Halide and Oxy-halide Eutectic Systems for High Performance High Temperature Heat Transfer Fluids

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Presentation outline

- Introduction to the key studies of the project
- Objectives and goals
- Approaches and the current budget period tasks
- Up-to-date key technical results and discussions
- Significance of the current results
- Challenges and barriers
- Planned future work
Introduction to the key studies of the project

- Ionic halide and covalent metal halide salts have dissimilar bonding mechanism that can be utilized to create deep eutectic systems.

- NaCl, KCl, AlCl$_3$, ZnCl$_2$, FeCl$_3$, are usually cheap and have large reserve.

- High boiling-point ionic halide salts in the eutectic system are expected to keep the eutectic system thermally stable at high temperatures (above 800 $^\circ$C).

- Lewis acid/base additives and network forming additives will be used to tune the thermodynamics and transport properties of the eutectic system simultaneously.
<table>
<thead>
<tr>
<th>Chloride salt</th>
<th>Melting (°C)</th>
<th>Boiling (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>800</td>
<td>1413</td>
</tr>
<tr>
<td>KCl</td>
<td>770</td>
<td>1420</td>
</tr>
<tr>
<td>LiCl</td>
<td>605</td>
<td>1382</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>772</td>
<td>1935</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>677</td>
<td>1023</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>na</td>
<td>315</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>714</td>
<td>1412</td>
</tr>
<tr>
<td>MnCl₂</td>
<td>654</td>
<td>1225</td>
</tr>
<tr>
<td>CuCl</td>
<td>426</td>
<td>1490</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>498</td>
<td>993</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>293</td>
<td>732</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>120</td>
<td>262</td>
</tr>
</tbody>
</table>
## Objectives and goal

The eutectic salt will be engineered to meet the following targeted property:

<table>
<thead>
<tr>
<th>Property</th>
<th>Target</th>
<th>Stretch Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Stability (liquid)</td>
<td>≥ 800 °C</td>
<td>≥ 1300 °C</td>
</tr>
<tr>
<td>Melting Point</td>
<td>≤ 250 °C</td>
<td>≤ 0 °C</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>≥ 1.5 J/g/K</td>
<td>≥ 3.75 J/g/K</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>≤ 1 atm</td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>≤ 0.012 Pa-s @ 300 °C; ≤ 0.004 Pa-s @ 600 °C</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>≤ 6,000 kg/m³ @ 300 °C; ≤ 5,400 kg/m³ @ 600 °C</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>≥ 0.51 W/m/K @ 300 °C; ≥ 0.58 W/m/K @ 600 °C</td>
<td></td>
</tr>
<tr>
<td>Materials Compatibility</td>
<td>Carbon Steel (&lt;425 °C), Stainless Steel (&lt;650 °C) and Nickel Alloys. Corrosion &lt;100μm/year</td>
<td></td>
</tr>
<tr>
<td>Materials Cost</td>
<td>≤ $1 / kg</td>
<td></td>
</tr>
</tbody>
</table>
Approaches and budget period tasks

- The primary mechanism to modify and meet both thermodynamics and transport properties lies in the choice of ternary and quaternary systems of ionic and covalent halide salts.

- The secondary level of control of the energetics, thermal conductivity, and viscosity is offered by Lewis acid/base additives and/or network forming additives.
- Optical Combinatorial Rapid Screening (OCRS)
- Computer-Assisted Rapid screening of Eutectic (CARE)
- Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) of the Eutectic salt
- Property measurement: thermal conductivity, viscosity, density, Cp, vapor pressure, radiation.
**Task 1.1:** Combinatorial analysis ionic/covalent low eutectic salts (KCl-NaCl-ZnCl₂, KCl-NaCl-AlCl₃)

**Task 1.2:** Explore vapor pressure reduction with additives (Lewis Acid-Base, oxy-halides)

**Task 1.3:** Determine corrosion rates of different container/piping alloys (iron and nickel alloys) in molten salts

**Task 1.4:** Determine thermal and transport properties up to 800°C
Up-to-date key technical results and discussions

- 1) Eutectic compositions and melting
- 2) Evaporation and vapor pressure
- 3) DSC and TGA tests
- 4) Corrosion test
- 5) Properties
1) Eutectic compositions and melting

KCl-NaCl-AlCl₃ ternary system

T = 132 °C at NaCl-KCl-AlCl₃ mole fraction of 36%-14%-50%.
T = 91 °C at NaCl-KCl-AlCl₃ mole fraction of 26.25%-15%-58.75%.
Overall, the current data from our research show that a ternary salt composition near 15KCl-35NaCl-50AlCl₃ will satisfy our milestone criteria of melting point <200ºC and vapor pressure <2 atm at 800ºC.

