SAND2010-3347C

Advanced Heat Transfer Fluid Development (CSP Agreement 16749)

2010 DOE CSP Program Annual Review

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CSP – Thermal Energy Storage

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Overview

Timeline

- Start date : Sept. 2007
- End date : Continued in FY11
- Percent complete: 50% (estimated, based on AOP-FY10)

Budget

- Total project funding 1645 K$
  - 100% DOE CSP program
- 507 K$ in FY09
- 835 K$ in FY10

Barriers

- Barriers addressed
  - Performance (G) – Improve CSP efficiency
  - Cost (E) – Reduce LCOE by advancing TES and collector systems
  - *Technology Risk (I)*

Partners

- No funded partners
- Interactions/collaborations
  - NREL, SQM, Abengoa, FOA awardees

Challenges, Barriers or Problems

- Challenges
  - Develop a broad base of inorganic heat transfer fluids (HTF) that can be used in Troughs and Towers.
    - Extend capabilities of molten salts beyond Solar Salt, organic HTF
    - Optimize properties and performance to match specific system needs and composition to attain least cost
  - Develop high energy density TES by encapsulating PCM cheaply and conveniently
- We are pursuing the development efforts by laboratory experiments and computational modeling.
- Importance - This project aims to develop the enabling technology of Advanced HTFs that will support construction of large-scale CSP power plants by commercial entities.

Relevance

- Discovery/characterization of low-melting nitrate-nitrite molten salts as HTF
  - Provides working fluid and TES media for advanced troughs
  - Enables Direct TES operation; reduces LCOE
- Evaluation of molten salts for high-temperature ($\leq$ 700°C) HTF
  - provides improved working fluid and TES capacity for Towers (SCR)
  - Improves thermal efficiency and exploits ultra-supercritical steam cycles
- Computational modeling of molten salt mixtures
  - A research effort to expand scope of investigated compositions beyond experimental range
  - Methodology will apply to other types of salts
- Evaluation of molten salt hydrates for Trough HTF
  - Extends lower temperature operation of molten salts to ambient or below
  - Avoids potential freeze-up in the collector field
- Encapsulation of PCM (phase change materials) for TES
  - Drastically reduces size and cost of TES system due to high energy density of phase changes compared to sensible heat capacity

Approach

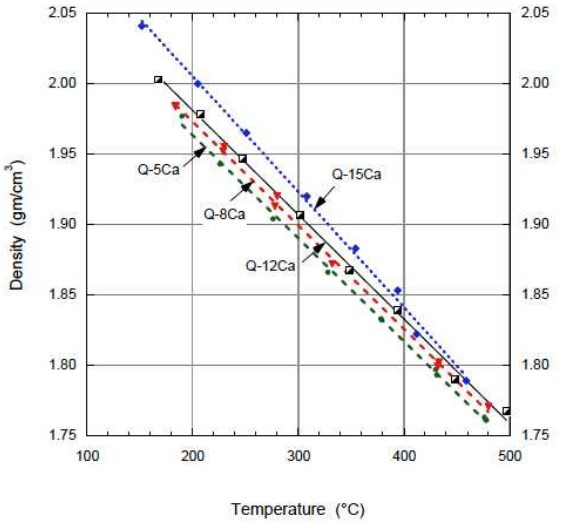
- Discovery/characterization of low-melting nitrate-nitrite molten salts as HTF
  - Laboratory-scale experiments to explore phase transition behavior vs. composition
  - Physical property measurements (various instruments) and chemical analysis of melts
- Evaluation of molten salts for high-temperature ($\leq$ 700°C) HTF
  - Laboratory-scale experiments to explore chemical stability vs. temperature and cation composition
  - Corrosion testing of variety of high-temperature alloys
- Computational modeling of molten salt mixtures
  - Molecular Dynamics calculations of liquidus temperature
  - Continuum thermodynamic calculations of liquidus temperature
- Evaluation of molten salt hydrates for Trough HTF
  - Laboratory-scale experiments to determine onset of crystallization vs. composition and temperature
- Encapsulation of PCM (phase change materials) for TES
  - Laboratory-scale development of novel technique to coat metal spheres by method suitable for mass production

