Supply	Examine projected commercial plant construction schedules with regard to domestic production capacity for the raw salts.

MOLTEN SALT HEAT TRANSPORT SYSTEM FOR SOLAR CENTRAL RECEIVERS

Molten salts offer advantages similar to sodium in heat transport applications, i.e. low vapor pressure at elevated temperatures, good thermal conductivity, low cost, and stability. Sodium- and potassium-nitrate based salts are inexpensive, readily available, have low melting points, and have a history of satisfactory industrial use. However, there is a paucity of information on the behavior of these salts over long periods at high temperatures.

Significant amounts of materials research and development will be required to ascertain the long-term stability of molten nitrate salts and the compatibility of these materials and their decomposition products with the alloys proposed for the containment vessels. There is no evidence that these salt systems will not work; to be determined are the replacement and makeup quantities needed over 10-30 year intervals and the corrosion allowances for the candidate containment materials.

Special handling procedures may be imposed upon nitrates and nitrites due to an ascribed link between these materials in food and an elevated incidence of stomach cancer. Also, public acceptance of systems using copious quantities of nitrates may be a problem, as nitrates have historically been associated with "explosives" and "violent reactions."

Corrosion of Containment Materials

We have been unable to find any published experimental or operational experience demonstrating successful (or unsuccessful) operation with molten nitrate salts near or above 1000°F. Screening experiments are under way at Martin Marietta Aerospace (MMA), Sandia Livermore (SLL), and Sandia Albuquerque (SLA) to evaluate the relative stability of candidate containment alloys. This preliminary screening should be followed by detailed experiments which will quantify the corrosion rates and characterize the mechanisms of corrosion for promising candidates.

The follow-on experiments should assess:

- The potential for chemical transport of alloy elements across temperature gradients;
- The corrosion enhancement due to galvanic coupling of dissimilar metals in the salt circuit;
- The influence of flow velocity upon corrosion rates
- The importance of closed, vented, or continuously air exposed salt systems;
- Thermal cycling;
- The potential for stress corrosion cracking.

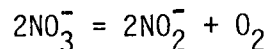
The corrosion mechanisms must be identified in order to select the containment material and predict material life times. Understanding the mechanisms of corrosion is important because they determine the change in corrosion rate as a function of time. For example, if passivation occurs by the formation of a stable oxide film, the corrosion rate will be a decreasing function of time, until it falls to zero. If passivation of the actual

surface does not occur, the rate of corrosion, although probably constant, will be primarily controlled by diffusion and interphase mass transport rates. In this case, the system geometry will be the overriding factor in determining corrosion rate. Differences between the experimental designs and the actual plant conditions, e.g. surface to fluid volume ratios, could result in continual corrosion. This in turn could lead to premature failure of the containment alloys. Examples of system dependent phenomena include mass and chemical transport and electrochemical corrosion. Temperature-induced concentration gradients cause the first two while the last involves these of dissimilar materials in the molten salt system; none can be modeled in laboratory isothermal studies.

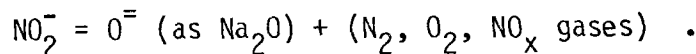
Determination of the corrosion mechanism is essential for the final selection of containment material and a precondition to attempting passivation of the containment alloys or chemical buffering of the melt to reduce corrosiveness. In addition to the problem of general corrosion, the susceptibility of candidate alloys to stress corrosion in the molten salt environment requires immediate evaluation.

Molten Salt Stability

In general, the thermal stability of molten nitrate salts has not been determined in the temperature range of interest. It has been assumed that nitrates tend to decompose according to the reaction



and the nitrite may undergo the continued decomposition



However, numerous secondary reactions can occur, especially if there is access to H₂O and CO₂; the formation of NaOH, Na₂CO₃, and Na₂O can be expected (similar potassium analogs will also form). The formation of specific decomposition species depends upon the environment and quality of starting materials. For example, Na₂O (sodium oxide) is a decomposition product of sodium nitrate. Any water present will react to form NaOH (caustic), which will react further with CO₂ to form Na₂CO₃ + H₂ (carbonate and hydrogen gas). It could be argued that the system should be designed to be water and CO₂ free, thus preventing the reaction sequence listed; however, in the absence of H₂O and CO₂, there is evidence that unstable NO_x can be formed. The current state of knowledge is that not only are reaction mechanisms and rates unknown, but even more fundamental is the fact that the reactions themselves are unidentified.

