Novel Molten Salts Thermal Energy Storage for Concentrating Solar Power Generation

Funding Organization: DE-Solar Energy Technologies Program

Performing Organization: The University of Alabama (UA)

Industrial Partner: United Technologies Research Center

Contract Number: DE-FG36-08GO18153

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Project Overview

1. Project Objective: To develop low melting point (LMP) molten salt mixtures 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$_{\text{thermal}}$ with > 93% round trip efficiency)

2. Major Accomplishments in this Year

- Thermodynamic modeling of high temperature (HT) stable molten salt mixtures: higher order carbonate-fluoride systems was completed
- Experimental determination of melting points of higher order carbonate-fluoride systems was completed
- Thermal stabilities of HT molten salt systems were determined
- Thermal conductivities of HT molten salt systems were determined
- Corrosion studies on SS316L stainless steel specimens in HT molten salt systems were determined
- Completed the TES system modeling

Major Accomplishments

(a) Nine salt mixtures were identified as possible TES materials (M.P. <222 C)

(b) Experimental determination of melting point, heat capacity, density, viscosity, thermal stability, thermal conductivity, and corrosivity of stainless steel in the nine salt mixtures was completed

(c) Atomic/molecular modeling of heat capacity, density, viscosity, thermal conductivity was completed for the salt mixtures

(d) All nine salt mixtures have melting temperatures in the range of 89-124°C, and energy storage density from 980 MJ/m^3 to 1230 MJ/m^3 which is a 29-63% improvement over the current salt

(e) Completed the TES system modeling and two novel changes were recommended (1) use of molten salt as a HTF through the solar trough field, and (2) use the salt to not only create steam but also to preheat the condensed feed water for Rankine cycle.

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

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

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

$\Delta G^{\circ}_{f,i}$ = Gibbs energy of fusion of '*i*'

$\overline{G}^{xs}_{i}$ = Partial excess Gibbs energy of '*i*'

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

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

D. Mantha, T. Wang, and R. G. Reddy, "Thermodynamic Modeling of Eutectic Point in the $LiNO_3$-$NaNO_3$-KNO_3 Ternary System," *Journal of Phase Equilibria and Diffusion,* Vol. 33, No. 2, pp. 110-114, 2012.

Thermodynamic Modeling (cont.)

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 ΔCp = [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**

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

- **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:

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

This is the standard Gibbs energy of fusion

The third term in equation (1) is given by

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

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:

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

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

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

R. G. Reddy, T. Wang, and D. Mantha, “Thermodynamic properties of potassium nitrate-magnesium nitrate compound $[2KNO_3.Mg(NO_3)_2]$,” *Thermochimica Acta*, Vol. 531, pp. 6-11, 2012.

Properties of Salts

Salt System		Melting Point (°C)	Density (g/cc)	Heat Capacity (J/g.K)	Energy Density (MJ/m³)
UA baseline ternary	**$LiNO_3$-$NaNO_3$-KNO_3**	**116 (117)**	**1.71**	**1.54**	**1056***
Solar Salt	$NaNO_3$-KNO_3	222	1.75	1.53	756

**Experimental determination*

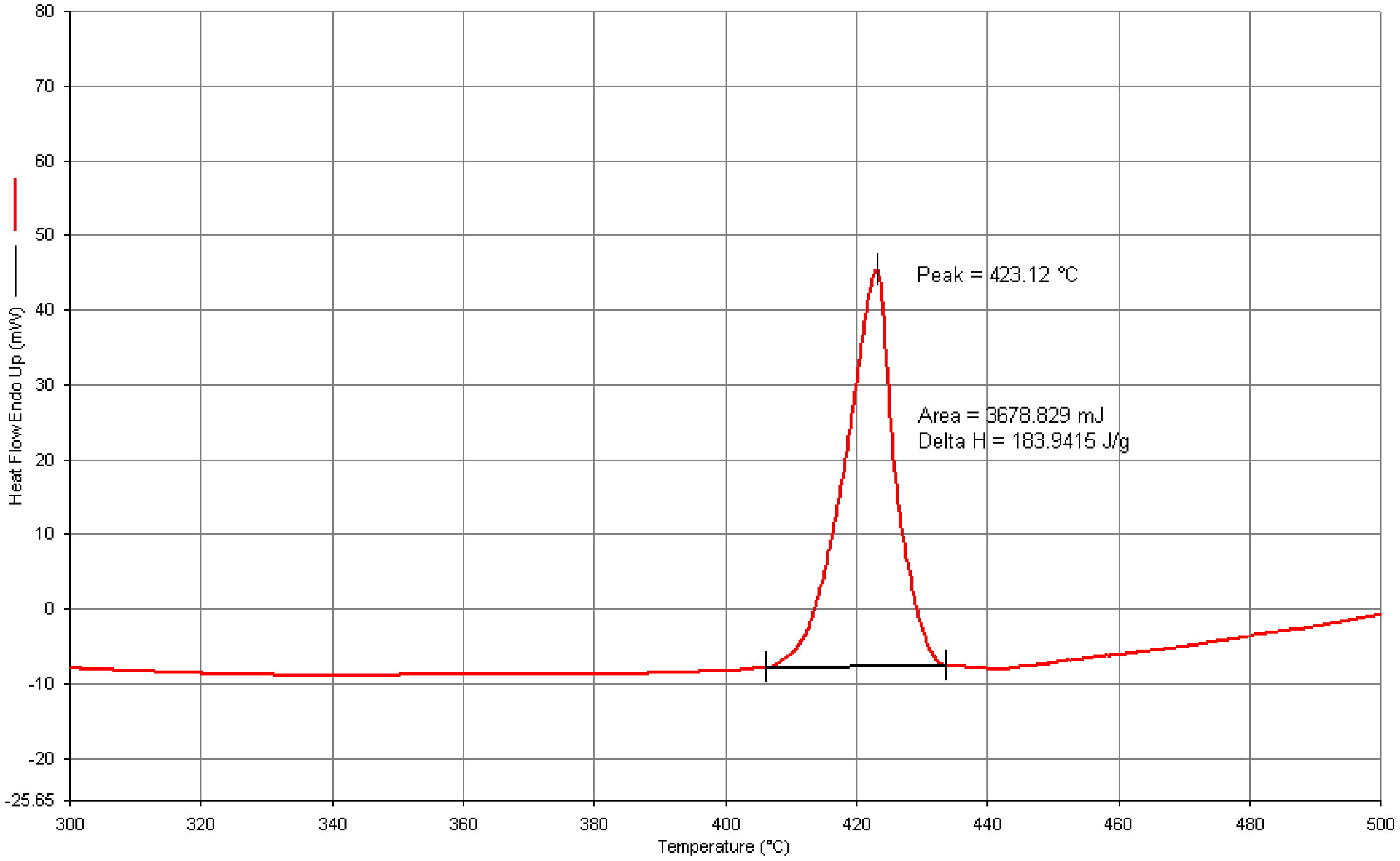
T. Wang, D. Mantha, R. G. Reddy, "Thermal stability of the eutectic composition in $LiNO_3$–$NaNO_3$–KNO_3 ternary system used for thermal energy storage," *Solar Energy Materials and Solar Cells*, Vol. 100, pp. 162-168, 2012.