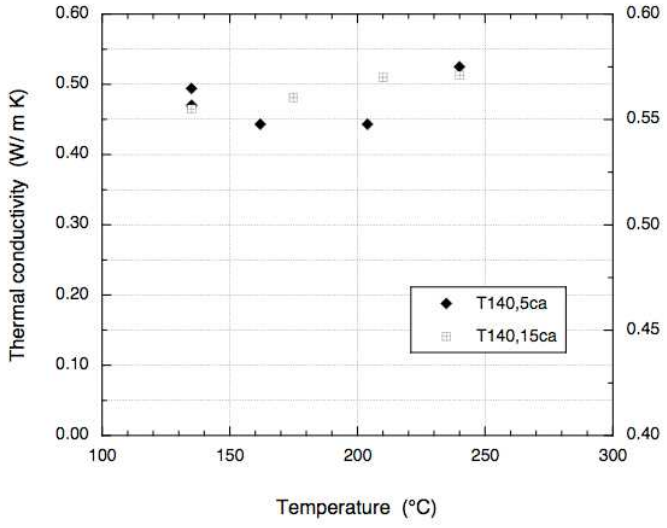
Characterization of Low-melting Nitrate Salts for Parabolic Trough HTF

(Accomplishments / Progress / Results)

- FY09 lab experiments and 3000-hour corrosion testing established that quaternary molten salt mixtures are stable at 500°C
- Physical properties determinations have progressed to demonstrate utility
  - Density – lab measurements agree with calculations based on partial molar volumes
  - Viscosity – non-Arrhenius temperature dependence well correlated by Fulcher equation
  - Thermal conductivity – preliminary measurements, up to 270°C, show minor effect of additions of $LiNO_3$ and $Ca(NO_3)_2$ compared to binary Solar Salt
- Metallographic examination of 3000-hour corrosion tests completed
  - 4 Stainless steels, 2 Cr-Mo steels, carbon steel, weldments, in 2 salt mixtures ; report in review

Take away - Quaternary nitrate molten salts have demonstrated useful engineering properties for CSP applications.



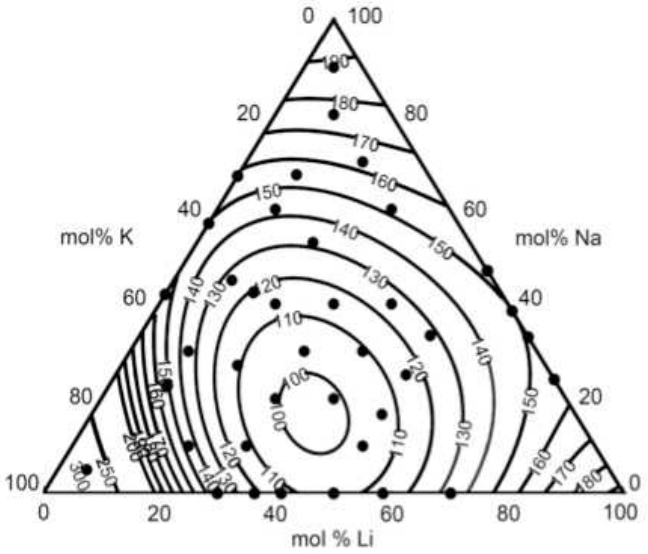


Discovery and Characterization of Low-melting Nitrate-Nitrite Salts for Parabolic Trough HTF

(Accomplishments / Progress / Results, Con't.)

- Expanded FY09 studies to experiments with additional NO_3^-/NO_2^- ratios
  - Lowest melting salt near 72 °C
  - Lithium content < 30 mol%
- Thermal stability limited by oxidation of NO_2^-
- Physical properties measurements in progress
  - Viscosity
  - Heat capacity
  - Heat of fusion

Take away – Molten salts containing significant proportions of alkali nitrates and nitrites offer reduced freezing points. Thermal stability must be further investigated to support CSP applications.