Experimental liquid/solid phase diagram of pseudo binary system determined by DSC.
Boiling point of binary systems NaCl-AlCl₃ at a pressure of 0.989 atm has been reported/tested.

KCl-NaCl-ZnCl$_2$ ternary system

T=213 °C at NaCl-KCl-ZnCl$_2$ mole fraction of 18.6%-21.9%-59.5%.
T=204 °C at NaCl-KCl-ZnCl$_2$ mole fraction of 13.4%-33.7%-52.9%.
T=229 °C at NaCl-KCl-ZnCl$_2$ mole fraction of 13.8%-41.9%-44.3%.
KCl-NaCl-FeCl$_3$ ternary system

T=139 °C at NaCl-KCl-FeCl$_3$ mole fraction of 34%-13%-53%.
T=141 °C at NaCl-KCl-FeCl$_3$ mole fraction of 35%-17%-48%.
T=240 °C at NaCl-KCl-FeCl$_3$ mole fraction of 2%-51%-47%.
2) Melting and evaporation

AlCl₃ salts: negligible vapor pressure up to 550°C

FeCl₃ salts: negligible vapor pressure up to 500°C

ZnCl₂ salts: negligible vapor pressure up to 450°C
AlCl₃ (50%) + NaCl (50%)

Mass loss

Onset: 149.8 °C, 0.75667 µV/mg

Value: 794.0 °C, 3.7072 µV/mg

AlCl₃ vapor loss through lid pinhole

Sample: Lucas, 2.9 mg

Sample car./TC: DSC/TG Cp S / S

Mode/type of meas.: DSC-TG / Sample

Segments: 1/1

Crucible: DSC/TG pan Al2O3

Atmosphere: N2 / N2

Instrument: NETZSCH STA 449F3 STA449F3A-0825-M

File: C:\NETZSCH\Proteus\data\TEST_AlCl3_high TG\TEST 900 0210 2ND.ngb-ss3

Project: TEST 900 0210 2ND

Identity: TEST 900 0210 2ND

Date/time: 2/10/2013 3:10:03 PM

Laboratory: 

Operator: 

Pre Mment Cycles: 3xVac

SunShot

U.S. Department of Energy
Mass loss occurs even with full Pt lid. DSC data unusable at high T because of composition uncertainty.

High pressure stainless steel crucible will be used in the future in non-oxidizing atmosphere.
MicroRaman collection performed with 514 nm excitation source using long focal objective on AlCl$_3$ sample encapsulated in glass.

All Raman modes are clearly resolved and consistent with literature.
Similarly, Raman modes of ZnCl$_2$ and FeCl$_3$ are clearly resolved and consistent with literature.
Normalized Raman spectra of ZnCl$_2$-NaCl-KCl salts

- Multiple species can be identified in ternary system
- Relative mode intensities can be measured to estimate species ratio

Normalized Raman spectra of ZnCl$_2$-NaCl-KCl salts

- 68%ZnCl$_2$-15.5%KCl-16.5NaCl
- 61.75%ZnCl$_2$-26.5%KCl-11.75NaCl
- 43.25%ZnCl$_2$-47.65%KCl-8.2%NaCl

ZnCl$_2$ $A_1$ mode

Na$_2$ZnCl$_4$ mode

$K_xZn_yCl_z$ mode
4) Corrosion testing

- **Gravimetric method is slow but accurate**: The weight loss by the gravimetric method is corrected for weight loss during surface preparation, e.g., from exposure to the sulfuric acid soak so the higher value using gravimetric method is not an artifact.

- **Electrochemical method is quick, precise but ~ 35% inaccurate**: The error in the electrochemical method arises from the assumptions used when applying Faraday’s Law of electrolysis to convert charge to mass when finding the weight loss.
  - Faraday’s Law of electrolysis is \( m = \frac{Q}{F} \left( \frac{M}{z} \right) \) in which \( m \) is the mass of the substance liberated from electrode in grams; \( Q \) is the total electric charge passed; \( F = 96,485 \text{ C mol}^{-1} \) is the Faraday constant; \( M \) is the molar mass of the substance and \( z \) is the number of electrons transferred per mole during the rate limiting step.
  - The only arbitrary assumption is that metal forms metal ions by the loss of 2 electrons (i.e., \( z=2 \)). Although reasonable, this may not be and appears not to be - exactly true.

- **Gravimetric method used to correct an Electrochemical sensor**: The time-dependent gravimetric and electrochemical weight-loss lines are straight.
  - The slopes of these lines differ by a constant, \( k \), and \( k \) can be used to correct the electrochemically-determined weight loss.
  - Finding \( k \) for each metal in each salt composition is an important task.
  - Knowing this constant, \( k \), for a specific metal in a specific molten salt, allows use of the electrochemical method to quickly and accurately monitor the rate of corrosion of metal.