Melting Point Determination

- **DSC technique was used to measure the melting point and heat capacities of the salt mixtures**
- **Each salt mixture was prepared by melting the weighed quantities of each component at 200 C and holding for 30 minutes in glove box under argon atmosphere**
- **Each salt mixture was run three times and at 2 heating rates (5 C/min and 20 C/min) and each run contains 6 -7 cycles**

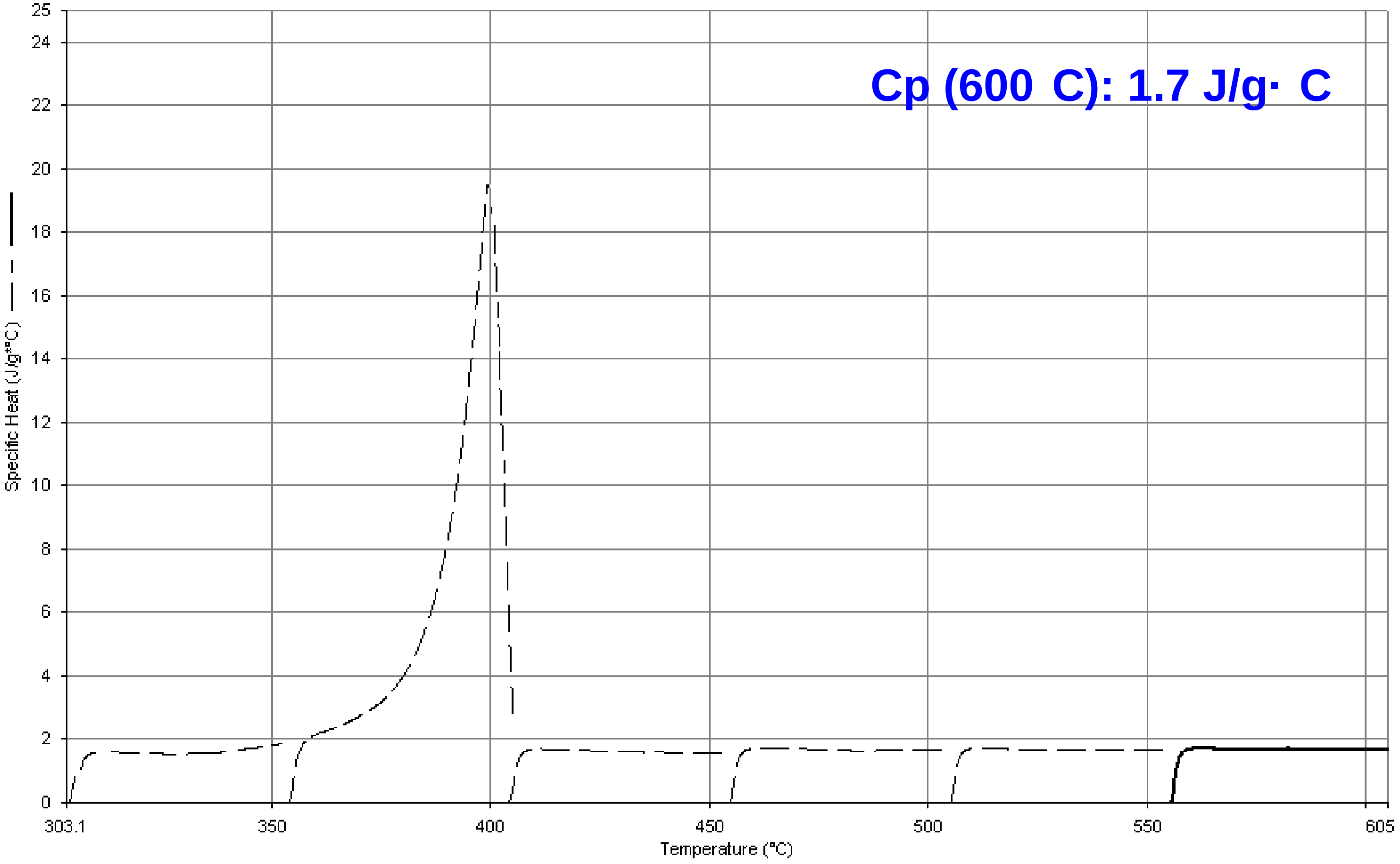
Model Diamond DSC
Temp: –50 C to 750 C
Solids and liquids
Reference: Empty pan
Computer controlled

Melting Point - LiF – NaF – K_2CO_3 System



DSC plot for the LiF-NaF-K_2CO_3 system showing the melting temperature.

Heat Capacity - Li_2CO_3 – Na_2CO_3 – K_2CO_3 System


Cp (600 C): 1.7 J/g· C

The heat flow is recorded as a function of temperature in "iso- scan-iso" steps at intervals of 50°C.

Melting point and Heat Capacities of Salt Mixtures

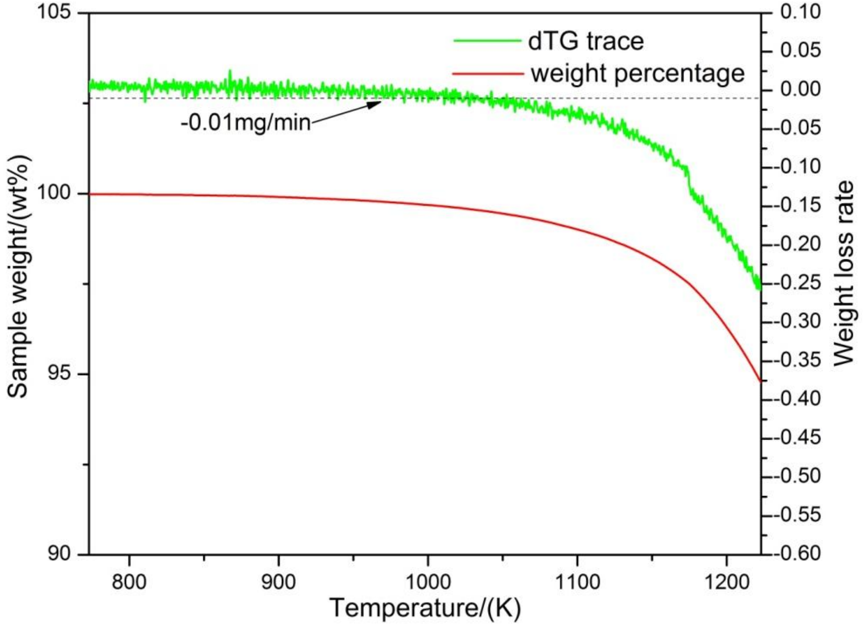
S. No.	System	Temperature, °C		Cp, J/g.°C at 600 °C
		Calc	Expt	
1	$LiF–K_2CO_3$	456	482	1.85
2	$LiF–Li_2CO_3$	612	608	1.88
3	$NaF–Na_2CO_3$	694	690	1.78
4	$Li_2CO_3–K_2CO_3$	503	503	2.03
5	$Li_2CO_3–Na_2CO_3–K_2CO_3$	397	398	1.7
6	$LiF–Na_2CO_3–K_2CO_3$	386	389	1.74
7	$LiF–NaF–K_2CO_3$	414	422	1.81
8	$LiF–KF–K_2CO_3$	412	438	
9	$LiF–NaF–Na_2CO_3–K_2CO_3$	373	423	1.85
10	$LiF–NaF–Li_2CO_3–Na_2CO_3$	444	444	1.88

