Thermal Storage Research and Development

Performing Organizations: Sandia National Laboratories (SNL)

Key Technical Contacts:
Nathan Siegel (SNL), 505-284-2033, npsiege@sandia.gov
Bob Bradshaw (SNL), 925-294-3229, rwbrads@sandia.gov
Greg Kolb (SNL), 505-844-1887, gjkolb@sandia.gov
David Raymond (SNL), 505-844-8026, dwraymo@sandia.gov
Rich Diver (SNL), 505-845-0195, rbdiver@sandia.gov
Tim Moss (SNL), 505-845-3366, tamoss@sandia.gov

DOE HQ Technology Manager: Thomas Rueckert, 202-586-0942, thomas.rueckert@ee.doe.gov

FY 2009 Budgets: $2.65M-total funds, carryover included (SNL)

Objectives

- Develop advanced heat transfer fluids and thermal storage media for power towers and parabolic troughs in an effort to improve dispatchability and achieve the LCOE cost goals outlined in the *DOE Solar Program Multi-Year Technical Plan*
- Develop the components and systems necessary for incorporating thermal storage into concentrating solar power (CSP) facilities.
- Support industrial partners who are developing thermal storage technologies.
- Develop cost-effective thermal energy storage (TES) for parabolic trough plants.
- Formulate heat transfer fluid (HTF) for advanced parabolic troughs enabling higher operating temperatures (500 ^{o}C) than current fluids and thus higher efficiency.

Accomplishments

- SNL: Began evaluating freeze recovery strategies necessary to enable the use of molten salt heat transfer fluids in parabolic trough facilities.
- SNL: Developed multi-component molten nitrate salt mixtures that solidify below 100°C.
- SNL: Demonstrated thermal stability of these salts to 500 ^{o}C and completed long-term corrosion testing of carbon and stainless steels.
- SNL: Produced a preliminary design of a test facility upgrade aimed at evaluating the components (pumps, valves, instrumentation) required by power plants using molten salt heat transfer and storage fluids.
- SNL: Began efforts to use computational chemistry to predict the physical properties of prospective new molten salt compounds.
- SNL: Identified salt mixtures that freeze below 80 ^{o}C.
- SNL: Performed an analysis of a 2X trough system showing a reduction in LCOE.

Future Directions

- Begin to expand our laboratory capabilities to better support the continued development of heat transfer and storage media and related systems (high temperature salt test lab, Pump and Valve upgrade, 2X trough development, central receiver testing with molten salt).
- Support funding opportunity announcement (FOA) awardees
- Begin to increase the focus on higher temperature heat transfer fluid and storage options for power towers.

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1. Introduction

Concentrating solar power (CSP) plants, both parabolic trough and power towers, are being built or planned that will generate significant electrical power output in the near-term. Thermal energy storage incorporated into such plants would reduce the levelized cost of energy and provide dispatchability at the most valuable time of day. Commercially available nitrate salts can provide high capacity storage and have properties that are readily adaptable to the operating characteristics of both trough plants and power towers. The purpose of this project is to develop improved heat transfer fluids, thermal storage media, and associated systems that are particularly suited to CSP applications.

The majority of the current R&D effort is focused on parabolic trough facilities. Sandia National Laboratories has developed and evaluated alternative inorganic molten salts that can be used at temperatures up to 500°C, increasing power cycle efficiency vs. oil-based HTFs, which are limited to 400°C. The molten salt HTF is amenable to use in large TES tanks because it is inexpensive relative to organic fluids and has negligible vapor pressure. The primary disadvantage of molten salt HTF is relatively high freezing point (for instance, 230°C for binary Solar Salt) as compared to about 13°C for organic fluids. As such, considerable care must be taken to ensure that molten salt HTF does not freeze in the solar field. In the event that it does, systems must be developed to allow the field to recover with minimal damage. In addition, there is a need for further development of components (valves, heat exchangers, pumps, and instrumentation) and systems appropriate for reliably handling molten salt fluids.

