Novel Molten Salts Thermal Energy Storage for Concentrating Solar Power Generation

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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/m³)
   - 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 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/m³ to 1230 MJ/m³ 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 \((\text{AX} + \text{BX})\) is represented as

\[
\text{AX}(s) + \text{BX}(s) = \text{AX}(l) + \text{BX}(l)
\]

Gibbs energies of fusion of both salts are given by

\[
\Delta G^\circ_{f,\text{AX}} = -RT \ln \left( K_{\text{AX}} \right) + G^\ell_{\text{AX}}
\]

\[
\Delta G^\circ_{f,\text{BX}} = -RT \ln \left( K_{\text{BX}} \right) + G^\ell_{\text{BX}}
\]

\[
\Delta G^\circ_{f,i} = \text{Gibbs energy of fusion of } 'i'
\]

\[
\overline{G^\ell_i} = \text{Partial excess Gibbs energy of } 'i'
\]

At eutectic point \((X_E, T_E)\), both the equations are satisfied. Similarly, eutectic points of LMP salt systems (other higher order) are evaluated.

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 \( \Delta C_p = [C_p(l) - C_p(s)] \) 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
  \[
  \Delta G_{f,i}^\circ + RT \ln(X_i) + \overline{G}_i^{xs} = 0 \quad \text{.................. (1)}
  \]
- Solve for composition and temperature using Newton-Raphson Algorithm

**What we get**
- Eutectic composition \((X_i)\) and temperature \((T)\) for the salt mixture
The first term in equation (1) is given by:

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

This is the standard Gibbs energy of fusion

The third term in equation (1) is given by

\[
G_i^{xs} = G^{xs} + \sum_{j=2}^{m} \Theta_{ij} - X_j \frac{\partial G^{xs}}{\partial X_j}
\]

where \( \delta_{ij} = 0 \) for \( i \neq j \)

\( \delta_{ij} = 1 \) 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:

\[
G^{xs} = \sum_{i=1}^{n} \sum_{j \neq i}^{n} G_{i-j}^{xs}
\]

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 \(J \cdot \delta x^{(k)} = -R\)

**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

\[ G_{\text{Li–K}}^{\text{xs}} = X_{\text{LiNO}_3} \cdot X_{\text{KNO}_3} \leq 1269.12 - 1.4359T \cdot \ln(T) + 7.2897T \]

\[ G_{\text{Li–Na}}^{\text{xs}} = X_{\text{LiNO}_3} \cdot X_{\text{NaNO}_3} \leq 4519.6 - 6.575T \cdot \ln(T) + 49.0607T \]

\[ G_{\text{Na–K}}^{\text{xs}} = X_{\text{NaNO}_3} \cdot X_{\text{KNO}_3} \leq 408.51 - 68X_{\text{NaNO}_3} \]

Excess Gibbs energy in the LiNO$_3$ – NaNO$_3$ – KNO$_3$ ternary system is given as

\[ G^{\text{xs}} = G_{\text{Li–Na}}^{\text{xs}} + G_{\text{Li–K}}^{\text{xs}} + G_{\text{Na–K}}^{\text{xs}} \]

# Properties of Salts

<table>
<thead>
<tr>
<th>Salt System</th>
<th>Melting Point (°C)</th>
<th>Density (g/cc)</th>
<th>Heat Capacity (J/g.K)</th>
<th>Energy Density (MJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA baseline ternary</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiNO₃-NaNO₃-KNO₃</td>
<td>116(117)</td>
<td>1.71</td>
<td>1.54</td>
<td>1056*</td>
</tr>
<tr>
<td>Solar Salt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaNO₃-KNO₃</td>
<td>222</td>
<td>1.75</td>
<td>1.53</td>
<td>756</td>
</tr>
</tbody>
</table>

*Experimental determination*

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$_2$CO$_3$ System

DSC plot for the LiF-NaF-K$_2$CO$_3$ system showing the melting temperature.
Heat Capacity - $\text{Li}_2\text{CO}_3 - \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$ System