Thermal Stability of Salt Mixtures

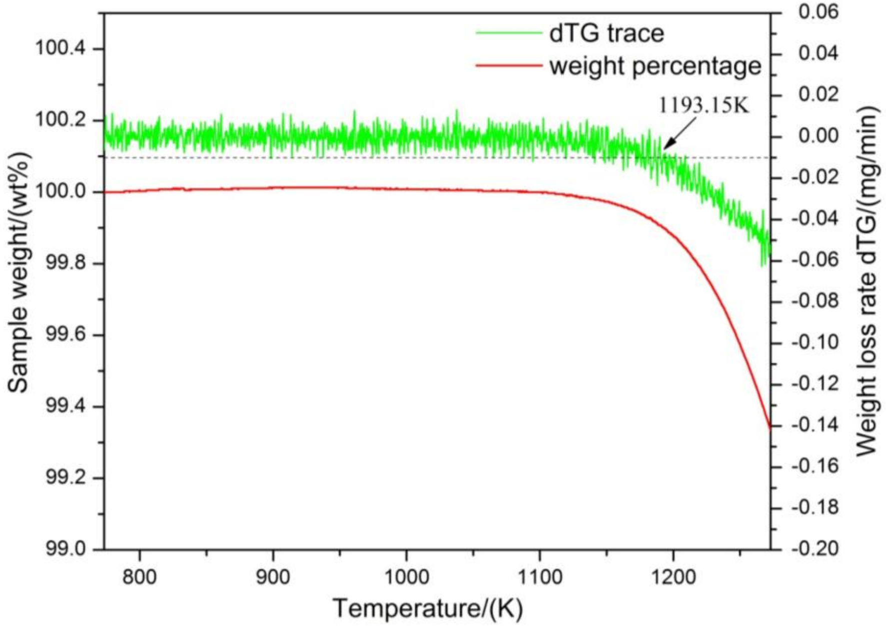
Model Pyris Diamond TGA-DTA;
Temp: 30˚C to1200˚C;
Solids and liquids; Platinum pan and Al_2O_3 reference material;
Computer operated.

- In order to determine the accurate upper limit of the working temperatures of the molten salts such as the LiF-Na_2CO_3-K_2CO_3, the salt mixture was heated continuously from 773.15 K to 1223.15 K with 10 K/min heating rate under argon atmosphere.
- The measurements were repeated at least 3 times with fresh prepared samples to ensure the accuracy and reproducibility.
- The weight change curve as function of temperature along with the rate of weight loss dTG will be analyzed.
- The temperature with 0.01mg/min of dTG trace is defined to be the upper limit of thermally stable working temperature of the HMP molten salt

Thermal Stability of Salt Mixtures



The upper limit of stable working temperature of LiF-Na_2CO_3-K_2CO_3 under argon atmosphere



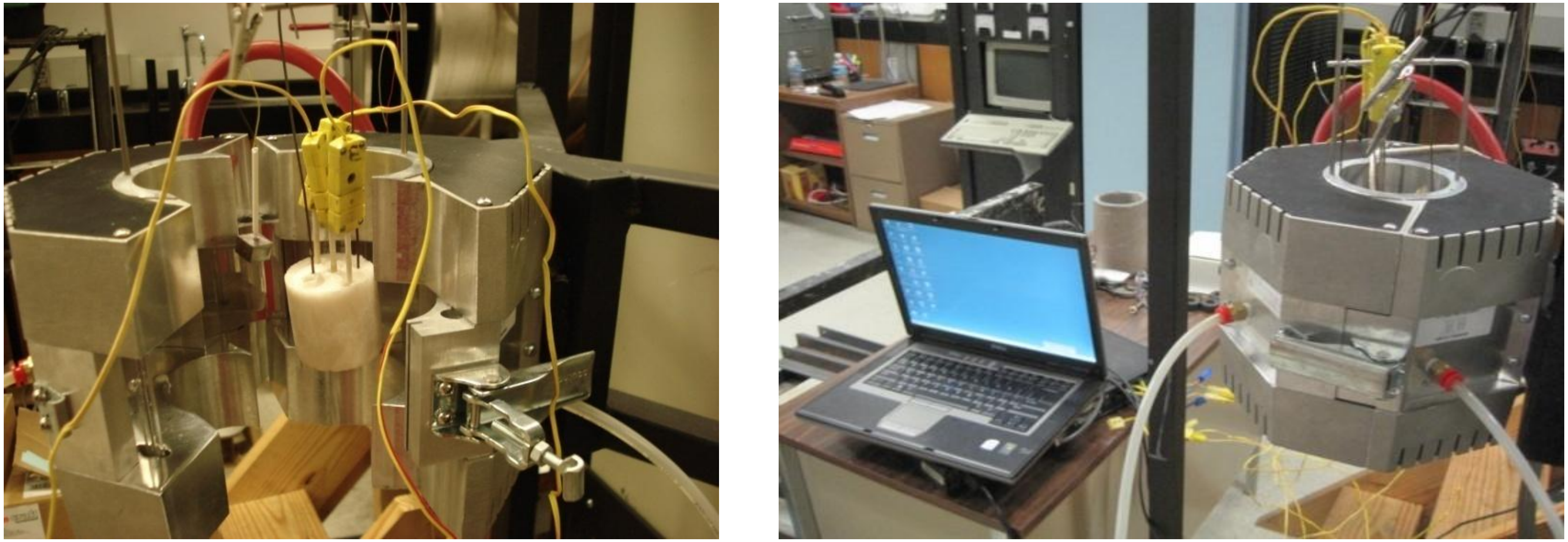
The upper limit of stable working temperature of LiF-Na_2CO_3-K_2CO_3 under carbon dioxide atmosphere