2. Technical Approach

Technical work in FY08 (and FY09) was focused in four general tasks outlined below:

- *Advanced heat transfer fluid development* - The strategy for developing improved molten nitrate salt HTF was to survey published phase diagrams for freezing point data, then expand the basis of formulations to include constituents that promised lower liquidus temperatures. A limited combinatorial experimental matrix was used to observe low-melting mixtures and to estimate the direction of optimal composition for the next sequence of experiments. The candidate low-melting salt mixtures were then subject to determinations of chemical stability, viscosity and corrosion activity.
- *Freeze recovery* – The issue of freeze recover for parabolic trough plants using a nitrate salt heat transfer fluid was investigated on a small scale using a string of heat collection elements (HCEs) equipped with an impedance heating system. The HCEs were exposed to successive freeze thaw cycles and evaluated for resultant damage. This work is ongoing.
- *Molten salt test facility design* – In the past Sandia has conducted experimental evaluation of components and instrumentation needed to handle molten salt in the field. The current facility used for this work requires an upgrade to support the near term needs of the CSP industry. In FY08 we produced a preliminary design for the upgraded facility along with an associated budget. We are now planning an industry workshop to fully define the necessary capabilities and upgrades.
- *Modeling* – We developed a model of an advanced parabolic trough system that incorporates several improvements relative to current technology including increased concentration ratio and higher operating temperature.

Agreement Title	FY 2009 Budget ($K)
Storage components (freeze recovery, facility design)	2000 (1400 c/o)
Storage systems (modeling)	100
Advanced HT fluid development	500
FOA support	50

Table 1. FY09 Budget Levels

3. Results and Accomplishments

<u>*Advanced heat transfer fluid development*</u>

- Developed multi-component molten nitrate salt mixtures that solidify below 100°C by limited combinatorial experiments
- Demonstrated chemical stability of these molten salts to 500°C
- Determined viscosity of molten salt HTF as suitable for applications in trough systems
- Completed long-term exposure phase of corrosion testing of container alloys ranging from stainless steels to carbon steel

This project achieved an innovation in an HTF capable of both low and high temperature operation and well suited for parabolic trough facilities as a direct replacement for the relatively costly organic HTF currently in use. Mixtures of the four salts (sodium, potassium, lithium and calcium nitrates) were identified that display liquidus temperatures less than 100°C.

The chemical stability limits of low-melting salt mixtures were determined by chemical analysis of decomposition products in molten salts maintained at progressively higher temperatures and are shown in Figure 1. The equilibrium concentrations of nitrite ion in several quaternary nitrate salt mixtures were measured between temperatures of 400°C and 520°C after holding for several days. The concentration of nitrite in the quaternary mixtures is somewhat less, but nevertheless comparable, to that calculated for the binary Solar salt at corresponding temperatures.

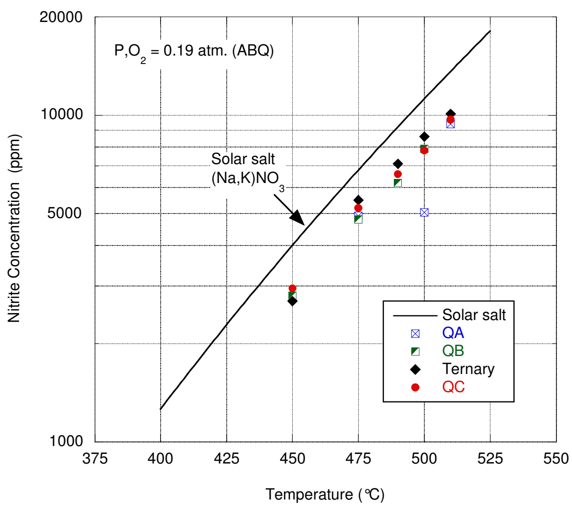

Figure 1. Low melting point salt (QA, QB, QC) stability data over the range of probable use in trough systems.

Viscosity measurements showed that calcium nitrate additions to the multi-component molten salts significantly increased the viscosity. The viscosity near the liquidus temperature (~90°C) was more than 100 cP, which is an acceptable value for handling in a TES system. The viscosity at temperatures in the upper range of normal operation of a trough system, e.g., 400°C, is 5-7 cP and is 4-5 cP at 500°C, as determined by extrapolating the data from the measurable temperature range.

To fully evaluate the properties of such molten salts, corrosion testing of materials that could be used to construct molten salt systems was conducted for 3000 hours. Materials tested at 500°C were several stainless steels (316L, 304, 321, 347) and alloy steel 9Cr-1Mo and, at 350°C, carbon steel A516 and alloy steels, 9Cr-1Mo and 2 ¼ Cr-1Mo. Welded specimens were included. The exposure period was completed and the specimens are being evaluated gravimetrically and metallographically to determine their performance. Salt samples were taken to confirm chemical stability by chemical analysis.

Exploratory laboratory work was conducted to investigate the properties of mixtures of nitrate (NO_3^-) and nitrite (NO_2^{-1}) salts. The cations added to the mixtures were sodium, potassium and lithium in varying proportions. The preliminary results indicate that low-melting salts are achievable with mixed anion compositions and melting points near 80 °C were observed for a 1:1 mol ratio of nitrate-nitrite. Particularly interesting are mixtures containing a low content of lithium, as this reduces the cost due to the most expensive constituent.