Salt decomposition can lead to performance degradation due to changes in the properties of the fluid (melting point, viscosity, specific heat, density, and conductivity), increased corrosion rates, and solids precipitation in

selected parts of the system. Clearly the thermal stability of the salt must be completely understood and characterized in order to predict the lifetime and performance of the solar plant. It is recommended that the decomposition rates, mechanisms, and extent of reaction as a function of design environment be determined for the candidate molten salt systems. The individual and possible synergistic effects of anticipated impurities (e.g., Cl^- , SO_4^{2-} , H_2O) also require examination.

TES Internal Tank Insulation

An internally insulated thermal energy storage tank has been proposed. The motivation is to reduce the temperature of the external surfaces of the storage tank which in turn leads to significant cost savings in that low cost carbon steels can be used. Severe requirements are placed on the insulation material: it must be compatible with the molten salt, and it must also withstand the stresses generated during the solidification and melting of the salt. Fibrous alumina-silicate is the leading candidate. However, a silicate matrix is susceptible to chemical attack by alkali nitrates, and the ability of the fibers to withstand the salt freeze-thaw volume changes is unknown. It is our opinion that the search for insulating materials and concepts has not been thorough, and the present selection is not a high confidence approach. It is recommended that other candidate insulation materials and concepts be examined with appropriate experimental verification.

Mechanical Properties of Receiver Containment Materials

In addition to the impact of the solar environment upon the structural properties of the candidate containment materials (see #1 in the liquid metal receiver section), the specific effect that a molten salt may have upon the structural properties of alloy materials in the receiver loop should be examined. These salt specific effects might include corrosion fatigue, surface layer alloy element dissolution, and sensitization.

Salt Purification

Impurities in commercial grade starting materials (chlorides, sulfates, water, and carbonates) can enhance or induce containment material corrosion or cracking; thus, the possibility of impurities should be quantified. Specifically, chloride is a known stress-corrosion cracking sensitizer for stainless steels and Incolloys. As a result, the chloride concentration is usually maintained in the decimal parts per million (ppm) range for steam power plant systems. Although the chemical activity of ions changes with the solvent, the commercial grades of nitrates will assay 1000-2500 ppm (0.1 - 0.25 wt%) sodium chloride, which is very high compared to water standards.

Caustic corrosion has occurred in liquid metal systems that will be cleaned with water. Two facets of this problem are that this corrosion is evidently dependent upon thermal cycling for sensitization to occur, and that pure hydroxide systems are less corrosive than those containing dilute caustic solutions. Either of these conditions could exist in the molten salt systems; however, the consequences may not be as severe as the aqueous solution cases.

TABLE II. SUMMARY OF MATERIALS CONCERNS FOR
LIQUID SODIUM METAL SOLAR LARGE POWER SYSTEMS

<u>Priority</u>	<u>Problem Area</u>	<u>Recommendations/Solutions</u>
1	Receiver Materials Mechanical Properties	Experimental verification of structural materials response to the high flux solar thermal stress field: high flux, single sided heating, large ΔT 's, and cycling frequency. Modelling and verification of these phenomena should be performed.
2	"Striping" Phenomena	Mechanism and impact upon sodium ACR's requires definition by experiment.
3	Valve Seat Hard Facing/Bearing	Mechanical and thermal cycling of candidate valve facing material required to verify performance and establish change-over periods.
4	Monitoring and Maintenance of Sodium Quality	Developed techniques of sodium clean-up and design of sodium piping should be employed to achieve adequate purity system and long life.
5	Generic Sodium System Materials Issues	Use-well developed sodium technology data base and proven designs where possible. Subcontract for consultation with those highly experienced in sodium technology for design review.

LIQUID SODIUM HEAT TRANSPORT SYSTEMS FOR SOLAR CENTRAL RECEIVERS

Up to 600°C (1100°F), sufficient material and design information exists such that liquid sodium systems can be considered commercially available. An extensive liquid metal technology has been developed in the United States, Europe, and Japan in support of liquid metal fast breeder (LMFBR) and other fission reactor technology. Operating experiences have been favorable; Experimental Breeder Reactor II has operated without incident for more than 15 years. However, subtle pitfalls do exist, and therefore it is desirable to have a contractor experienced in sodium systems. Advanced central receivers (ACR's) proposed to utilize a sodium working fluid can and should use this wealth of materials technology.