System	**Upper limit (°C)**
Li_2CO_3-Na_2CO_3-K_2CO_3	**857**
LiF-Na_2CO_3-K_2CO_3	**920**
LiF-NaF-K_2CO_3	**951**
LiF-NaF-Li_2CO_3-Na_2CO_3	**In progress**
LiF-NaF-KF-Li_2CO_3-Na_2CO_3	**887**

Thermal Conductivity of Salt Mixtures

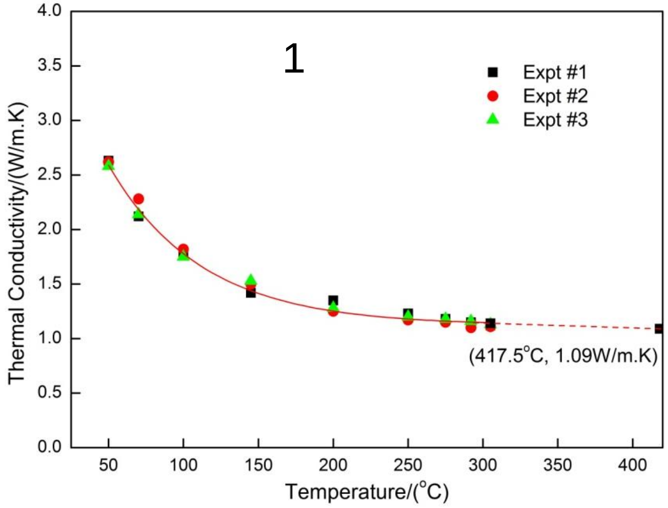
Thermal conductivity of Phase I salts have been measured experimentally using the technique as described in our earlier quarterly report. At least three experiments were conducted on each salt and the resulting thermal conductivity as a function of temperature is plotted in the following figure. The data are extrapolated to the respective melting points.

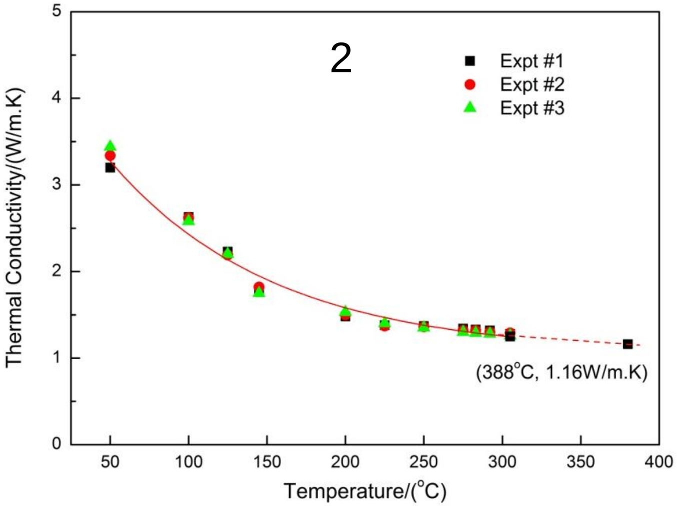
Thermal conductivity set-up

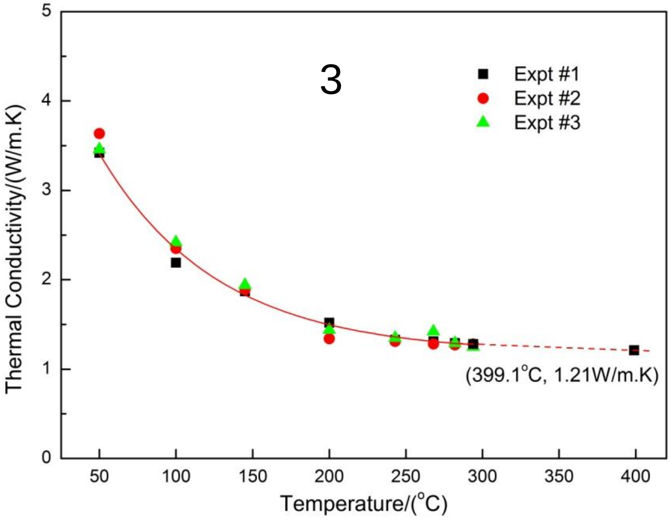


T. Wang, S. Viswanathan, D. Mantha, and R. G. Reddy, Thermal conductivity of the ternary eutectic $LiNO_3$–$NaNO_3$–KNO_3 salt mixture in the solid state using a simple inverse method, *Solar Energy Materials &Solar Cells (SOLMAT)*, 102, pp. 201-207, 2012.