1:1 Nitrate-Nitrite Phase Diagram

Evaluation of Molten Nitrate Salts for Advanced CSP Tower Systems

(Accomplishments / Progress / Results, Con't.)

- Assembled experimental apparatus to investigate chemical stability of molten nitrate salts up to 700°C
  - Experimental evaluation of stabilizing binary molten nitrate salts by oxygen partial pressure
  - Began experiments with (Na,K)NO_3 mixtures.
  - Effect of alkali metal nitrate proportions on melt chemistry
- Apparatus being assembled to conduct corrosion tests of high-temperature alloys in stabilized molten nitrate salts to 700°C
- Previous work using oxygen-stabilized Solar Salt at 650°C
  - Two nickel-based alloys showed good corrosion resistance during 3000 hour tests

Take away – Binary Solar Salt shows good promise as an HTF capable of increasing the temperature limit of Tower systems to 650°C or more.

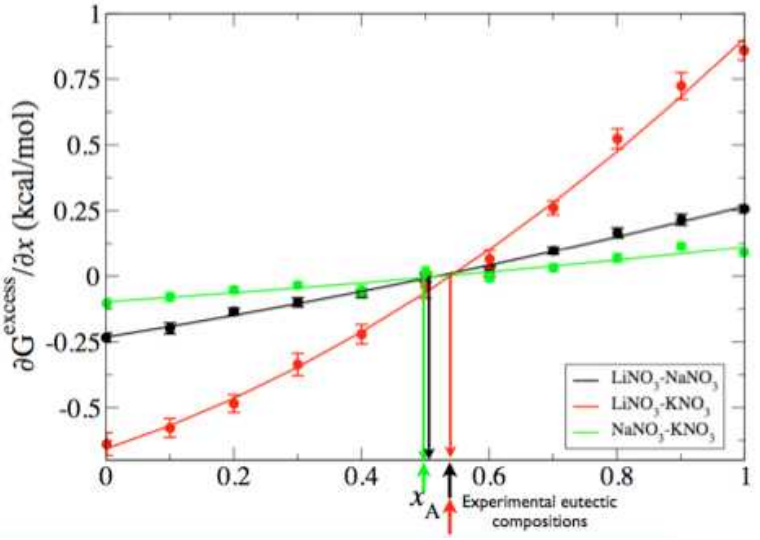
Controlled-atmosphere molten salt chemistry apparatus

Molecular Dynamics Modeling of Molten Salt Liquidus Properties

(Accomplishments / Progress / Results, Con't.)

- Aim: To develop and apply a method to compute low-melting compositions of alkali nitrate salt mixtures using MD simulations implemented in LAMMPS. Current approaches can't handle molten salts.
- Approach: Compute minimum in free energy of liquid mixture which is an estimate of the eutectic composition. Free energy computed via alchemical transformation of one cation to another, an iterative method.
- Accomplishments: Developed method and computed free energies and hence estimates of eutectics of $LiNO_3$-$NaNO_3$, $NaNO_3$-KNO_3, and $LiNO_3$-KNO_3 mixtures. Computed results compare well with experimental values.

Take away – Molecular Dynamics simulations of multi-component ionic fluids are very complex to develop but significant porgress has been made. MD can be applied to other salts and can also compute physical properties.