<u>Freeze recovery</u>

- Constructed an impedance heating test platform (Figure 2)
- Performed preliminary freeze/thaw studies

Several industry partners have proposed using molten salt in the field for parabolic trough plants. A strategy must be developed that would enable the facility to recover from a freeze. One option is to treat the HCEs as electrical resistors that can be used to thaw the frozen salt within them when an electrical current is applied. Questions remain as to whether the HCEs can be adequately heated in this manner without damage. We are currently exposing the HCEs, which have been filled with salt, to successive freeze thaw cycles. Preliminary results show some tube motion during cycling due to induced stresses. Understanding the behavior of this system will allow us to design HCEs specifically for moltent salt service. Additionally Solar Millennium, a FOA awardee, has requested test support using this platform.

<u>Molten salt test facility design</u>

- Preliminary facility design has been completed
- Industry workshop planning to further define the required upgrades and test and evaluation needs is underway
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There is an industry-wide need for test support related to the development of the components used to handle heat transfer and thermal storage media, particularly molten salts.

Currently a suitable test and evaluation platform does not exist. In the past, Sandia had a suitable facility but it has since fallen into disrepair and, even if restored to its former condition, would not meet current industry needs. We have completed a design for an upgraded facility that would build off of existing infrastructure and be able to accommodate an expanded suite of component testing and development. We are soliciting input from industry partners and DOE to aid in fully defining the capabilities of the upgraded facility.

Fig. 1. Two HCEs equipped with an impedance heating freeze recovery system at SNL.

Modeling

- Performed an initial system analysis of an advanced parabolic trough system (2X Trough) having double the concentration ratio of current systems

Lowering the LCOE for parabolic trough power plants requires several technical advances including increased concentration ratio, better selective surfaces, higher temperature operation, and thermal storage. We modeled a facility having these attributes to determine the level of the specific performance and cost gains. The results indicate that high temperature operation (500 ^oC) can only be efficiently achieved if the concentration ratio is doubled, better selective coatings are used on the HCE, and an appropriate fluid is developed. At this point we feel that R&D related to the system design of the 2X trough is justified and plan to include this in our future activities.

4. Planned FY 2009 Activities

Advanced heat transfer fluid development

- Extend physical property determinations of molten nitrate salt HTF to include density, heat capacity and thermal conductivity.
- Complete evaluation of 3000-hour corrosion test specimens to confirm suitable materials of construction corresponding to the new molten salt HTF.
- Complete exploratory study of nitrate-nitrite molten salt system for low-melting compositions and preliminary evaluation of viscosity and chemical stability.
- Determine effects of impurities expected in bulk commodity grades of constituent nitrate salts, e.g., carbonate, chloride, sulfate, on freezing behavior.
- Explore molecular dynamics computational methods to discover better low-melting salt compositions.
- Investigate higher temperature heat transfer fluids for power tower applications

Freeze recovery

- Continue evaluating the impedance heating strategy – identify technical hurdles
- Develop inroads with international partners working on similar technologies
- Support FOA awardees interested in this technology

Molten salt test facility design

- Complete the conceptual design – likely to be done in two stages
- Place a contract with an A&E firm to begin the detailed design
- Place construction contracts
- Begin construction

Modeling

- Construct a finite-element structural/optics model of the advanced 2X trough initially analyzed in FY08

5. FY 2008 Special Recognitions, Awards, and Patents

Patent application S-112,575, Low-Melting Point Inorganic Nitrate Salt Heat Transfer Fluid, R. W. Bradshaw and D. A. Brosseau, Allowed Dec. 2008, in USPO review.

Patent application S-114-222, Low Melting Point Heat Transfer Fluids, J. Cordaro and R.W. Bradshaw, filed Dec. 2008.

6. Major FY 2008 Publications

Improved Molten Salt Formulations for Heat Transfer Fluids in Parabolic Trough Solar Power Systems, SolarPACES 2008, Las Vegas, NV, Mar. 4-7, 2008, R. W. Bradshaw and D. A. Brosseau

Molten Nitrate Salt Development for Thermal Energy Storage in Parabolic Trough Solar Power Systems, Paper ES2008-54174, ASME 2nd International Conference on Energy Sustainability, Jacksonville, FL, Aug. 10-14, 2008, R. W. Bradshaw and N. P. Siegel

Conceptual Design of an Advanced Trough Utilizing a Molten Salt Working Fluid, SolarPACES 2008, Las Vegas, NV, Mar. 4-7, 2008, G. J. Kolb and R. B. Diver

7. Acknowledgements

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.