Thermal Conductivity of Salt Mixtures



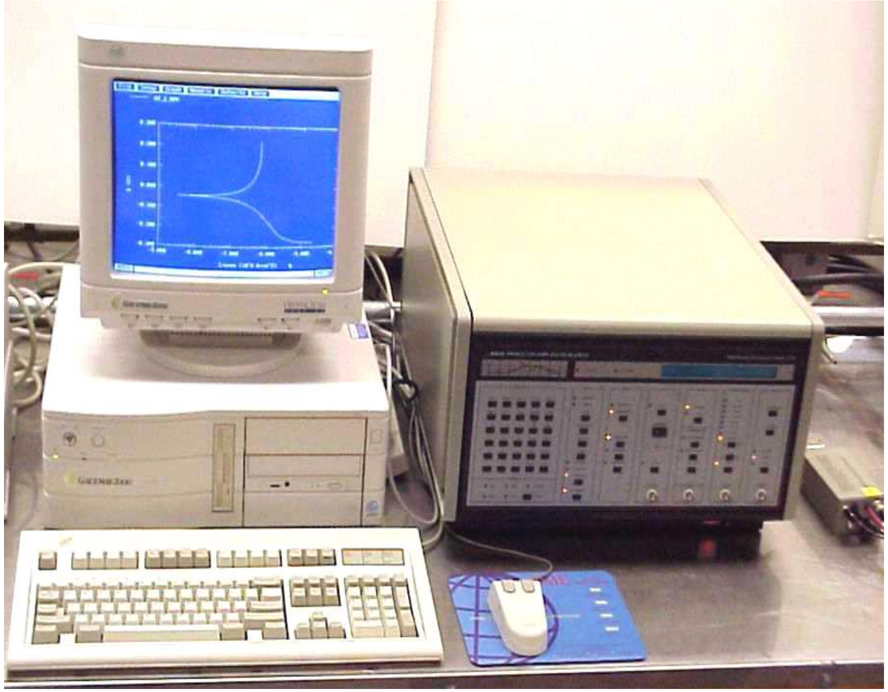




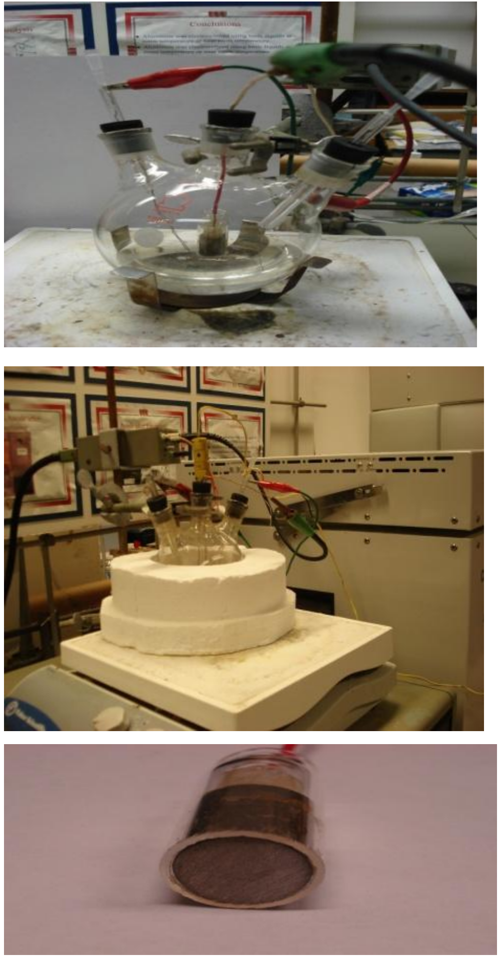
Expt. No.	**Salt Systems**	**Thermal Conductivity (W/m. K) at M.P.**
1	**LiF-NaF-KF-Li_2CO_3-Na_2CO_3**	**1.09**
2	**LiF-NaF-Li_2CO_3-Na_2CO_3-K_2CO_3**	**1.16**
3	**LiF- Li_2CO_3-Na_2CO_3-K_2CO_3**	**1.21**

Corrosion Studies

Corrosion of of SS316L stainless steel coupons in high temperature stable molten salt systems was accomplished by the electrochemical corrosion experiments. The SS 316L rod and coupon were used as test samples.