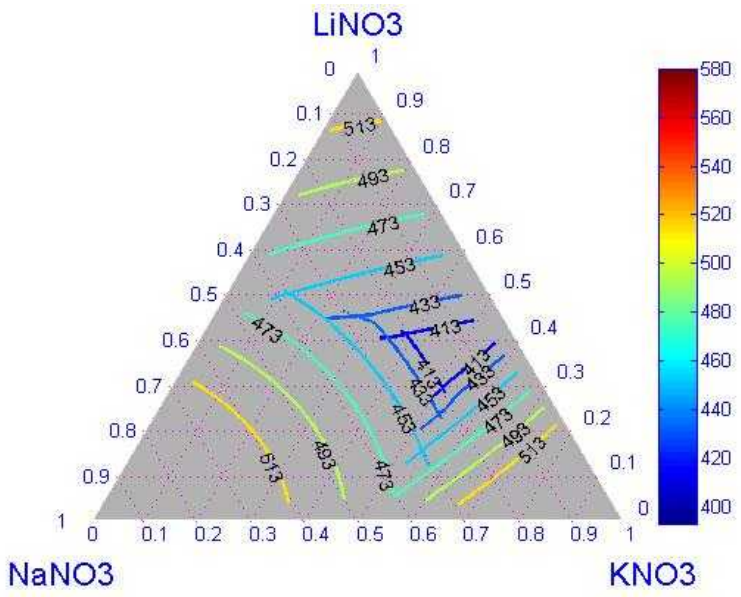


Continuum Thermodynamics Modeling of Molten Salt Liquidus Properties

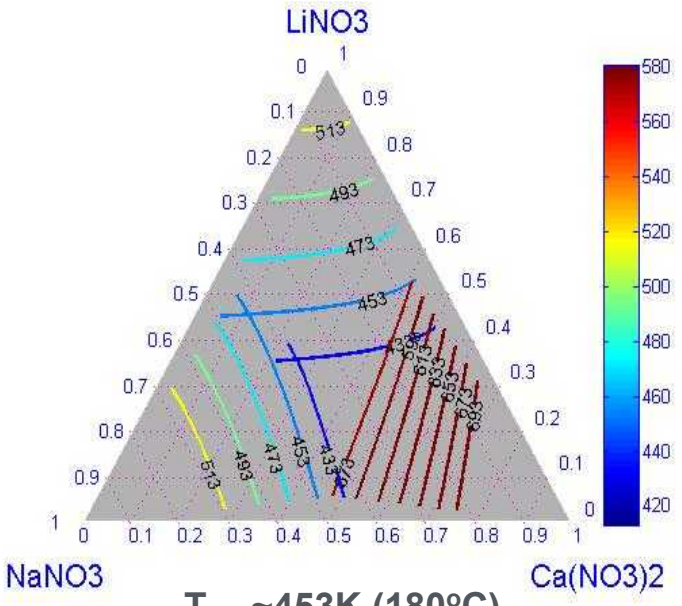
(Accomplishments / Progress / Results, Con't.)

- Programmed in-house computation tool based on Wilson equation to model liquid phase activity with binary interaction parameters.
- Prediction of ternary eutectic points of $LiNO_3$, $NaNO_3$, KNO_3, and $Ca(NO_3)_2$.

Take away – Classical thermodynamics methods for excess free energy calculations provide a means to extend phase diagram prediction to additional constituents.



T_{eut} ~393K (120°C)
Data = 120°C



T_{eut} ~453K (180°C)
Data = 170°C

Investigation of Molten Salt Hydrates for Parabolic Trough HTF

(Accomplishments / Progress / Results, Con't.)

- Molten salt hydrates are mixtures in which water is the minority component
- Reviewed literature concerning phase diagrams of metal-nitrate-water systems for individual metals (Na, K, Li, Ca, Mg) and mixed-cation salt hydrates
  - Additions of $LiNO_3$ and $Ca(NO_3)_2$ expected to reduce water content required for single phase at low temperature
- Experiments started to determine water content vs. temperature and multi-component salt composition at which initial phase separation occurs at low temperatures (ambient or below)

Take away – Application of molten salt hydrates to parabolic troughs leverages industrial systems used to start molten salt heat exchangers. The properties of hydrates of multi-component molten salt mixtures may enable low solidification temperatures.

