

SANDIA LABORATORIES IN-HOUSE ACTIVITIES IN SUPPORT OF
SOLAR THERMAL LARGE POWER APPLICATIONS*

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SUMMARY

Research activities have been planned and carried out in direct support of the development of thermal energy storage subsystems for solar thermal large power applications. The emphasis has been on characterizing the behavior of molten nitrate salts with regard to thermal decomposition, environmental interactions, and corrosion. The results to date and future activities are summarized in this paper.

INTRODUCTION

Sandia's in-house activities are defined with the overall objective of advancing solar thermal large power systems. As such, many of these activities are equally supportive of STOR and TPS interest, and generic in-house research programs have evolved. No attempt is made here to partition the in-house activities according to funding division, since a clear demarcation does not exist in many cases.

MOLTEN NITRATE SALT STUDIES

Molten nitrate sensible heat thermal energy storage systems have emerged as one of the leading choices of primary heat transfer and thermal storage media in advanced solar power systems (ref. 1). The salt composition of greatest interest is draw salt (nominally a 50-50 molar mixture of NaNO_3 and KNO_3), and most of the activities to date have concentrated on this composition. Numerous problems have been identified which require resolution in order to prove technical feasibility, carry out detailed designs, and predict long term performance. An in-house program (supplemented by subcontracted activities) has been developed to solve these problems. These activities can be conveniently divided into the following technical areas:

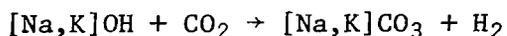
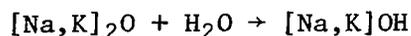
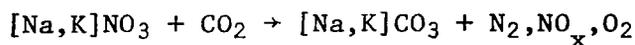
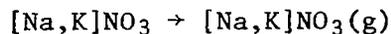
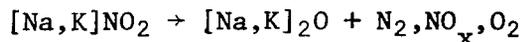
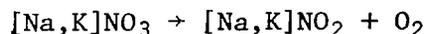
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- Thermal Stability
- General Corrosion
- Environmental Corrosion Cracking
- Electrochemical Studies
- Thermal Properties

Each of these areas are discussed below with regard to (1) the nature of the problem, (2) accomplishments to date, and (3) future activities.

Thermal Stability

It is recognized that nitrate salts can degrade by numerous processes; some examples are given below (unbalanced):



All of these reactions are thermodynamically favored to some extent. The problem is to define the extent and rate at which these reactions occur.

Many parameters conceivably influence the degradation process, a partial list being temperature, surface area, surface to volume ratio, ullage gas composition, salt purity and gas flow rate over the salt. A Plackett-Burman experimental design (ref. 2) has been run in order to determine the main effect variables. Preliminary analyses of the data indicate temperature is by far the most important variable; detailed data analyses are currently being carried out. In addition to these main effect screening studies, in-depth studies are underway using a TGA/EGA (thermogravimetric/evolved gas analysis) apparatus capable of simultaneously measuring sample weight changes and analyzing evolved gas species in vacuum and controlled pressures up to one atmosphere. Results to date show it is incorrect to assume the reduction reaction ($[\text{Na,K}]\text{NO}_3 \rightarrow [\text{Na,K}]\text{NO}_2 + .5\text{O}_2$) is the only major decomposition process as suggested by others (ref. 3). Rather, numerous modes of decomposition appear to be active; N_2 and NO_x are generated as products of decomposition along with O_2 .

Future activities will be aimed at isolating the different decomposition processes, and determining their individual rates. The prime mode of study will be with the TGA/EGA apparatus. Several supplementary subcontracted activities have been defined: (1) phase diagram determinations and (2) H₂O/CO₂ interaction rates and mechanisms. Requests for proposals have been prepared and are scheduled for release in early FY80.

General Corrosion

Molten nitrates do not appear to create an overly severe general corrosion environment. Static immersion tests have indicated that general corrosion takes place by oxidation. Parabolic rates have been observed for high chromium alloys, suggestive of protective oxide formation. The oxide layers appear to be adherent, and are not susceptible to thermal cycling. However, in order to extrapolate this data to 30 year time periods with confidence, mechanistic understanding of the corrosion process is needed. Furthermore, a cause for concern has arisen; chromium has been observed in the salt, which implies a potential mass transport problem in an operating system with thermal gradients and flowing fluids. Static immersion tests have led to the selection of Incoloy 800 as the prime candidate for high temperature use (1050°F), although the less costly stainless steels cannot be discounted on the basis of general corrosion.