The potential for sodium systems to operate at 700°C (1300°F) is good from a materials standpoint; however, extensive testing of full-size components will be required because corrosion and material transport are design sensitive at temperatures above 1100°F.

The effect of the solar system characteristics of high flux, single-side tube heating, and diurnal thermal cycling on sodium compatible materials must be determined. Presently the thermal cycling data on containment alloys seldom exceed 300 cycles.

Mechanical Properties of Receiver Materials

Response of the structural material to the high solar flux environment, the effect of single-side tube heating, and the effect of diurnal temperature change upon receiver tube materials requires modelling and experimentation. For any central receiver design, a major concern is the performance of structural materials in the solar environment. Phenomena of concern are creep-fatigue, corrosion fatigue, and thermal shock--not the best understood dynamic processes. These phenomena ultimately influence the design selection of allowable flux levels, longitudinal and transverse tube temperature gradients, and cycling frequency and amplitude. A long-term materials research and development program is needed that addresses both fundamental (generic) and applied (point design) aspects.

The advantages of addressing these issues in a generic sense is that an optimum receiver design would ultimately result; the disadvantage is that a great deal of time is required compared to point design evaluation. It is felt that a combination of both approaches could be used, with testing of selected components and designs at the Central Receiver Test Facility (CRTF) coordinated with laboratory studies and analytical modeling.

Concern over the structural materials response in the solar environment is not unique to sodium systems. Major differences among the receiver designs are primarily flux levels through and temperature gradients within the receiver tubes (transverse and longitudinal). Understanding the response of structural metals in the solar environment is the most important and least understood materials problem for central receiver designs.

Thermal 'Striping'

Crazing or superficial cracking has occurred in header assemblies where individual sodium inlet jets of with 15-20°C temperature difference mix and impinge upon the header wall. A suggested mechanism is that a combination thermal shock and fatigue state develops, which leads to surface cracking. The long-term operational significance of this phenomena is unknown. Where it has occurred in liquid sodium systems, weld overlays of Inconel 617 were used for repair and no subsequent crazing of the I-617 was observed. If tube-to-tube temperature differences of this magnitude exist in the panels of liquid sodium receivers, allowance for crazing should be made in header materials. Inspection of the headers for crazing or lining of header impingement surfaces with a suitable alloy should be included in the design. Experimental determination of the mechanism is required.

Valve Seat/Bearing Hard Facing

The durability of the hard facing materials proposed for valve seats/bearings as well as for sodium pump bearings should be evaluated under simulated solar plant operating conditions. Some of this effort would be a continuation of LMFBR studies; however, the number of thermal cycles (10,000 versus 120 for the LMFBR) and the diurnal temperature extremes are unique to solar systems. One concern is that the hard facing may scale or flake, thereby altering fluid flow. Hard-facing elements may also be "leached out" by the sodium, which would destroy the wear resistance properties and lead to "galling of the moving surfaces. Further development of hard-facing application techniques will be required if the substrates are not austenitic stainless steels, or if valve designs deviate significantly from tested configurations.

Monitoring and Maintenance of Sodium Quality

Corrosion rates and compatibility are mainly controlled by the fluid sodium quality, i.e., oxygen content, carbon level, and trace metal concentration. The importance of monitoring and maintaining the sodium purity and quality can not be exaggerated. A major emphasis in design should be to insure that the purity of the sodium is not degraded. Plant start-up procedures should also be carefully delineated to prevent caustic formation in the sodium system.

Generic Sodium System Materials Issues

Appendix I discusses the performance aspects of materials in service in liquid sodium systems. These items are important only if the solar requirements deviate significantly from the design or operating guides developed for the LMFBR.

GENERIC SODIUM MATERIALS ISSUES

The property data compiled on sodium and sodium compatible materials for LMFBR applications are extensive. The following "generic sodium materials issues" reflect this depth of knowledge. Our consultants infrequently interpolate between test point data and never extrapolate beyond the existing data. Where data ranges are cited, material performance outside a range may be acceptable once the data are obtained.