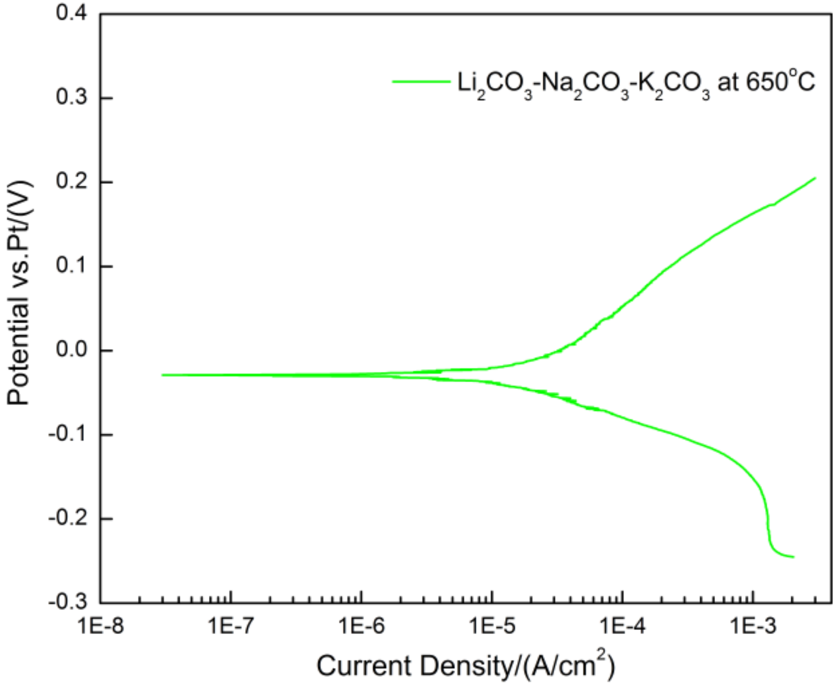


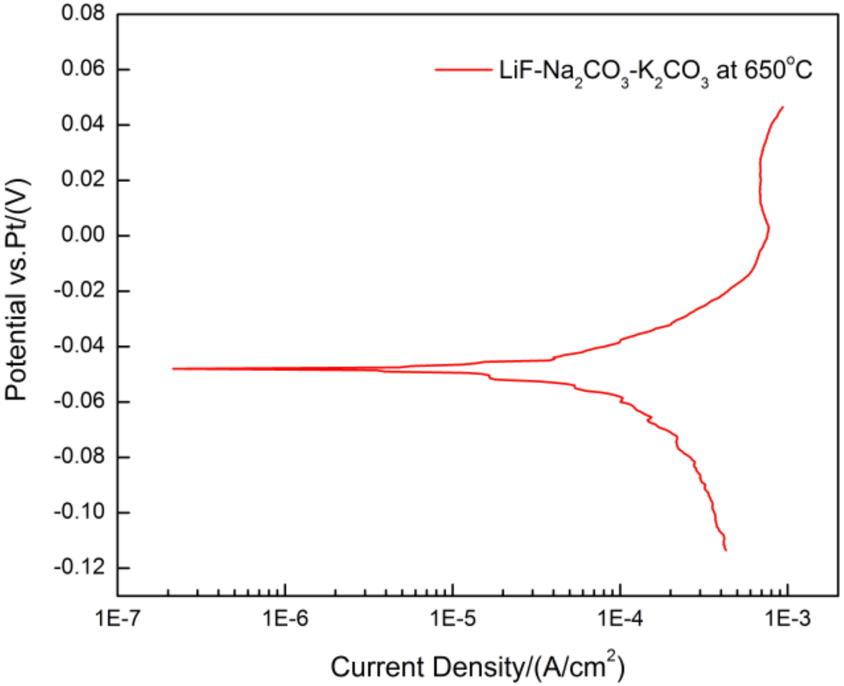
Potentiostat / galvanostat set-up



Corrosion cell set-up

Electrochemical Corrosion of SS 316L coupons



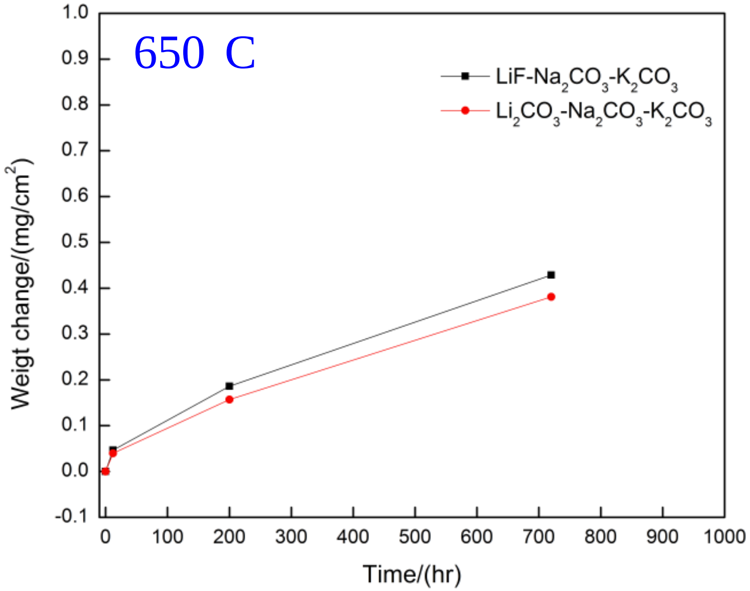


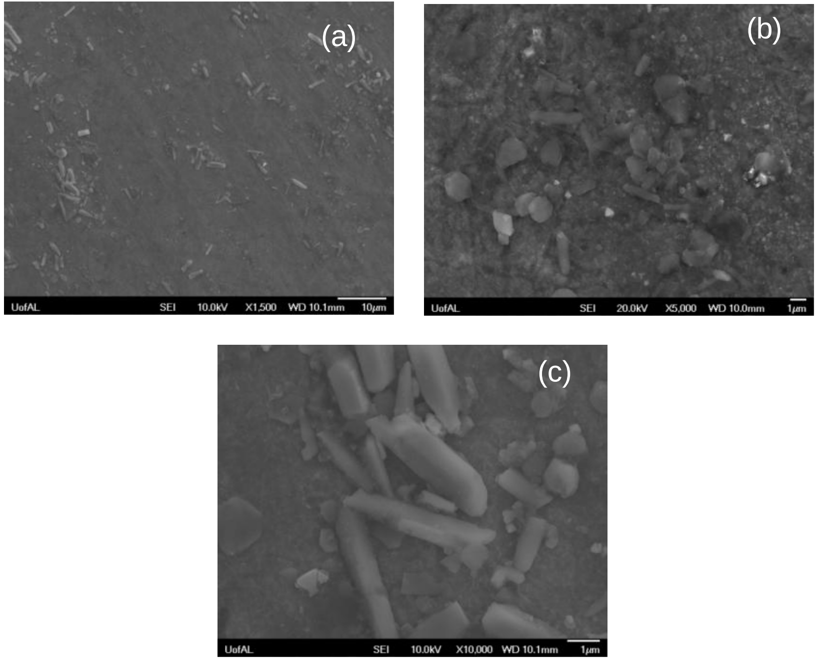
Corrosion rate calculations:

$$r = \frac{3.27 i_{corr} W_i}{\rho}$$

Salt system	**Temperature of testing °C**	**Current density μA/cm²**
Li_2CO_3-Na_2CO_3-K_2CO_3	650	15.7
LiF-Na_2CO_3-K_2CO_3	650	17.9

Corrosion of SS 316L coupons





The SEM of oxides adherent to SS316L after 12hr dipping corrosion test under (a) ×1500 magnification, (b) at ×5000 magnification, (c) at ×10000 magnification

Major corrosion products in Li_2CO_3-Na_2CO_3-K_2CO_3 and LiF-Na_2CO_3-K_2CO_3 systems

Salt system	after 0 hr	after 200hr	after 720hr
Li_2CO_3-Na_2CO_3-K_2CO_3	Base metal	Base metal, Fe(Cr, Ni)$_3$O$_4$, $LiFeO_2$, $LiFe_5O_8$	same as 200hr
LiF-Na_2CO_3-K_2CO_3	Base metal	Base metal, Fe(Cr, Ni)$_3$O$_4$, $LiFeO_2$, $LiFe_5O_8$	same as 200hr

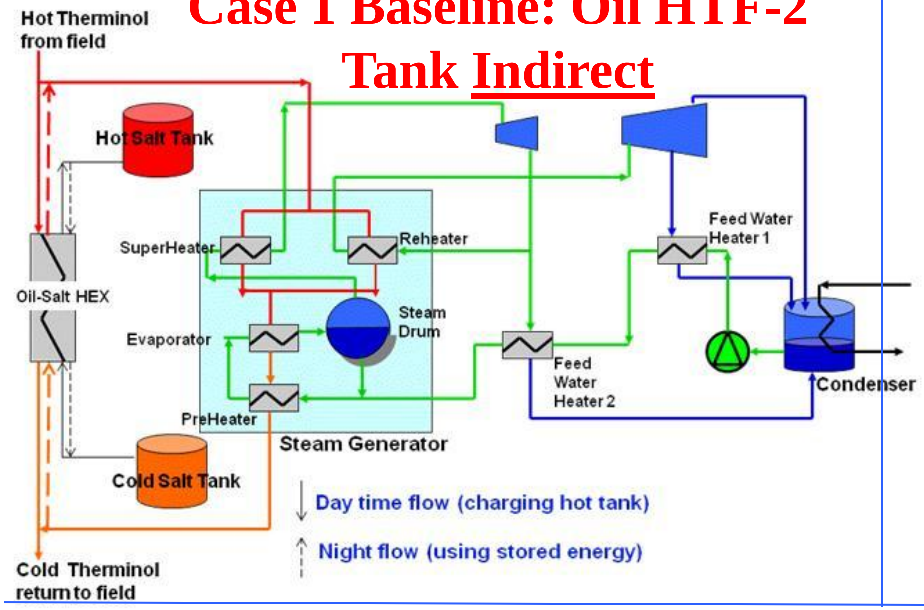
Thermal Energy Storage (TES) system

The heat transfer and fluid dynamics modeling enables the selection of the best Thermal Energy Storage (TES) system, including system geometry for laboratory scale testing, and required data such as heat transfer coefficient and thermal conductivity.