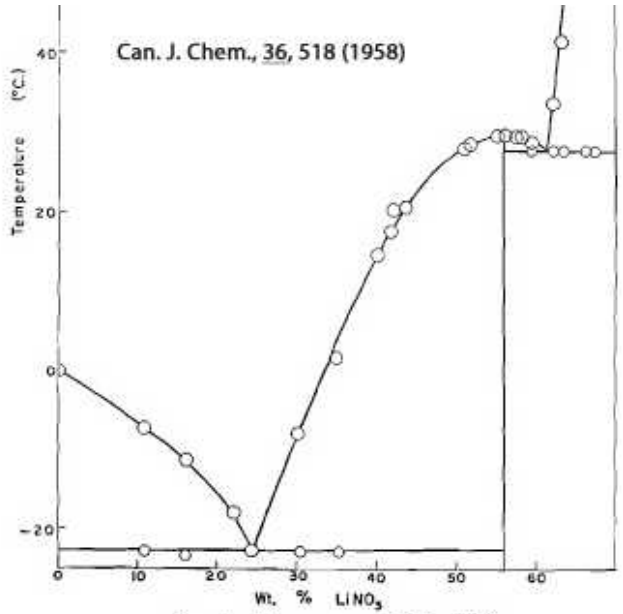


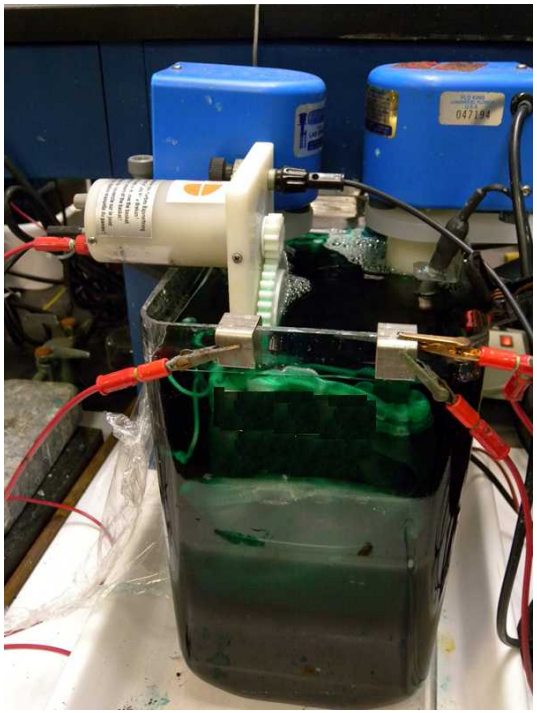
FIG. 4. The system $LiNO_3$–H_2O.

- Demonstrated an encapsulation technique for metallic PCM to produce media compatible with molten salt HTF
- Zinc (T_m 417°C) and lead (328°C) are target PCM media
- Lead balls were electroplated with nickel, subjected to melt/freeze cycle and remained intact.
- Encapsulation technique is suitable for mass production.
- Patent application in preparation

Take away – A small, but significant, advance has been made to enable high-density thermal energy storage with PCM.

<u>Furnace test</u>
Left – plated balls
Right – lead ball

Lab-scale barrel plating apparatus



Future Plans (FY 2011 and beyond)

- Discovery/characterization of low-melting nitrate-nitrite molten salts as HTF
  - Complete physical property measurements (FY10)
  - Issue corrosion report (FY10)
  - Address carry-over technical issues (FY11)
- Evaluation of molten salts for high-temperature ($\leq$ 700°C) HTF
  - Continue laboratory experiments of chemical stability vs. temperature and cation composition (FY10); study other aspects of melt chemistry (FY11)
  - Corrosion testing at 650°C (FY10) and 700°C (FY11)
- Computational modeling of molten salt mixtures
  - Molecular Dynamics – Extension of method to ternary mixtures (FY10); Extension to divalent cations; very challenging (FY11).
  - Continuum thermodynamics – Refine ternary calculations (FY10); Quaternary mixtures (FY11)
- Evaluation of molten salt hydrates for Trough HTF
  - Complete initial matrix of phase separation vs. composition, temperature (FY10)
  - Conduct high temperature experiments at pressure (FY11)
- Encapsulation of PCM (phase change materials) for TES
  - Extend electroplating method to zinc balls (FY10)
  - Optimize mechanical properties of plated shells (FY11)

Collaborations

- NREL
  - Co-operation among technical staff to leverage laboratory capability for physical properties at high temperatures
- SQM
  - Extending physical property and corrosion studies of molten salt HTF
- Information exchanges with Private-sector companies (public information)
  - Response to inquiries for technical information typically related to corrosion, physical or chemical properties of molten salts
  - Assisted FOA awardees within the DOE Solar Program
- University contacts
  - Informal discussions with U. Wisconsin and U. Alabama regarding thermodynamic approach to phase diagram calculations
- Licensing activities
  - Discussions in progress with a US company

