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Novel Molten Salts Thermal Energy Storage for Concentrating Solar Power Generation

CSP

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1. Project Description: develop low melting point (LMP) molten salts that have the following characteristics :
   - Lower melting point compared to current salts (<225 °C)
   - Higher energy density compared to current salts (> 300-756* MJ/m^3)
   - Lower power generation cost compared to current salts (target DOE 2020 goal of Thermal Energy Storage(TES) cost < $\$15/kWh_{thermal}$ with >93% round trip efficiency)
2. Major Activities in 2009
   (a) Extensive thermodynamic modeling on various multicomponent salt systems to identify possible TES materials
   (b) Experimental determination of heat capacity, thermal stability, viscosity and corrosivity and other materials properties characterization of the possible TES materials
   (c) Performed economic assessment on the salt systems
   (d) Carry out system level modeling of the TES salt systems
3. Planned Milestones in 2009
   (a) Identify primary low melting point (LMP) molten salt candidates for TES systems that satisfy the DOE 2020 goals as outlined in the project description
4. Budget (2009)
   (a) \$500,000, sub-contract (UTRC): \$ 165,000

Overview

Timeline

- Jan 2009
- Dec 2012
- 33%

Barriers

- Barriers addressed
  - We have addressed the issue of low melting point salt system and identified six such molten salt systems that have melting point lower than the current salts
  - Thermal stability of the six salt systems has been determined and was found to be excellent for all the salt systems up to 500 C

Budget

- $1,894,633
  - $1,500,000
  - $ 394,633 (non-federal)
- Funding received in FY09
- Funding received in FY10

Partners

- UTRC

Table-3: Matrix of some possible LMP salt compounds to be examined

Challenges, Barriers or Problems

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Currently very limited data on the proposed salt systems is available for solar energy storage applications. The long term thermal stability of these salts at the operating temperature is best served by eutectic systems. Careful and systematic evaluation of the matrix of materials listed in the table below and a combination of experimentation and atomic scale modeling for various salt systems is expected to significantly increase chances for success.

		Li	**Na**	**Mg**	**K**	**Ca**	**Mn**
ANIONS	**Cl**	LiCl	NaCl	$MgCl_2$	KCl	$CaCl_2$	$MnCl_2$
	F	LiF	NaF	MgF_2	KF	CaF_2	MnF_2
	O						
	CO_3		Na_2CO_3				
	NO_3	$LiNO_3$	$NaNO_3$	$Mg(NO_3)_2$	KNO_3	$Ca(NO_3)_2$	$Mn(NO_3)_2$
	SO_4		Na_2SO_4				
	BO_4						
	PO_3						
	$ABNO_3$	$LiK(NO_3)_2$ $LiNH_4(NO_3)_2$	$(K,Na)NO_3$ $NaNH_4(NO_3)_2$		$K_2Mg(NO_3)_4$ $KNH_4(NO_3)_2$	$(Ca,Mg)(NO_3)_2$	

Major Accomplishments in 2009

(a) 18 salt systems were identified as possible TES materials (M.P. <222 °C)

(b) $LiNO_3$-$NaNO_3$-KNO_3 ternary eutectic mixture was experimentally confirmed as a potential TES material (M.P. 117 °C)

(c) Experimental determination of heat capacity, thermal stability, viscosity and corrosivity of the ternary eutectic mixture was completed

(d) Melting points and thermal stabilities of selected six salt systems was completed

(e) Thermal stabilities of all six salt systems range from 0.02 to 0.38 % wt loss at 500 °C

(e) Atomic/molecular modeling of heat capacity and density was completed for binary solar salt and extended to the ternary eutectic mixtures

(f) Selected TES salt mixtures showed improved cost per unit stored energy than that of current salts

(f) Three salt mixtures were near the DOE 2020 goal of $15/kWh and three salt mixtures were near $18/kWh

(g) An TES model was defined and potential improvements in power cycle preheating was proposed based on the ternary eutectic salt mixture properties

Future Activities (2010)

Planned Milestone for 2010

Define and optimized LMP molten salt composition and TES system geometry that potentially meets the year 2020 goals (the potential to reduce the cost of TES to less than $\$15/kWh_{thermal}$ and achieve round trip efficiencies greater than 93%), including recyclability and environmental impact plan (by the end of Phase II – Dec 2010)

Activities for 2010

(a) Synthesis and detailed evaluation of thermodynamics of candidate salts identified in Phase I

(b) Measurement of key properties such as heat capacity, melting point, etc. for salts identified in Phase I

(c) Heat transfer and fluid dynamics modeling to enable selection of best TES materials and system.