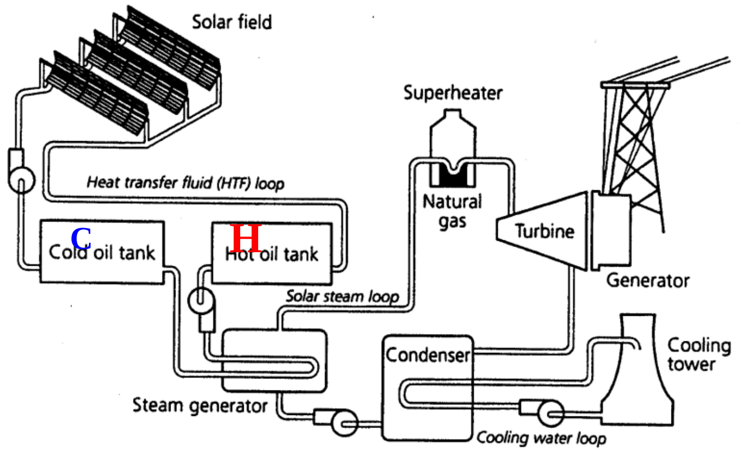
Several concepts evaluated; two proposed for use of salt latent heat

- **Use of 500C heat capability for higher efficiency steam Rankine cycle (salt as HTF)**
- **Use of low temp range for feedwater preheating**
- **Use of low temp salt in an “additional” low pressure turbine reheater**
- **Incorporate a separate bottoming cycle to utilize available thermal energy**

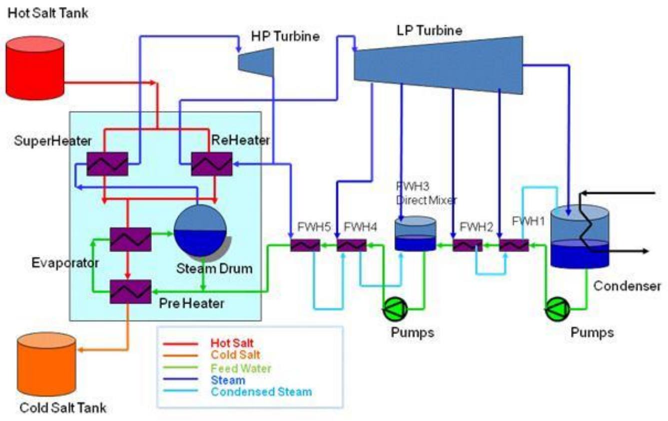
Case 1 Baseline: Oil HTF-2 Tank Indirect



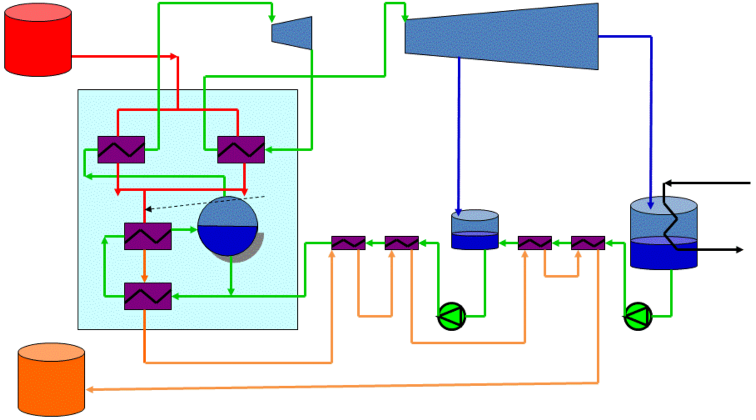
Solar Parabolic Trough



Case 2: U-A Salt HTF - 2 Tank Direct



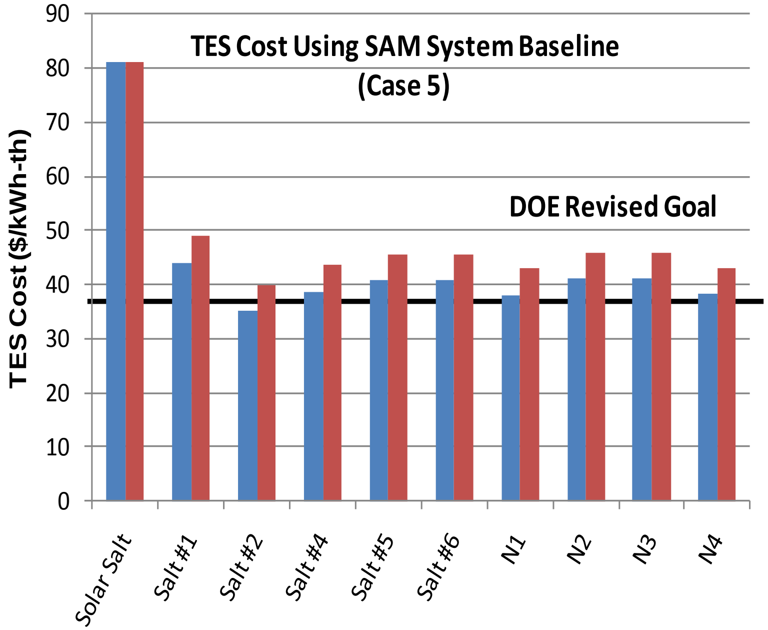
Case 5: U-A Salt HTF - 2 Tank Direct w/ salt heating all FWHs



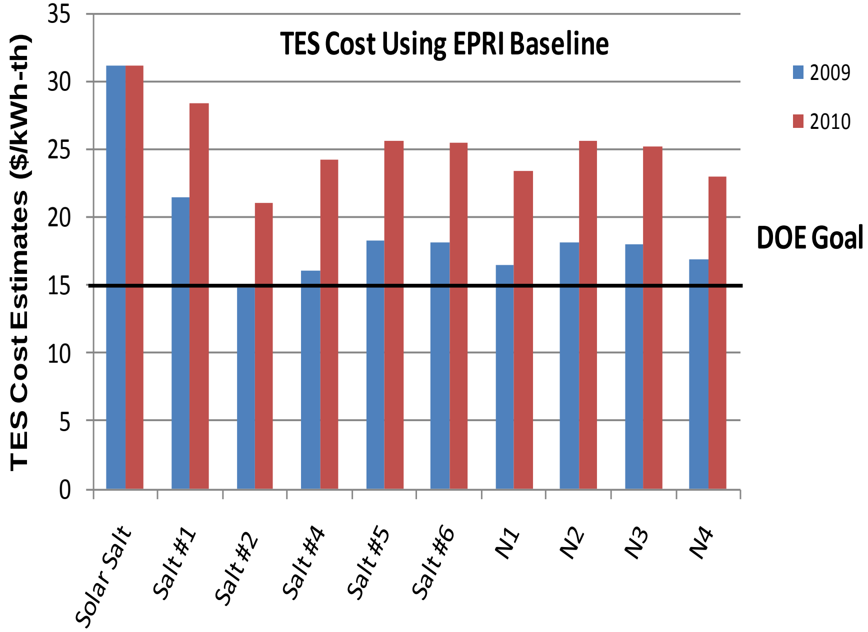
Alternative TES system configurations

Graphical Comparison of TES Cost estimates

(SAM and EPRI Baselines – linear (blue) and .07 power (red) scaling)



Comparative TES costs using 2009 salt component prices. Blue bars use "linear" equipment cost scaling, red bars utilize "0.7 power law" equipment cost scaling.



