2008 Solar Annual Review Meeting

Session: Thermal Storage
Company or Organization: Sandia National Labs
Funding Opportunity: CSP Advanced Systems Solicitation

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Relationship to Solar Program Goals

“…to develop low-cost HTFs that facilitate direct thermal energy storage"

1. Project overview - Molten Salt Heat Transfer Fluid Development

a) Project description - develop molten salt HTF's based on simple mixtures of nitrate and/or nitrite salts with primary objective of low freezing point

b) Major FY08 Activities

   a) Determine liquid-solid phase transition temperature vs. composition

   b) Evaluate chemical stability at high temperature

   c) Measure viscosity and other thermophysical properties

   d) Evaluate compatibility with stainless and carbon steels

   e) Perform basic economic assessment

   f) Investigate the operational considerations of salt in the field

   g) Begin computational materials discovery efforts

c) Planned Milestones (all Q4 FY08)

   a) Complete physical/chemical evaluation of all-nitrate molten salt mixtures

   b) Document results of FY08 development testing

   c) File I.P. documents

d) Budget Table (FTEs, $FTE, Subcontract Info)

   a) 1.2 FTE, 350 K$, no subcontracts (FY08)

Relationship to Solar Program Goals
(continued)

1. Project overview (continued)
   a) Personnel contributing to the project
      a) Tech Staff - Bob Bradshaw, Nate Siegel, Joe Cordaro, Sandia/CA&NM
      b) Tech Support - Kai Chisman, Bill Anderson, Tom Zifer, Sandia/CA&NM

2. Link project to Program Plans & Goals
   a) Solar Multi-year Program Plan
      a) Develop efficient, dispatchable electrical power from parabolic trough systems
   b) CSP Subprogram Goals -
      a) Enable economical thermal energy storage in parabolic trough plants
      b) Increase system efficiency via working fluid capable of higher operating temperature

This work also supports central receiver systems that use molten salt HTFs

FY08 Progress Report

1. What has been accomplished thus far?

a) Technical highlights

- a) Identified nitrate salt compositions that are liquids at Temp. <100°C
- b) Verified chemical stability of these molten salts to Temp. >500°C
- c) Viscosity increased by $Ca(NO_3)_2$ additions but acceptable
- d) Started materials compatibility tests (stainless and carbon-alloy steels)

b) Cost estimation of commodity constituents has lagged

- a) Need input from potential suppliers
- b) The price of some constituents is very dynamic and difficult to estimate

c) Costing (current level; projected end-year balance)

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Project Beginning Date	**FY07 Budget**	**FY08 Budget**	**Total Budget**
Oct. 2006	$ 280K	$ 330K	$ 510K

FY08 Progress Report (continued)

1. What will be accomplished in the 3rd and 4th Quarters?

   a) Complete screening experiments to identify low-melting compositions of Nitrate-Nitrite salts

   b) Complete corrosion tests of container alloys molten Nitrate salts

   c) Write report summarizing data from FY08 development activities

   d) File I.P. documents

   e) Determine effect of CO_2 absorption on nitrate salts

   f) Evaluate effects of impurity constituents on solidification properties

   g) Begin Molecular Dynamics Computational Modeling of phase-change temperatures and molten salt physical properties

Future Activities

1. FY09 Planned Activities

a) Follow-on efforts

   a) Evaluate fluid physical properties, compatibility with solid TES media, compatibility with seals, packing materials, other non-metallics

   b) Complete metallographic analysis of corrosion specimens,

   c) Complete Molecular Dynamics Calculations to screen for additional compositions

   d) Combinatorial studies to further screen for additional compositions

b) New directions

   a) Begin working with FOA partners

   b) Begin to investigate ways to raise the upper temperature stability limit of salts

c) Budget Table (FTEs, $FTE, Subcontract Info)

   a) 1.8 FTE, 600 K$, no subcontracts

d) Projected Milestones

   a) All nitrate salt sub-tasks complete by Q4-FY09

   b) Nitrate-Nitrite salt tasks TBD, pending discovery of promising compositions

Future Activities

2. FY10 and Beyond Ideas

a) **Salt in the field** – evaluate advanced HTF mixtures on sun in a trough loop

b) **Solid Thermal Energy Storage (TES) media** – customize the chemistry TES media to improve compatibility/stability with HTFs

c) **Expanding the thermal range of salts** – Ultra supercritical steam cycles will require 700^{o}C to achieve >50% efficiency. We need to develop HTF formulations and operating strategies to support this technology on a ***central receiver platform***

d) **Phase Change TES -** develop encapsulated PCM's for high temperature systems, e.g., those using molten salt HTF