(d) Recycling characteristics and corrosion behavior of candidate salt systems.

(e) Optimized LMP salt composition and TES system geometry

Future Work Plan

- **Synthesize the selected TES materials and study the thermal and physical properties**

- **Apply heat transfer models to select preferred TES system design and LMP molten salt composition (utilizing thermal conductivity data)**

- **Evaluate options to optimize the thermal systems model for the performance of the power cycle**

- **Estimate the total cost for the TES systems based on the storage density of TES materials**

Approach

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The approach to the stated project is based on sound thermodynamic principles and modeling in the identification of novel low-melting molten salt systems and experimental determination of the properties to meet the DOE 2020 goals

Timeline of Phases

PHASE 1: Identification of primary LMP molten salt candidates for TES systems
PHASE 2: Optimization of LMP molten salt composition and identification of preferred TES system design
PHASE 3: Optimize LMP molten salt for application in TES systems including energy efficiencies and system economic feasibility

		2009				2010				2011			
Task	**Description**	**Phase 1**				**Phase II**				**Phase III**			
I-1	Thermodynamics/synthesis	■	■	■									
I-2	Property characterization	■	■	■	■								
I-3	Heat and fluid flow modeling	■	■	■	■								
I-4	Assessment of salt systems			■	■								
I-5	Identify potential salt systems				■ ◆								
II-1	Thermodynamics/synthesis					■	■	■					
II-2	Property characterization					■	■	■	■				
II-3	Heat and fluid flow modeling					■	■	■	■				
II-4	Assessment of salts							■	■				
II-5	Material selection							■	■				
II-6	Identify optimized salts								■ ◆				
III-1	Setup lab scale system									■			
III-2	Conduct detailed tests									■	■	■	
III-3	Heat and fluid flow modeling									■	■	■	
III-4	Economic and cost analysis										■	■	
III-5	Final report											■	■ ◆

Methodology of Study

Thermodynamic modeling to calculate eutectic compositions of salt mixtures

↓

Conduct experiments using eutectic compositions to determine melting point

↓

Determine heat capacity, thermal stability, viscosity and calculate thermal storage energy density

↓

Total TES cost estimation per unit energy using an EPRI study of the Andasol 1 plant as a baseline

Thermodynamic Modeling

Melting of an LMP binary salt mixture (AX + BX) is represented as

$$AX(s) + BX(s) = AX(l) + BX(l)$$

Gibbs energies of fusion of both salts are given by*

$$\Delta G^{\circ}_{f,AX} = -RT\,ln\left(X_{AX}\right) - \overline{G}^{xs}_{AX}$$

$$\Delta G^{\circ}_{f,BX} = -RT\,ln\left(X_{BX}\right) - \overline{G}^{xs}_{BX}$$

$\Delta G^{\circ}_{f,i}$ = Gibbs energy of fusion of '*i*' (AX or BX)

$\overline{G}^{xs}_{i}$ = Partial excess Gibbs energy of '*i*' (AX or BX)

At eutectic point (X_E,T_E), both the equations are satisfied

Similarly, eutectic points of LMP salt systems (other higher order) are evaluated

***Thermodynamics, 2nd Edition, N. A. Gokcen and R. G. Reddy, Plenum Press, NY, (1996)**

Thermodynamic Modeling

Eutectic composition and temperature in a salt mixture is calculated by minimizing the Gibbs energies of fusion of the constituents

What we need

- Melting point, Enthalpy and entropy of fusion of the constituents
- Change of heat capacity $\Delta Cp = [Cp(l) - Cp(s)]$ of the constituents (if available)
- Excess Gibbs energies of mixing of constituent binaries

What we do

- Generate a system of fusion equations for the constituents of the salt mixture

$$\Delta G^{\circ}_{f,i} + RT\,ln(X_i) + \overline{G}_i^{xs} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