$C_p (600 \, \text{C}): 1.7 \, \text{J/g} \cdot \text{C}$

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

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>Temperature, °C</th>
<th>Cp, J/g.°C at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calc</td>
<td>Expt</td>
</tr>
<tr>
<td>1</td>
<td>LiF–K$_2$CO$_3$</td>
<td>456</td>
<td>482</td>
</tr>
<tr>
<td>2</td>
<td>LiF–Li$_2$CO$_3$</td>
<td>612</td>
<td>608</td>
</tr>
<tr>
<td>3</td>
<td>NaF–Na$_2$CO$_3$</td>
<td>694</td>
<td>690</td>
</tr>
<tr>
<td>4</td>
<td>Li$_2$CO$_3$–K$_2$CO$_3$</td>
<td>503</td>
<td>503</td>
</tr>
<tr>
<td>5</td>
<td>Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$</td>
<td>397</td>
<td>398</td>
</tr>
<tr>
<td>6</td>
<td>LiF–Na$_2$CO$_3$–K$_2$CO$_3$</td>
<td>386</td>
<td>389</td>
</tr>
<tr>
<td>7</td>
<td>LiF–NaF–K$_2$CO$_3$</td>
<td>414</td>
<td>422</td>
</tr>
<tr>
<td>8</td>
<td>LiF–KF–K$_2$CO$_3$</td>
<td>412</td>
<td>438</td>
</tr>
<tr>
<td>9</td>
<td>LiF–NaF–Na$_2$CO$_3$–K$_2$CO$_3$</td>
<td>373</td>
<td>423</td>
</tr>
<tr>
<td>10</td>
<td>LiF–NaF–Li$_2$CO$_3$–Na$_2$CO$_3$</td>
<td>444</td>
<td>444</td>
</tr>
</tbody>
</table>
• In order to determine the accurate upper limit of the working temperatures of the molten salts such as the LiF-Na$_2$CO$_3$-K$_2$CO$_3$, 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$_2$CO$_3$-K$_2$CO$_3$ under argon atmosphere is 857°C.

The upper limit of stable working temperature of LiF-Na$_2$CO$_3$-K$_2$CO$_3$ under carbon dioxide atmosphere is 920°C.

System | Upper limit (°C)
--- | ---
Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ | 857
LiF-Na$_2$CO$_3$-K$_2$CO$_3$ | 920
LiF-NaF-K$_2$CO$_3$ | 951
LiF-NaF-Li$_2$CO$_3$-Na$_2$CO$_3$ | In progress
LiF-NaF-KF-Li$_2$CO$_3$-Na$_2$CO$_3$ | 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**

### Thermal Conductivity of Salt Mixtures

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Salt Systems</th>
<th>Thermal Conductivity (W/m. K) at M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiF-NaF-KF-Li$_2$CO$_3$-Na$_2$CO$_3$</td>
<td>1.09</td>
</tr>
<tr>
<td>2</td>
<td>LiF-NaF-Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$</td>
<td>1.16</td>
</tr>
<tr>
<td>3</td>
<td>LiF-Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$</td>
<td>1.21</td>
</tr>
</tbody>
</table>
Corrosion Studies

Corrosion 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.
Electrochemical Corrosion of SS 316L coupons

Corrosion rate calculations:

\[ r = \frac{3.27 i_{corr} W_i}{\rho} \]

<table>
<thead>
<tr>
<th>Salt system</th>
<th>Temperature of testing °C</th>
<th>Current density μA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}_2\text{CO}_3-\text{Na}_2\text{CO}_3-\text{K}_2\text{CO}_3 )</td>
<td>650</td>
<td>15.7</td>
</tr>
<tr>
<td>( \text{LiF}-\text{Na}_2\text{CO}_3-\text{K}_2\text{CO}_3 )</td>
<td>650</td>
<td>17.9</td>
</tr>
</tbody>
</table>
Corrosion of SS 316L coupons

650 C

Major corrosion products in Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ and LiF-Na$_2$CO$_3$-K$_2$CO$_3$ systems

<table>
<thead>
<tr>
<th>Salt system</th>
<th>after 0 hr</th>
<th>after 200hr</th>
<th>after 720hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$</td>
<td>Base metal</td>
<td>Base metal, Fe(Cr, Ni)$_3$O$_4$, LiFeO$_2$, LiFe$_5$O$_8$</td>
<td>same as 200hr</td>
</tr>
<tr>
<td>LiF-Na$_2$CO$_3$-K$_2$CO$_3$</td>
<td>Base metal</td>
<td>Base metal, Fe(Cr, Ni)$_3$O$_4$, LiFeO$_2$, LiFe$_5$O$_8$</td>
<td>same as 200hr</td>
</tr>
</tbody>
</table>
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

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

Solar Parabolic Trough

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.

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.
Archival Technical Journal Publications:


Conference Publications:

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