Comparison of I-800 and 304/316 Stainless Steels Considered by ACR Contractors for Liquid Sodium Service

I-800 and 304/316 stainless properties and other considerations critical to liquid sodium service are summarized in Table A-I. These alloys are considered to be the prime candidate receiver and hot leg piping materials, and the majority of liquid sodium experience has been obtained with them.

Corrosion Aspects of I-800 and 304 Stainless

The corrosion of I-800 and 304 stainless by liquid sodium has been thoroughly studied. The important considerations are summarized in Table A-II.

Temperature Limitations

When considering mechanical property limitations, design problems, corrosion, and the available experimental data base, 1150°F is the upper operational temperature limit for sodium-cooled loops in nuclear reactor technology at this time. This apparent limit may also be expected to apply to solar receivers using I-800, and the limit may be 50-100°F lower for 304 stainless steel. Thermal gradients and cyclic operation may lower the limits still further.

Mass Transport and Deposition

The solubility of almost all alloy elements and nonmetals in sodium is in the parts per million range. Solubility is a function of temperature; therefore material removed from mass loss regions must be deposited somewhere

TABLE A-I. SUMMARY COMPARISON OF INCOLOY 800 AND
304/316 STAINLESS STEELS FOR LIQUID SODIUM SERVICE

<u>Component</u>	<u>Property or Concern</u>	<u>Incoloy 800</u>	<u>304/316 Stainless</u>	<u>Remarks</u>
Receiver	1. stress repture time or creep rates in response to temperature cycling and gradients	Unknown	Probably acceptable	Basic mechanisms are not known. Micro-structural instabilities in IN800 need study
Steam Generator	2. Stress Allowables @ Temperature (1100°F)	75 MPa	50 MPa	Thinner walls can be specified for I-800
Evaporator	3. Stress Corrosion	Superior	Sensitizes	On the water side of heat exchangers, 304/316 is sensitive to chloride stress corrosion cracking (a problem only in <u>liquid</u> water)
Receiver	4. Sodium Corrosion Rate	1 mil/yr	1/2 mil/yr	Corrosion rates for both decrease with time
-	5. Sodium Compatibility Data	Some Data	Extensive	I-800 data is being compiled
All	6. Material Availability		Common	The supply of I-800 is adequate with appropriate lead time for fabrication
-	7. Fabrication Techniques	Similar to 304	Defined	
-	8. Cost	More Expensive Per Unit Mass		There is clear advantage, as less I-800 may be required due to higher allowables

TABLE A-II. CORROSION OF INCOLOY 800 AND
TYPE 304 STAINLESS STEEL

Alloy Composition	High nickel compositions are deleterious at low oxygen concentrations (0-2 ppm); 304 stainless steel is superior to Incoloy 800.
Alloy Purity	Non-metallic inclusions are very bad, especially near or on the surface
Oxygen Level in Na	Controls the corrosion rate
Temperature	Operation limit of ~620°C (1150°F), design sensitive 600-650°C (1100-1150°F)
Mass Transport	Controllable by standard practices
Carburization/Decarburization	Controllable and detectable over the range 0.05-15 ppm. At a carbon content of >3 ppm, carburization occurs in stainless with no loss of stress allowables.
Sodium Flow Rate	The materials are sensitive up to 10 fps; no additional effect is noted at higher rates.

else in the fluid loop. Significant mass transport can occur even though solubilities are in the ppm range. Deposition frequently occurs in heat exchangers, and a 10-20 percent oversize is usually allowed in these components to accommodate reduction in heat transfer area.

Mass transport data in the literature are less quantitative than corrosion information. Mass transport is sensitive to component and system design, which makes laboratory results more severe than those observed in actual reaction loops. Frequently, mass transport rates will decline with time due to localized depletion of a specific element, such as silicon; however, chromium is usually deposited as a carbide, the source of carbon being lubricating oil which is continually available.

Stabilized stainless steels or I-800 would be carburized at the temperatures proposed for operation (590°C). However, data for stainless steels indicate no significant alternation of stress rupture times or creep rates with carburization. No significant loss of stress or ductility allowables would occur on the sodium side with exposure.

Decarburization of all unstabilized annealed austenitic stainless steels will occur at temperatures above 550°C. Although appearing to be

similar to intergranular attack, dissolution of $M_{23}C_6$ type carbides occurs very slowly. Long-term deposition of these carbides in zones with temperatures below $550^{\circ}C$ is the major concern.