- Solve for composition and temperature using Newton-Raphson Algorithm

What we get

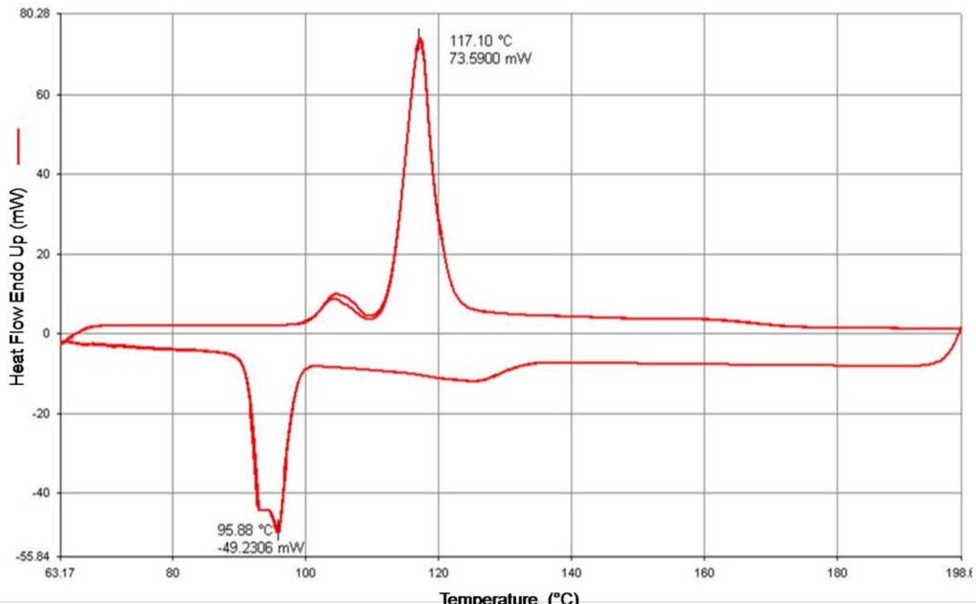
- Eutectic composition (X_i) and temperature (T) for the salt mixture

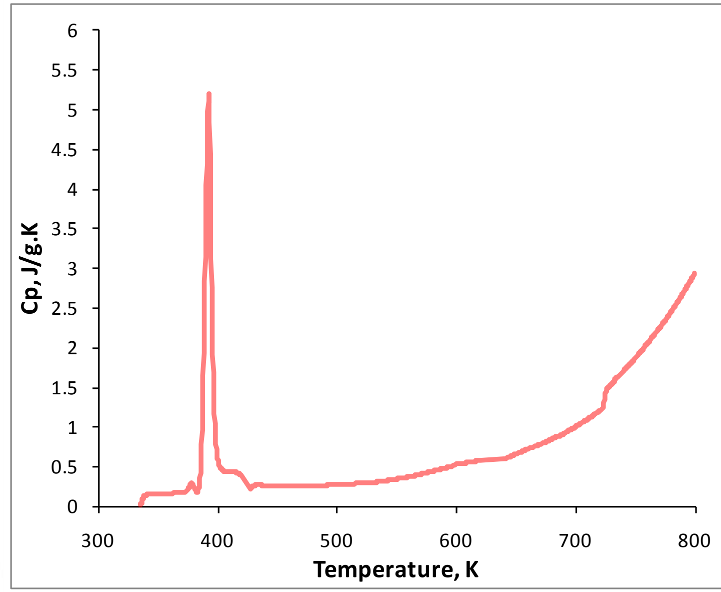
Model Calculated UA Baseline Ternary Salts

	Composition, wt%			Melting Point, °C
	$LiNO_3$	$NaNO_3$	KNO_3	
Our Model-Ideal (without excess terms)	21.94	29.32	48.74	154
Our Model-Regular (with excess terms)	25.92	20.01	54.07	116 (117)
Literature *	30	18	52	120

*_Russ. J. Inorg. Chem._ Vol. 9 (6),(1964), 771-773

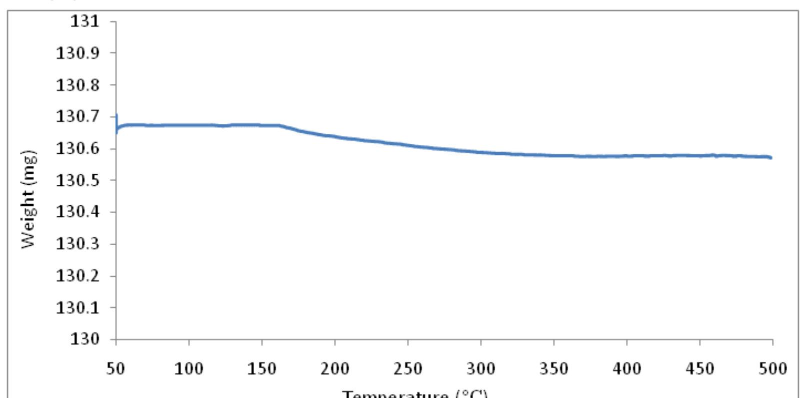
Thermal Data Validating $LiNO_3$–$NaNO_3$–KNO_3 Eutectic Salt