Heat Transfer Fluids - Key Properties for TES

- Working temperature range
  - Freezing point
    - Liquidus temperature, at which a solid phase first appears
  - Thermal stability limit
    - Maximum temperature allowing prolonged use
- Cost
- Viscosity
  - Moderate values over working temperature range
  - Particularly near lower temperature limit
- Fluid engineering properties
  - Heat capacity
  - Thermal conductivity
  - Density

Molten Nitrate Salt - Formulating Low-Melting Mixtures

- Blend mixtures to optimize properties of individual constituents

- Sodium, Potassium
  - Highest temperature stability
  - Low cost

- Lithium
  - High temperature stability
  - Low viscosity
  - Highest cost

- Calcium
  - Moderate temperature stability
  - Increases viscosity
  - Lowest cost

Simple Combinatorial Experiment for Molten Salt Mixtures

Aluminum block with cavities for Pyrex tubes

Molten salt mixtures were cooled to successively lower temperatures and appearance of solid phases observed

Residual molten salt phase sampled by a 'cold finger'

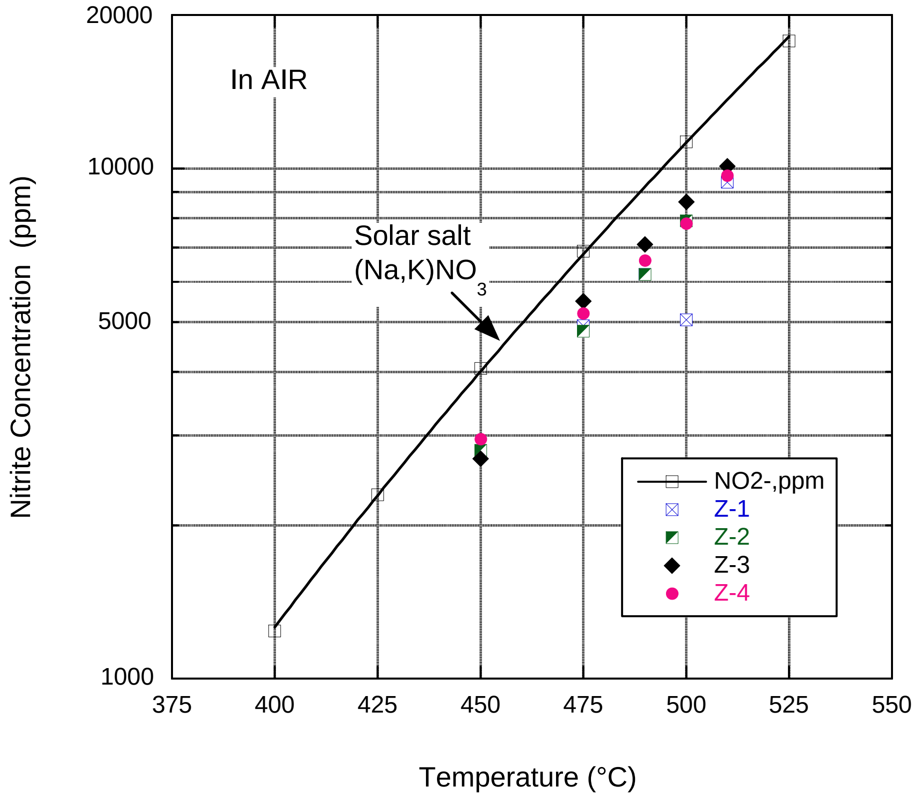
Gradient in composition of liquid indicates subsequent starting points

Liquidus Temperatures of Molten Nitrate Mixtures

- Multi-component mixtures of nitrate salts remain liquid at relatively low temperatures compared to binary and ternary mixtures

Na	K	Ca	Li	Liquidus Temp.	Notes
mol%	mol%	mol%	mol%	°C	
50	50			221	Na-K-NO_3 eutectic
21	49	30		133	Ca-Na-K-NO_3 eutectic
18	52		30	120	Li-Na-K-NO_3 eutectic
	58	11	31	117	Ca-Li-K-NO_3 eutectic
High	+	+	+	< 95	QA
Med.	+	+	+	< 95	QB
Low	+	+	+	< 95	QC