Three single-material thermal convection loops have been constructed out of 304, 316, and I800, and they are currently in operation. To date, the loops have experienced 4000, 1000 and 1000 hours of operation respectively. Sample coupons have been extracted at 500 hour intervals and analyzed for extent of corrosion. Thin oxide layers formed on the alloys; net weight changes are negative for 304, and positive for 316 and I800.

Future activities include the continued operation of these loops and complementary immersion tests will be carried out with the objective of determining the rates of the various processes involved (e.g. oxide formation, Cr₂O₃ dissolution, Cr diffusion). The in-house studies will be supplemented by a subcontracted study at ORNL, where 304, 316, and I800 loops experiments will be carried out in sealed environments.

Environmental Corrosion Cracking

A major concern to design engineers is the coupled interaction of an aggressive environment and applied stress on containment materials. A well known problem of this type is chloride stress corrosion cracking, where the chemical action of the environment acts on tips of propagating cracks to greatly accelerate crack growth. It is not known whether the nitrate salt environment induces corrosion cracking; no data are available to suggest that there is or isn't a problem.

A plan has been developed to determine the potential for environmental cracking; slow strain rate, stress corrosion, and corrosion fatigue

experiments are planned, and will be initiated in FY80.

Electrochemical Studies

Currently, decomposition and corrosion processes are being studied independently as discussed above. It is also recognized that one can expect strong synergistic interactions between the salt chemistry (ionic species), decomposition processes, and corrosion processes; therefore, an ability to determine ionic species (quantitatively and qualitatively) in the salt melt is clearly desired. Electrochemical techniques can provide the capability; however, techniques must be developed and perfected. Electrochemical approaches can also be used for real time studies of corrosion, providing a potential for a sensitive corrosion tool complementing other corrosion activities discussed above.

In-house activities have concentrated on the development of an oxide ion sensitive electrode. Because the oxide ion (O^{2-}) is purported to be a key component in thermal decomposition, corrosion, and CO_2/H_2O interaction processes, it is felt that a means to directly measure its presence is required to gain a fundamental understanding of salt behavior. An oxide ion sensitive electrode of the form $Pb, PbO/ZrO_2Y_2O_3//$ has been developed and Nernst behavior demonstrated over the range of 10^{-10} - 10^{-4} molal O^{2-} with excellent stability, response, and reproducibility. A cyclic voltammetric set-up has been completed, and preliminary studies on nitrate melts have demonstrated the potential for using cyclic voltammetry to identify ionic melt species.

Techniques to determine the ionic species in the melt will continue to be developed, and eventually used to monitor the salt chemistry as thermal decomposition, atmospheric interaction, and corrosion processes occur. Subcontracted electrokinetic studies are also planned in which the kinetics of passive oxide film formation on candidate alloys will be investigated.

Thermal Properties

The high temperature viscometer has been modified to study molten salts, and experiments will be carried out to measure viscosity, surface tension, and density as a function of temperature, salt composition and gaseous environment. If it is determined that accurate high temperature thermal conductivity and heat capacity data are required, studies will be initiated.

OTHER STUDIES

The major emphasis of Sandia's in-house program has been on molten draw-salt behavior. For the sake of completeness, other in-house thermal energy storage related activities are mentioned here. It is known that the use of hydrocarbon fluids as a thermal storage medium is temperature limited due to the degradation of the oil. Rates of fluid loss have been determined for three different hydrocarbon oils: Caloria HT43, SUN 21, and Therminol 66. In

addition, fluid loss rates pertinent to oil/granite and oil/sand dual media systems were also determined; the filler material (granite and sand) caused enhanced fluid loss rates in all cases.

Dual media systems have also been proposed for nitrate salt systems. The compatibility of nitrate salts with granite rock and pelletized iron ore (taconite) have been cursorily examined; the results indicate the salts are not compatible with granite rock materials, but may possibly be used in direct contact with taconite at temperatures up to 550°C.

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