Melting point
117 °C

Heat Capacity
2.32 J/g.K



Thermal Stability
< 0.1 %

Properties of UA Baseline Ternary and Current Salts

Salt System		Melting Point (°C)	Density (g/cc)	Heat Capacity (J/g.K)	Energy Density (MJ/m^3)
UA baseline ternary	**(#1) $LiNO_3$-$NaNO_3$-KNO_3**	**116 (117)**	**1.72**	**2.32**	**1524***
Solar Salt	$NaNO_3$-KNO_3	222	1.75	1.54	756
Hitec Salt	$NaNO_3$-$NaNO_2$-KNO_3	142	1.87	1.42	955

**Experimental determination or calculations based thereon*

Accomplishments / Progress / Results, Con't.

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TES Material Candidates from Thermodynamic Modeling

Salt #	SALT SYSTEM	Melting Point °C	Density g/cc	Heat Capacity J/g.K	Energy Density MJ/m^3	Thermal Stability % wt loss
	Group 1 (70 – 80 °C)					
9	$LiNO_2$-$LiNO_3$-$NaNO_3$-KNO_3-KNO_2	70.7	1.68	1.58	1141	
8	$LiNO_3$-$NaNO_3$-KNO_3-$LiNO_2$	77	1.68	1.61	1146	
3	$LiNO_2$-$NaNO_3$-KNO_2-KNO_3	79	1.69	1.50	1073	
7	Li(metal)-$LiNO_3$-$NaNO_3$	80.7	0.63	2.39	632	
	Group 2 (80 – 100 °C)					
12	$LiNO_2$-$LiNO_3$-KNO_2-KNO_3	90.7	1.67	1.57	1070	
11	$LiNO_2$-$NaNO_3$-KNO_3	92.7	1.68	1.57	1075	
6	$LiNO_3$-$NaNO_2$-$NaNO_3$-KNO_2-KNO_3	95.7	1.78	1.54	1110	
10	$LiNO_2$-$LiNO_3$ -KNO_3	98.4	1.67	1.61	1076	
5	$LiNO_3$-$NaNO_3$-KNO_3-$NaNO_2$	98.6 (99)	1.78	1.56	1114	0.38
4	$LiNO_3$-$NaNO_3$-KNO_3-**MgK**	98.6 (101.2)	1.71	1.66	1211	0.05
	Group 3 (100 – 116 °C)					
14	$LiNO_3$-$NaNO_3$-KNO_3-$AgNO_3$	103 (107)	2.79	1.08	1192	
13	$LiNO_2$-$LiNO_3$-$NaNO_3$	108.4	1.66	1.73	1125	
1	$LiNO_3$-$NaNO_3$-KNO_3	116 (117)	1.72	2.32	1524	0.08
18	$LiNO_3$-$NaNO_3$-KNO_3-$Ca(NO_3)_2$	113 (108.8)	1.73	1.58	1055	0.09
17	$LiNO_3$-$NaNO_3$-KNO_3-$Mg(NO_3)_2$	113.5 (111.6)	1.73	1.61	1081	0.07
15	$LiNO_3$-$NaNO_3$-KNO_3-LiCl	114.1 (115.5)	1.71	1.60	1057	0.02
16	$LiNO_3$-$NaNO_3$-KNO_3-LiF	115.9	1.72	1.60	1057	
2	KNO_3-$NaNO_2$-$NaNO_3$	123 (99)	1.84	1.46	1080	