In summary, mass transport and deposition are important effects which should influence design. Although the possibility does exist for carburization and decarburization to occur simultaneously in different portions of a sodium system, design care minimize these reactions and allow for their occurrence.

Hardware - Materials Considerations

Drag Discs

Drag discs, which reduce the pressure head from the receiver to the heat exchangers, may experience 1) erosion due to solids in the sodium and high sodium velocities, and 2) galling of load bearing surfaces that undergo relative motion.

Pumps

Mechanical pumps require good seals in order to minimize hydrocarbon leakage into the sodium, which can cause carburization. Hydrostatic bearings are usually employed to prevent the friction problems that occur as a result of the sodium environment.

Heat Exchangers

Heat exchangers present problems similar to those experienced in the nuclear power industry, only without the need to contain radioisotopes. Most corrosion problems occur on the water side of heat exchangers; therefore, separate heat exchangers are usually employed for preheating, boiling, and superheating. At the lower temperatures, the 2-1/4 Cr-1 Mo alloys are employed for resistance to water corrosion. In the superheater, 304 SS or I-800 are recommended for high-temperature sodium compatibility.

Special care should be taken in design and fabrication to minimize small leaks between the sodium and water sides of heat exchangers. On-line monitoring of OH , H_2 , or O_2 should be required so that leaks can be detected prior to catastrophic failure. (A catastrophic leak is one sufficiently large to require shutdown.) Emergency shutdown procedures should be established based on this early warning system. On-line monitoring devices should be designed to provide meaningful data. For example, if the O_2 and H_2 concentration in sodium is detected at the output of the heat exchangers where leaks might occur, the required measurement sensitivity is much less than if the measurement is performed after the fluid stream has passed through the storage system.

Treatment of the entire water system on each pass, not just partial stream processing, should be performed. Components should be evaluated for compatibility. When defining water quality standards, reference should be made to AEC RDT Standard A1-1T for pressurized water reactors and RDT-A1-1 for boiling water reactors.

Alternate Materials

One of the principal limiting factors which controls the use of austenitic stainless steels at elevated temperature is their susceptibility to stress corrosion cracking in the presence of chloride ions on the liquid water side of the heat exchangers. This problem could be eliminated if ferritic steels, which are immune to chloride cracking, were employed. However, unlike austenitic stainless steels, these alloys do not generally possess either the high-temperature strength or compatibility with sodium. Recent European investigations indicate that a new alloy based on 9Cr-1Mo may be able to replace austenitic alloys at least to operating temperatures of 1050°F. Unfortunately, a more complete data base is required before 9Cr-1Mo can be recommended for the sodium systems. It is appropriate that the solar community participate in this effort, particularly since some of the information required may be peculiar to the solar environment.

APPENDIX B

Consultation Listing
Solar Materials Task Group

TABLE AII-1. SOLAR MATERIALS TASK GROUP
CONSULTATION LISTING

<u>Date</u>	<u>Organization</u>	<u>Purpose/Expertise</u>
4/25/78	Martin Marietta	Review design proposed for ACR and materials experiments/compatibility studies
4/26/78	SLL/SLA	Molten salt R&D review
5/22/78	G.E. San Jose	Review liquid sodium test facilities/heat exchanger, H ₂ O chemistry
5/23/78	Badger Chemical Texas City	Chemical processing industry field experience with molten salt systems/user history
6/13/78	Atomics International	Review materials aspect of ACR design/large sodium systems
6/14/78	Energy Technology Engineering Center	Review sodium test experience with small and large components/ valves, hardfacing materials, heat exchangers
7/14/78	G.E. San Jose	Materials development program review
7/17/78	Argonne National Laboratory	Review sodium compatibility work (open meeting)/structural response
9/13/78	SERI	Materials aspects of ACR's information exchange
9/14/78	Martin Marietta	Technical exchange molten salt screening studies/alloy compatibility studies
9/22/78	Westinghouse LMTC, CRC	Capabilities of LMTC for sodium materials testing/liquid metal - structural metals interactions
10/5/78	Hanford Engineering Development Laboratory	High temperature liquid metal experience/STTF component testing
10/12/78	Honeywell	Molten nitrate salts safe use discussions/TES system

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