Novel Molten Salts Thermal Energy Storage for Concentrating Solar Power Generation

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Project Objectives

The project objective is to develop low melting point (LMP) molten salts that have the following characteristics:

1. **Lower melting point compared to current salts (<222°C)**
2. **Higher energy density compared to current salts (>756 MJ/m^3)**
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)**

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											■	■ ◆

Planned Milestones

✓ **Identification of two or more potential salt system candidates that have lower melting points and higher energy density compared to current salts. In addition to being technically superior, these salt system candidates must be economically viable. (by the end of Phase I – Dec 2009)**

❑ **Define and optimize 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)**

❑ **Demonstrate the novel LMP molten salt in a (lab scale) TES system. (by the end of Phase III – Dec 2011)**

Significant Achievements

- Extensive thermodynamic modeling was carried out on various multi-component salt systems and 18 salt mixtures have been identified as possible TES materials.
- $LiNO_3$–$NaNO_3$–KNO_3 ternary eutectic mixture was experimentally confirmed as a potential TES material.
- Experimental determination of melting point, heat capacity, thermal stability and viscosity for the ternary eutectic mixture was completed.
- Experimental verification of melting point for eight of the salt mixtures was completed. Selected heat capacity (one salt) and thermal stabilities (six salts) were also experimentally determined.

Significant Achievements (cont.)

- **Thermal stabilities of the selected salts range from 0.02 to 0.38 wt% loss at 500°C.**
- **Atomic/molecular modeling of heat capacity and density were completed for binary solar salt and extended to ternary mixtures.**
- **Selected TES salt mixtures(six salts)showed improved cost per unit stored energy than that of current salts.**
- **Three salt mixtures were near the DOE 2020 goal of $15/kWh and three salt mixtures were near $18/kWh.**
- **A TES model was defined and potential improvements in power cycle preheating were proposed based on the LMP ternary eutectic salt properties.**

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

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

- Solve for composition and temperature using Newton-Raphson Algorithm

What we get

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

The first term in equation (1) is given by:

$$\Delta G_f^\circ = \Delta H_f \frac{\left(T_{mp} - T\right)}{T_{mp}} - \Delta C_p \left[T.ln\left(\frac{T}{T_{mp}}\right) + T_{mp} - T \right]$$

This is the standard Gibbs energy of fusion

The third term in equation (1) is given by

$$\overline{G}_i^{xs} = G^{xs} + \sum_{j=2}^{m} \left(\delta_{ij} - X_j\right) \frac{\partial G^{xs}}{\partial X_j}$$

where $\delta_{ij} = 0 \text{ for } i \neq j$

$\delta_{ij} = 1 \text{ for } i = j$

This is the partial excess Gibbs energy of the component 'i'

We get the total excess Gibbs energy of the salt mixture G^{xs} **from the constituent binaries as:**

$$G^{xs} = \sum_{i=1}^{n} \sum_{j \neq i}^{n} G_{i-j}^{xs} \quad \text{......... (2)}$$

Equation (2) represents the total excess Gibbs energy for each novel salt mixture

Algorithm using Newton-Raphson method

STEP 1 Generate fusion equations for the system

STEP 2 Give the initial guess values of the variables (X_i, T)

STEP 3 Calculate the Jacobian (J) and Residual (R) Matrices

STEP 4 Solve the equation $J.\ \delta x^{(k)} = -R$

STEP 5 Calculate the new guess values

STEP 6 Check for convergence; if YES exit, if NO go to STEP 3

Examples for Excess Gibbs Energies

Excess Gibbs energies in the $LiNO_3 – KNO_3$, $LiNO_3 – NaNO_3$ and $NaNO_3 – KNO_3$ binary systems

$$G^{xs}_{Li-K} = X_{LiNO_3}.X_{KNO_3}\left[-1269.12 - 1.4359T.ln(T) + 7.2897T\right]$$

$$G^{xs}_{Li-Na} = X_{LiNO_3}.X_{NaNO_3}\left[-4519.6 - 6.575T.ln(T) + 49.0607T\right]$$