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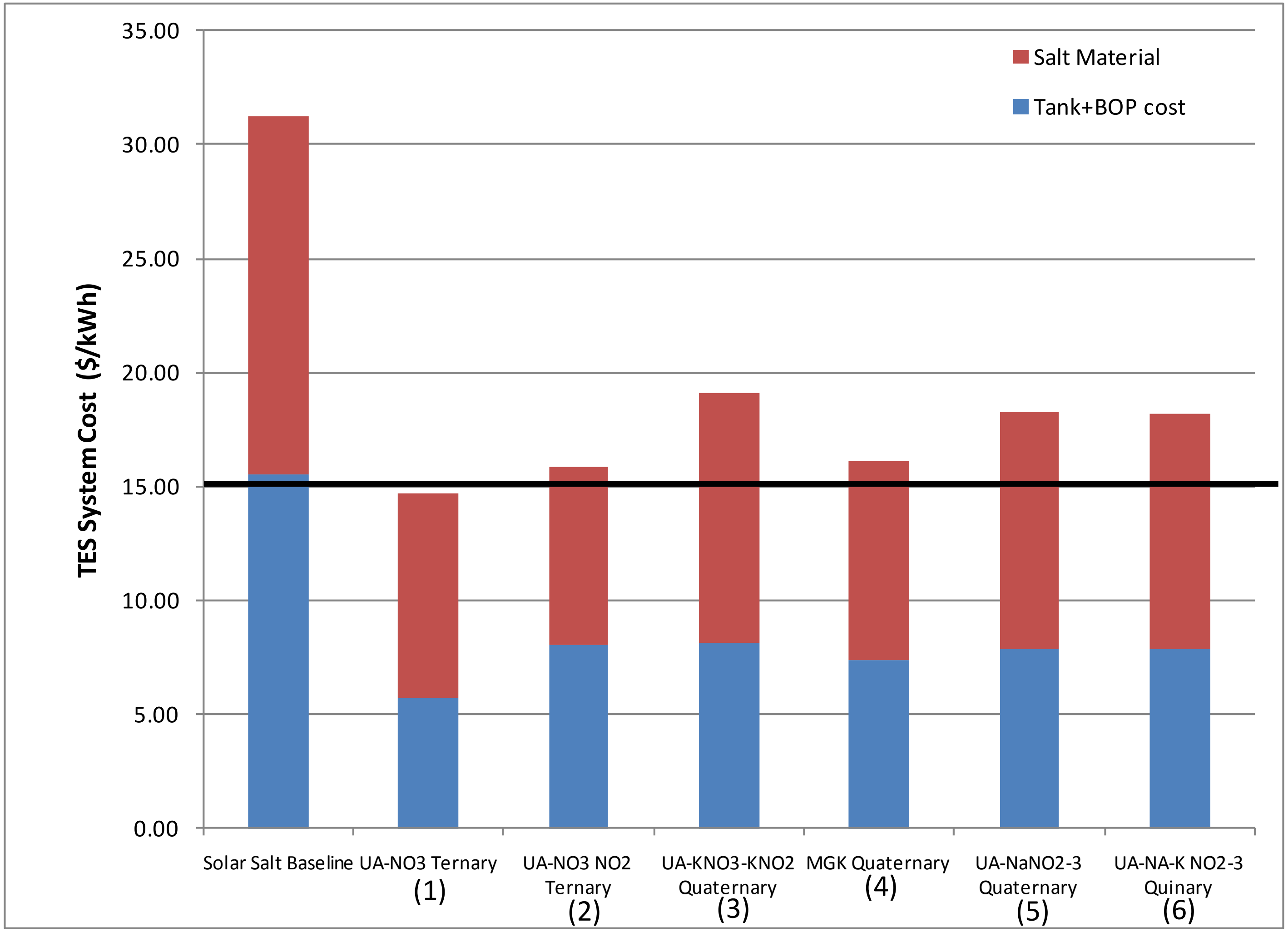
Selected TES Candidate Salt Mixtures with Cost Estimates