Summary Slide

- Development of low-melting molten salt HTF has attained a relatively advanced state
  - concept of adding constituents validated, good properties demonstrated, I.P. created, licensing and partnering to scale-up is in progress, other DOE-funded projects will extend the original scope.
- Prospects for using molten nitrate salts at high temperatures in Tower systems are very promising
  - Prior studies of melt chemistry and corrosion behavior support extension of a Solar Salt-like mixture to 700°C
- Encapsulation method for PCM has been demonstrated
  - Significant process development and material validation work needs to follow
- Project team has breadth of skills to continue progress in HTF development and applications

Supplemental Slides

Project Schedule

1. Initiation Date – FY07 (This project started as a single task incorporated under another larger project.)
2. Original Expected Completion Date – not specified. This work is an on-going research project that adapts to meet evolving needs of CSP systems as communicated by system design engineers.
3. Current Expected Completion Date – n/a
4. Reasons for Delay – n/a

Budget

- All funding for this project derives from DOE-EERE.
  - The project is within budget and consistent with spend plan.
  - Tasks that could be added given additional funding
    - Broaden experimental effort to evaluate molten salt chemistry and corrosion at temperatures up to 700°C.
    - Focus more resources on development of encapsulation technique for metallic PCM.
    - Accelerate computational chemistry modeling effort to include physical property modeling and explore other constituents.

Responses to Previous Year Reviewers' Comments

- Previous year's reviewers' comments - This project was not reviewed as a stand-alone in 2009 but was included in the review of the Storage Systems project. Regardless, reviewers commented that they were skeptical that molten salt could be used in a parabolic trough field due to possible freezing.
- This is a significant issue that we are addressing by seeking fluid mixtures with lower freezing points and by conducting freeze-thaw testing with full-scale heat collection elements (HCE) to evaluate recovery techniques and potential damage to HCEs. We are also cooperating with two trough system design companies to establish programs to evaluate molten salt in trough test loops.

Publications

- Bradshaw, R.W. and Siegel, N.P., "Development of Molten Nitrate Salt Mixtures for Concentrating Solar Power Systems", Paper 11538, SolarPACES 2009, Berlin, Germany, Sept. 2009.
- R.W. Bradshaw, "Effect of Composition on the Density of Multi-Component Molten Nitrate Salts", SAND2009-8221, Dec. 2009.
- Bradshaw, R.W., Cordaro, J.G. and Siegel, N.P., "Development of Inorganic Molten Salt Mixtures for Solar Thermal Energy Systems", ASME Energy Sustainability 2009, Paper ES2009-90140, San Francisco, CA.
- Jayaraman, S., Thompson, A.P., von Lillienfeld, O.A. and Magnin, E.J., "Molecular Simulation of the Thermal and Transport Properties of Three Alkali Nitrate Salts, Ind. Eng. Chem. Res., vol. 49 (2), pp. 559-571 (2010).
- R.W. Bradshaw, "Viscosity of Multi-Component Molten Nitrate Salts – Liquidus to 200°C", SAND2010-1129, March 2010.

Publications (continued)

- J.G. Cordaro, N.R. Rubin and R.W. Bradshaw, “Multi-Component Molten Salt Mixtures Based on Nitrate/Nitrite Anions”, submitted to SolarPACES 2010, Parpignon, France, Sept. 2010.
- Bradshaw, R.W. and Goods, S.H., “Corrosion Resistance of Nickel-base Alloys in Molten Nitrate Salts”, submitted to Corrosion Science.

Patents and Applications

- Bradshaw, R.W. and Brosseau, D.A., Low-Melting Point Inorganic Nitrate Salt Heat Transfer Fluid, US Patent #7,588,694, awarded Sept. 15, 2009.
- Cordaro, J.G. and Bradshaw, R.W., Low-Melting Point Inorganic Nitrate-Nitrite Salts, Patent Application #12/336,657, in USPO review.