$$G^{xs}_{Na-K} = X_{NaNO_3}.X_{KNO_3}\left[-408.51 - 68X_{NaNO_3}\right]$$

Excess Gibbs energy in the $LiNO_3 – NaNO_3 – KNO_3$ ternary system is given as

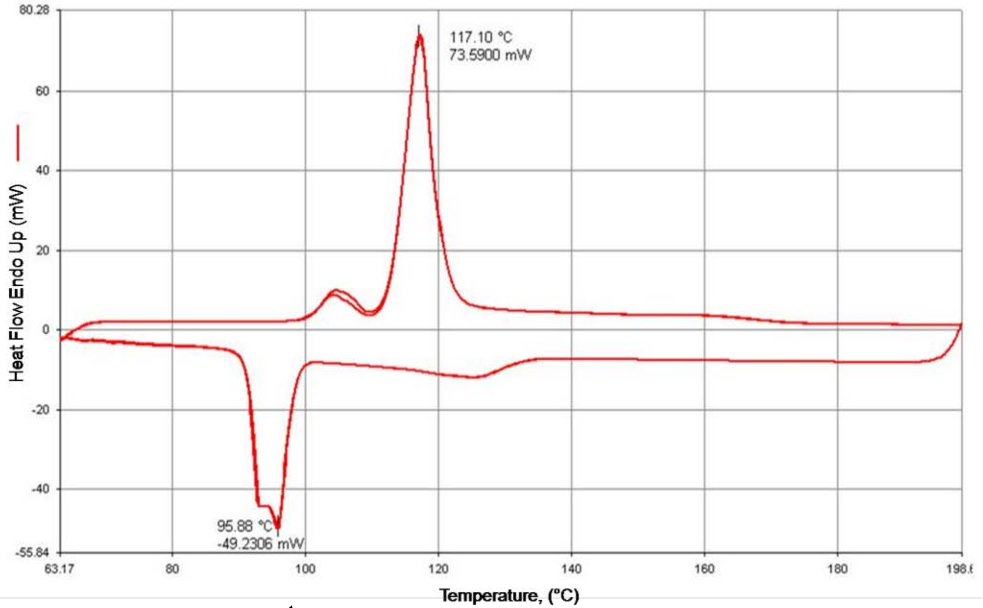
$$G^{xs} = G^{xs}_{Li-Na} + G^{xs}_{Li-K} + G^{xs}_{Na-K}$$

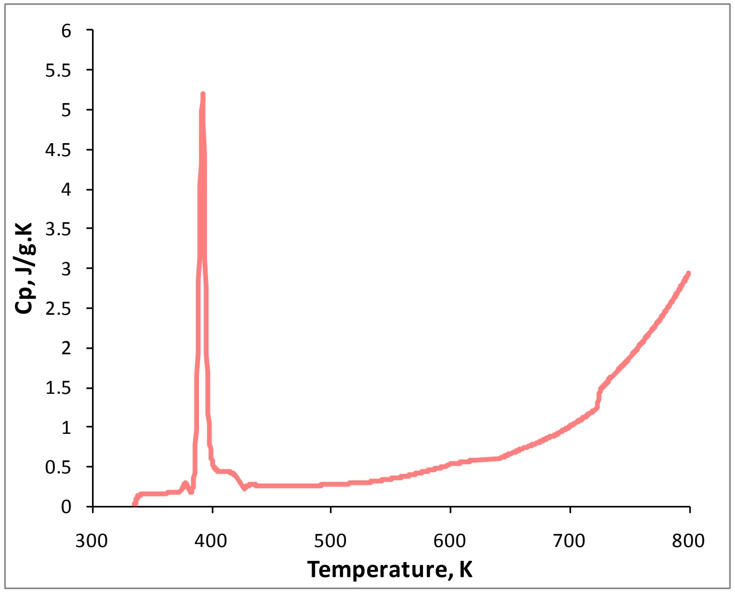
Model Calculated UA Baseline Ternary Salts

	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

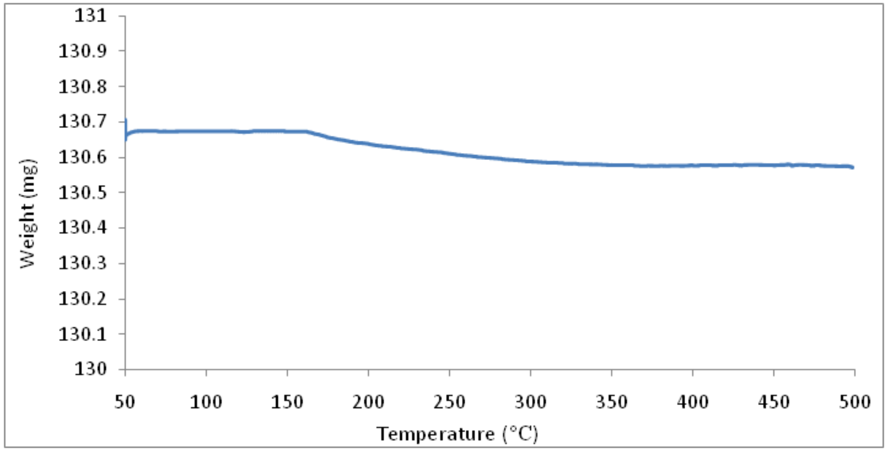
******Russ. J. Inorg. Chem.* **Vol. 9 (6),(1964), 771-773**

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/m³)
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*