Chemical Stability of Low-Melting Nitrate Salts



Low-melting mixtures track Solar Salt stability to 500°C or higher

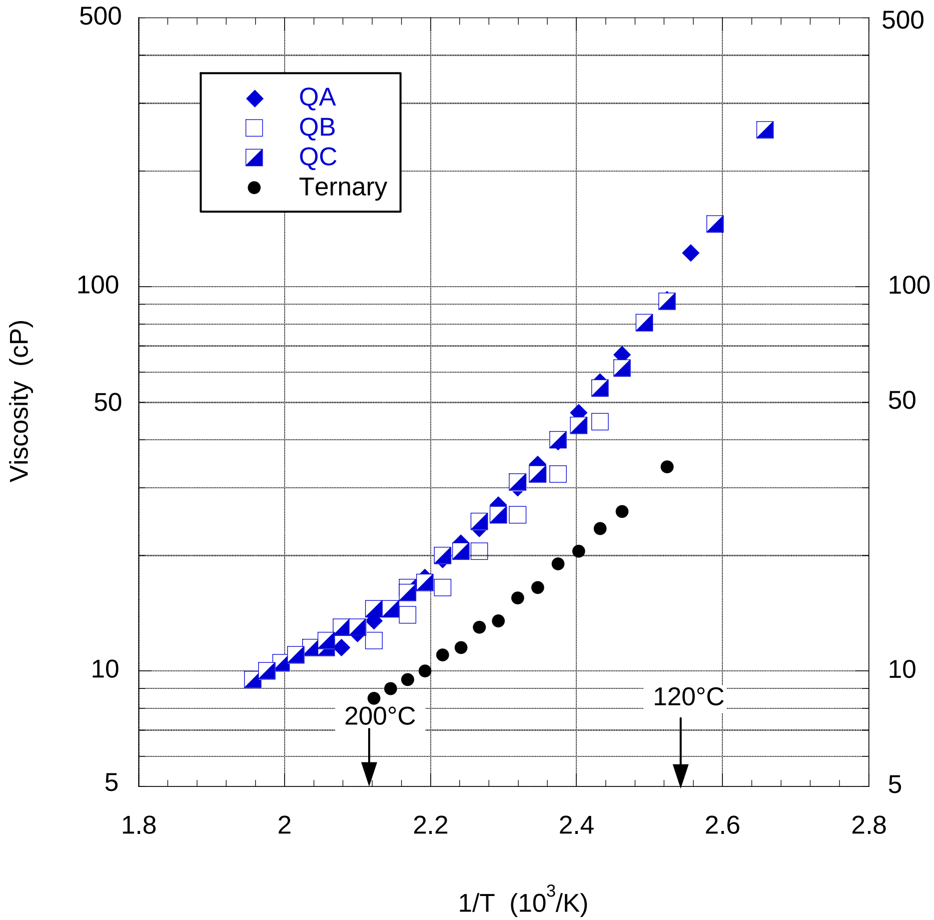
An equilibrium reaction governs initial dissociation of nitrate anion in melts

- $MNO_3 = MNO_2 + 1/2\ O_2$

Subsequent decomposition occurs at high temperature

- $MNO_2 >> M\text{-oxide}, NO_x$

Viscosity of Low-Melting Nitrate Mixtures



Viscosity measurements performed using a Brookfield DV-II+ viscometer

<u>Comparison data</u>

Binary Solar Salt 4.7 cP at 250°C

Hitec XL 65 cP at 150°C

"Ternary" mixture refers to the Li-Na-K-NO_3 eutectic

Estimated Costs of Constituent Nitrates

- Cost data for commodity quantities of industrial purity nitrates have not yet been obtained

- Relative costs of individual constituent nitrates are expected to follow order
  - Li > Na, K > Ca

- Cost data from B. Kelly (SE-2007 ASME, 2007)
  - Binary Solar Salt 0.5 $/kg
  - 30% (wt.) $Ca(NO_3)_2$ 0.9 $/kg
  - Hitec (with nitrite) 1.1 $/kg

- Compare to organic heat transfer fluids at $3-4/kg

End of slides