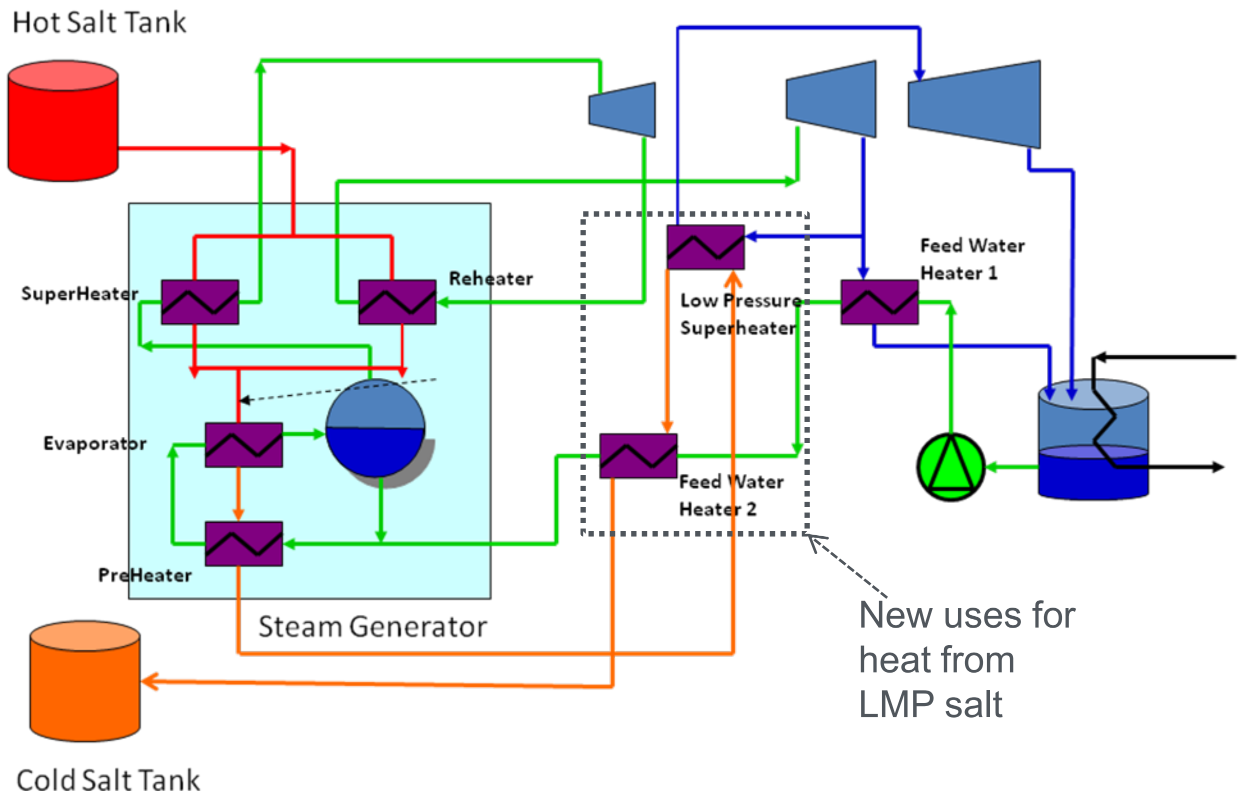
Salt #	Material	Composition	Melting Point	Heat Capacity	Energy Density (500C-M.P.)	Salt Compd. Price	2 Tank System Cost / Stored Energy
		Wt%	(ºC)	(J/g-K)	(MJ/m^3)	($/kg)	($\$/kW\text{-}h_{thermal}$)
	Today's Solar Salt	40% KNO_3 60% $NaNO_3$	222	1.5381	756	$1.080	$31.21
1	Baseline Ternary (in proposal)	KNO_3 – $LiNO_3$ – $NaNO_3$	117*	2.32	1524*	$2.206	$14.66
2	Nitrate- nitrite Ternary	KNO_3 – $NaNO_2$ – $NaNO_3$	99	1.4623	1080*	$1.266	$15.87
3	UA K-Nitrate-nitrite Quaternary	KNO_3 – $NaNO_2$ – $LiNO_2$ – $NaNO_3$	79	1.5048	1073	$1.928	$19.11
4	"AB" nitrate compound	KNO_3 – $LiNO_3$ $NaNO_3$ – MgK* * $2KNO_3.Mg(NO_3)_2$	101	1.5788	1181	$1.537	$16.15
5	UA Na- nitrate-nitrite Quaternary	$LiNO_3$ – $NaNO_2$ $NaNO_3$ – KNO_3	99	1.5569	1114	$1.809	$18.27
6	UA Na-K-nitrate-nitrite Quinary	$LiNO_3$ – $NaNO_2$ $NaNO_3$ – KNO_2 – KNO_3	95.7	1.5455	1110	$1.797	$18.23

Cost Estimates for Proposed HTF Systems vs. Baseline



Using EPRI baseline

Development of a LMP Salt Thermal System



- A low temperature, high specific heat eutectic mixture has large potential for benefits.