TES Material Candidates from Thermodynamic Modeling

Salt #	SALT SYSTEM	Melting Point °C	Density g/cc	Heat Capacity J/g.K	Energy Density MJ/m³	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	

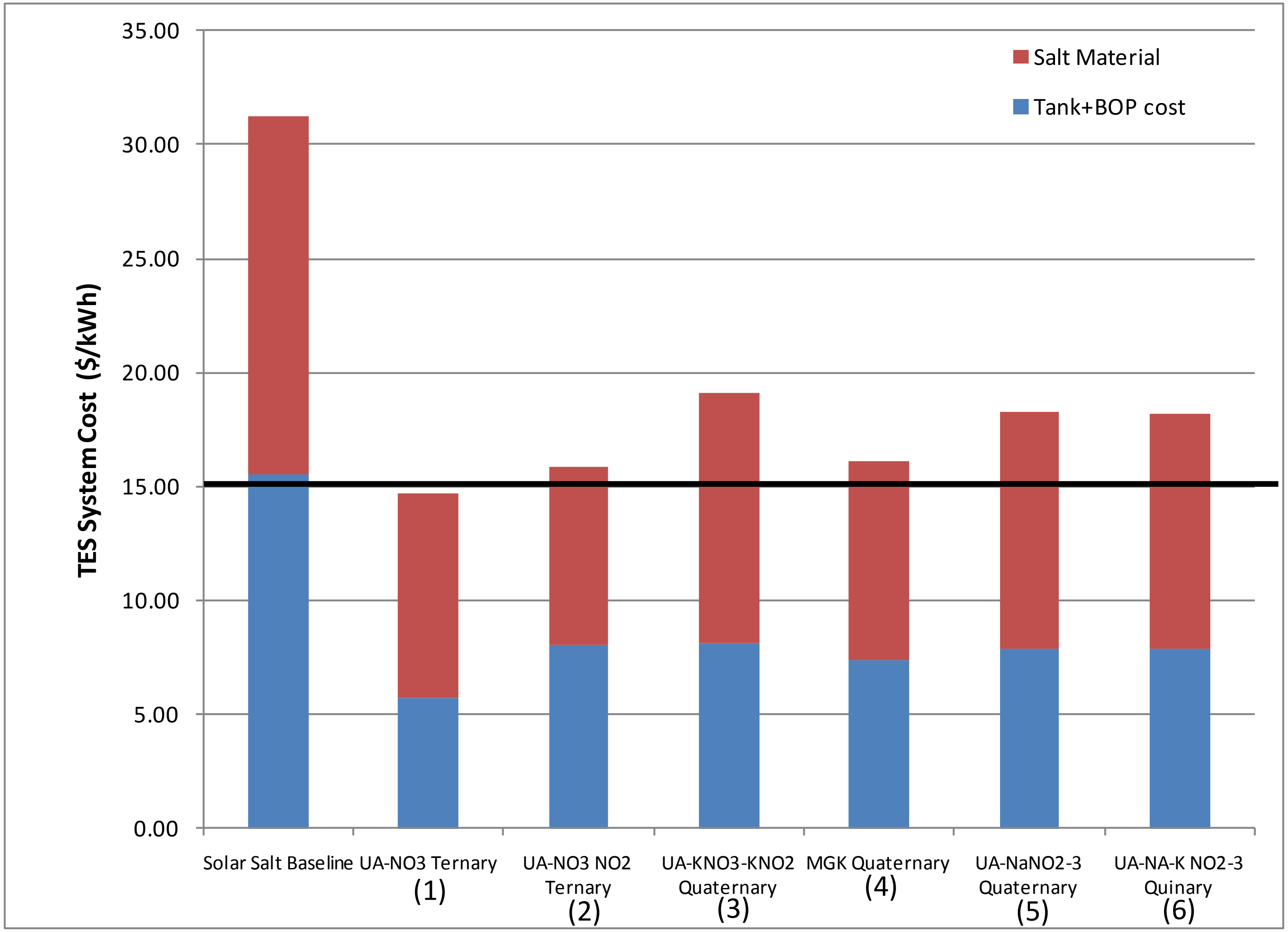
*crimson type indicates experimental data; black type indicates calculated values