TES Calculations using 2009 EPRI Baseline (from Phase I report). Blue bars assume full delta T and linear equipment scaling; red bars assume average properties at 350 C and 0.7 power scaling.

Linear TES scaling calculates to be lower than cost target – reasonable because of dramatic reduction in TES size (only 1/3 baseline)

Power factor scaling very close to cost targets

Summary

- High order carbonate - fluoride molten salt systems have been developed using thermodynamic modeling method.
- Experimental determination of melting points of higher order carbonate-fluoride systems was completed
- Experimental determination of heat capacities of higher order carbonate-fluoride systems was completed
- Onset temperatures for weight loss for the higher order carbonate-fluoride systems can be as high as 900 degree C under carbon dioxide atmosphere.
- $LiCrO_2$, $LiFeO_2$ or similar protective oxide layers were formed as oxidation scale products on the SS316L specimens after isothermal corrosion experiment

Planned Activities for 2013

- Thermodynamic modeling of novel high temperature molten salt mixtures.
- Experimental verification of melting point and heat capacities.
- Thermal stability measurements for HT molten salt mixtures.
- Corrosion mechanism study in HT molten salt mixtures.
- Communicate research results to journals.

Publications

Archival Technical Journal Publications:

•Ramana G. Reddy, Tao Wang and Divakar Mantha, Thermodynamic Properties of potassium nitrate – magnesium nitrate compound [$2KNO_3.Mg(NO_3)_2$], *Thermochemica Acta,* 531, pp. 6-11, 2012.

•Tao Wang, Divakar Mantha and Ramana G. Reddy, Thermal stability of the eutectic composition in $LiNO_3$–$NaNO_3$–KNO_3 ternary system used for thermal energy storage, *Solar Energy Materials &Solar Cells (SOLMAT)*, 100, pp. 162-168, 2012.

•D. Mantha, T. Wang and R. G. Reddy, Thermodynamic Modeling of Eutectic Point in the $LiNO_3$-$NaNO_3$-KNO_3 Ternary System, *Journal of Phase Diagrams and Diffusion* (JPED), 33 (2), pp. 110-114, 2012.

•Tao Wang, Srinath Viswanathan, Divakar Mantha, and Ramana G. Reddy, Thermal conductivity of the ternary eutectic $LiNO_3$–$NaNO_3$–KNO_3 salt mixture in the solid state using a simple inverse method, *Solar Energy Materials &Solar Cells (SOLMAT)*, 102, pp. 201-207, 2012.

•T. Wang, D. Mantha and R. G. Reddy, "Novel low melting point quaternary eutectic system for solar thermal energy storage", Received 23 April 2012Revised 24 August 2012 Accepted 2 September 2012*Journal of Applied energy, 2013* (in press). http://dx.doi.org/10.1016/j.apenergy.2012.09.001

• T. Wang, D. Mantha and R. G. Reddy, "Available online 6 October 2012Thermodynamic properties of $LiNO_3$–$NaNO_3$–KNO_3–$2KNO_3.Mg(NO_3)_2$ system", *Thrmochemica Acta,* 2013 (in press). http://dx.doi.org/10.1016/j.tca.2012.09.035

Conference Publications:

• Tao Wang and R. G. Reddy, Thermal Stability of Low Melting Point $NaNO_3$–$NaNO_2$– KNO_3 Ternary Molten Salts for Thermal Energy Storage, Preprint 12-112, CD, SME, Littleton, CO, USA, pp.1-4, 2012.

•T. Wang, D. Mantha and R. G. Reddy, High Thermal Energy Storage Density $LiNO_3$-$NaNO_3$-KNO_3-KNO_2 quaternary Molten Salt for Parabolic Trough Solar Power Generation, Energy Technology 2012: Carbon Dioxide Management and Other Technologies, TMS, Warrendale, PA, USA, pp. 73-84, 2012.

•R. G. Reddy, Molten Salt Thermal Energy Storage Materials for Solar Power Generation, Ninth International conference on Molten Slags, Fluxes and Salts (Molten 12), The Chinese Society for Metals, Beijing, China, CD, 2012, pp. 1-18.

•T. Tao and R. G. Reddy, "Thermodynamic Properties of Novel Low Melting point LiNO3-NaNO3-KNO3 Ternary Molten Salt For Parabolic Trough Solar Power generation, Energy Technology 2013: Carbon Dioxide Management and Other Technologies, TMS, Warrendale, USA, pp. 5-16, 2013.

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  - Joe Stekli, DOE HQ Engineer
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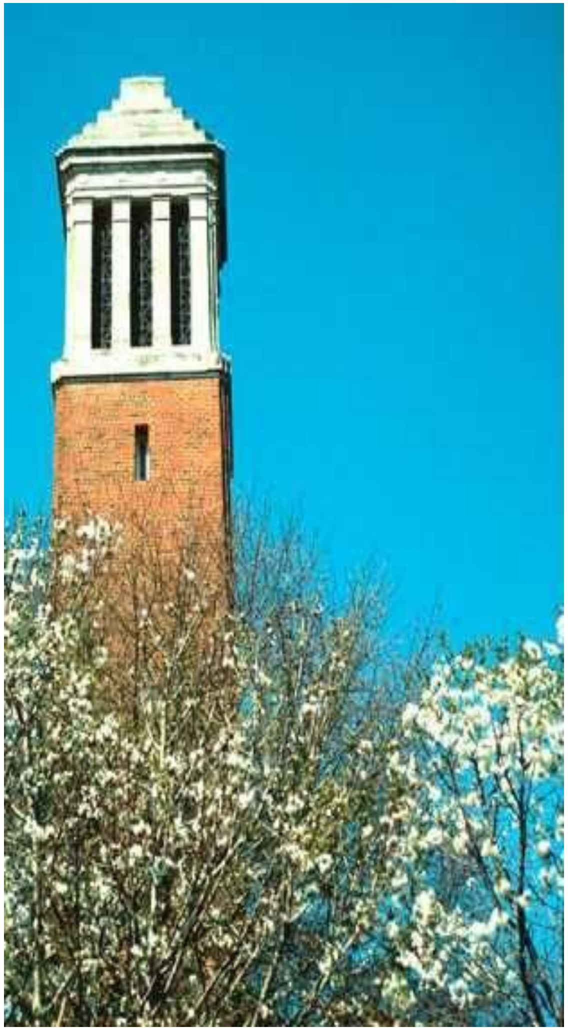
- Michael McDowell, Pratt Rocketdyne
- United Technologies Research Center (UTRC)
- The University of Alabama
  - Department of Metallurgical and Materials Engineering
- ACIPCO Endowed Chair Professorship



Thank you