Acknowledgements

- Department of Energy
- The University of Alabama
- ACIPCO
- Department of Metallurgical and Materials Engineering

Collaborations

- United Technologies Research Center
  - Sub-contract
  - The collaboration is on three tasks of the project, (i) Atomic/molecular modeling of properties, (ii) Heat and fluid flow modeling, (iii) Optimization of molten salt composition and TES system geometry to meet the DOE 2020 goals

Summary

- **Ternary eutectic ($LiNO_3$-$NaNO_3$-KNO_3) salt mixture was experimentally verified to be a candidate TES material**
- **Melting points and thermal stability of six molten salt mixtures were experimentally determined**
- **Total TES cost estimate for ternary eutectic salt met the DOE goal of $15/kWh**
- **TES cost estimates for three salt mixtures (including the ternary eutectic) were close to the DOE goal**
- **Six salt mixtures were found to be thermally stable at 500°C**

Responses to Previous Year Reviewers' Comments

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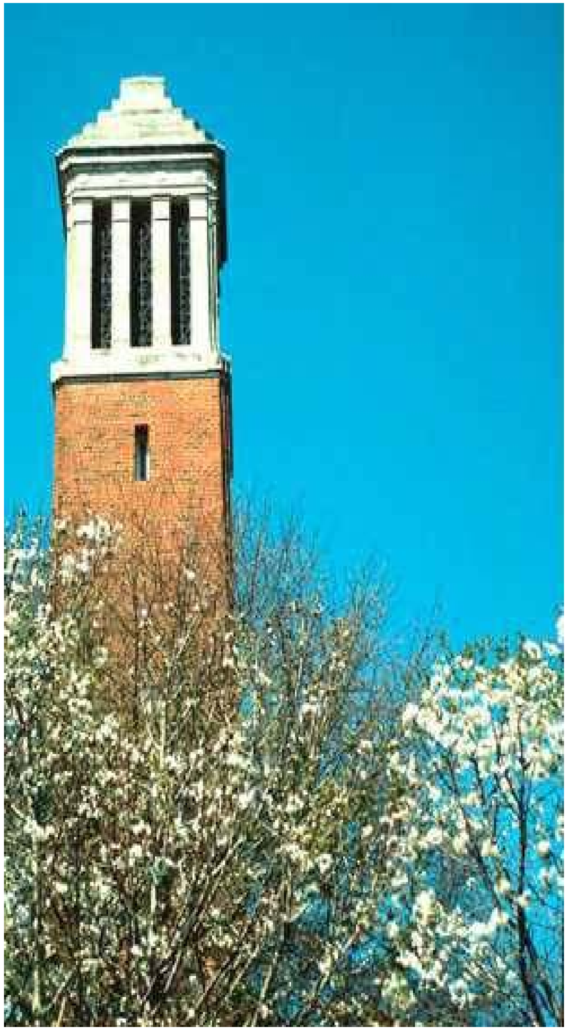
- **Heat and Fluid flow modeling (Task 1.3): The status of this task was inquired**
  - During Phase I, this task was confined only to system level modeling since we have not down-selected any single low-melting material. Detailed component modeling which includes boundary conditions for a specific molten salt will be appropriate when we consider the pilot-plant configuration for testing in Phase III, but notional analysis is possible during Phase II.
- **Viscosity and Thermal conductivity: results of these properties were inquired.**
  - Viscosity data are already presented in the annual report, thermal conductivity calculations for the UA base ternary were presented and compared along with those of the current salts in the supplementary report to the annual report.
- **Assessment of Salt systems (Task 1.4): Corrosivity, cycle life, recyclability of salt systems was inquired**
  - During Phase I, thermodynamic calculations were done to understand the corrosion behavior of stainless steel in molten salts both in air and in inert gas environment. Coupon tests on short-term corrosion of stainless steel were carried out in UA base ternary salt mixture at 500 C for 6 hours for 5 cycles and no weight loss was recorded. Cycle life of the molten salt and recyclability were presented in the annual report and was mentioned in our supplementary report. Efficiency of recyclability of six salt mixtures listed in the annual report were greater than 99.6%.

Publications

- One paper titled "Thermodynamic Modeling of Eutectic Point in the $LiNO_3$-$NaNO_3$-KNO_3 Ternary System," D. Mantha, T. Wang, and R. G. Reddy," Journal of Phase Equilibria and Diffusion, (2010) (submitted).



Thank you