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

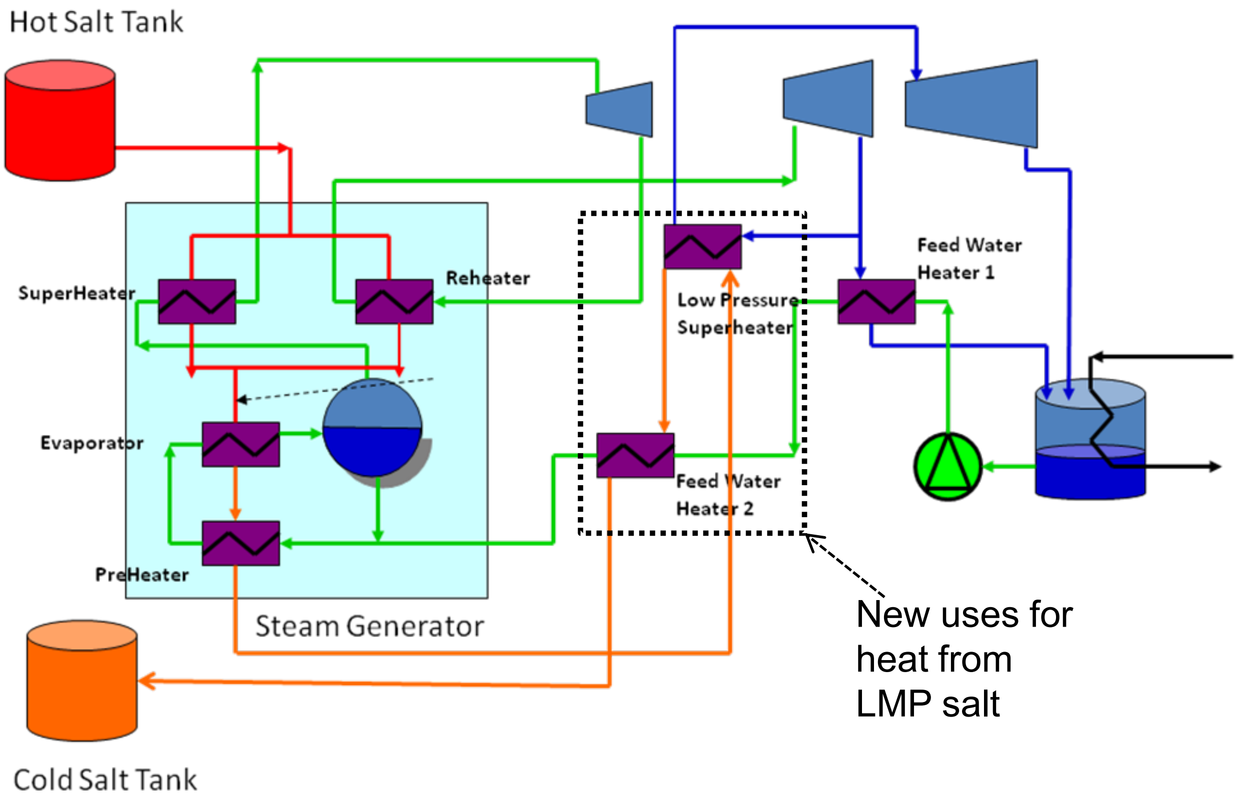
*Blue type indicates experimental data or calculations based thereon; black type shows calculated values

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.**

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.

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**

Acknowledgements

- Department of Energy
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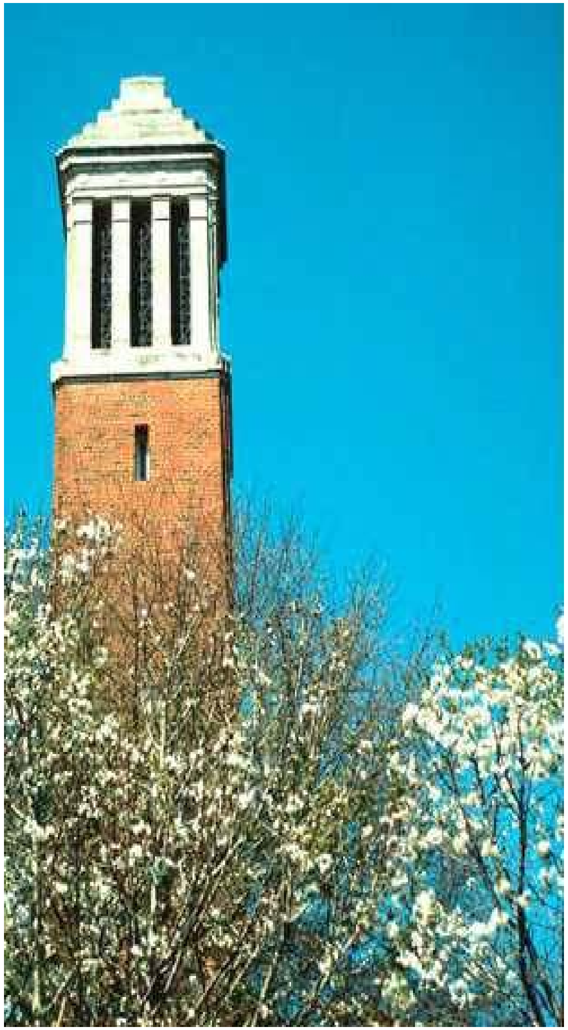

Thank you