Weight loss of 1008 steel in aerated water with 1000 ppm sodium sulfate in time. Measured by the
1. gravimetric method (red line)
2. electrochemical method (blue line).
Polarization curves in molten salt

Electrochemical measurement set-up connected to the corrosion cell in the high temperature furnace. Right panel shows the blown-up view of the corrosion cell and the connecting wires going to the electrodes.

Polarization curve ($\log_{10} |I|$ versus $E$) for a stainless steel electrode in 13.4NaCl- 33.7KCl- 52.9ZnCl$_2$ eutectic molten salt at 250°C.
## Summary of corrosion data in molten salts

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Alloy Sample</th>
<th>Salt Composition</th>
<th>Temperature &amp; Atmosphere</th>
<th>Corrosion Rate ($\mu$m/yr)</th>
<th>$E_{corr}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stainless Steel (430)</td>
<td>1M NaCl aqueous solution</td>
<td>RT/Air</td>
<td>10</td>
<td>n/a -229 -222</td>
</tr>
<tr>
<td>2</td>
<td>Stainless Steel (430)</td>
<td>NaCl-ZnCl$_2$ (40-60)</td>
<td>300 $^\circ$C/Air</td>
<td>12</td>
<td>n/a 9 27</td>
</tr>
<tr>
<td>3</td>
<td>Stainless Steel (430)</td>
<td>NaCl-KCl-ZnCl$_2$ (13.4-33.7-52.9)</td>
<td>250 $^\circ$C/Air</td>
<td>45</td>
<td>n/a -76 n/a</td>
</tr>
<tr>
<td>4</td>
<td>Hastelloy (C 276)</td>
<td>NaCl-KCl-ZnCl$_2$ (13.4-33.7-52.9)</td>
<td>250 $^\circ$C/Air</td>
<td>12</td>
<td>-39 -25 -37</td>
</tr>
</tbody>
</table>
5. Thermal and Transport Properties

Thermal conductivity by Ga-Tech.
Density, Cp, viscosity, radiation by UA
Indirect measurement - Laser Flash Diffusivity method

- $\lambda = \rho \alpha C_p$
  - $\rho$: Density $\rightarrow$ literature or measured (UA)
  - $\alpha$: Thermal diffusivity $\rightarrow$ measured by LFD
  - $C_p$: Specific heat $\rightarrow$ measured by DSC (UA)

- Test mixture measurements by Netzsch Instruments Application Laboratory, Burlington, MA
  - KNO$_3$/NaNO$_3$ eutectic mixture (54 % mol KNO$_3$)
  - Temp. Range: 523 K-723 K
  - Reported error: 10-15%

- Collaboration with Oak Ridge National Lab (ORNL)
  - Will require re-design of the sample holder for high temperatures
Netzsch Results and Comparisons

KNO₃/NaNO₃ eutectic mixture

\[ \lambda \text{ (W/m/K)} \]

Temperature (K)

- New Data, LFD (2012)
- Diguilio (1992) - 54% KNO₃
- Tufeu (1985) - 50% KNO₃
- Omotani (1982) - 50% KNO₃
Transient Hot Wire apparatus improvements

- **Existing system**
  - Mercury filled glass capillary (suitable up to 523 K)

- **Proposed set up**
  - Alumina sample holder and cell
  - Capillary filled with gallium
Model Development

- **Thermal conductivity correlation and prediction**
  - alkali-nitrates from NaNO₃ data
  - alkali-chlorides from NaCl data
High temperature HTF density (UA)

(a) Schematic diagram of the test apparatus.
(b) Actual setup.

Future work (calibration with NaCl and KCl up to 1200 C, with nickel block as the weight rather than Cu for now).
High temperature HTF density (UA)

- Oxidation of nickel weight at high temperatures
  - Nickel rod: 99.98% from Good Fellow

- Color turns green during NaCl calibration
- Ni will be oxidized above 400 °C to form NiO (even before dipping into NaCl melted at 800 °C)

- Deposit 100 nm Pt on Ni rod
- Less NiO still forms after taking out
High temperature HTF density (UA)

- **NaCl calibration result**
- **Nickel:**
  - Volume expansion $\beta(T) \approx 3\alpha(T)$
  - 4.19% volume expansion from 25 to 800 °C
- **NaCl density at 800-850 °C**
  - 1610 kg/m$^3$, 3.47% higher than literature value
  - It may be due to slight surface oxidation on Ni rod
Challenges and barriers

- All three ternary eutectic systems showed a vaporization at temperature about 500 C in ambient pressure. Before we find the proper quaternary system or additives to reduce the vapor pressure, we face challenges in conducting tests of thermal and transport properties under pressure. This requires equipment to hold pressures of up to 2.0 atm as expected.
Planned future work

- Pressurized test of vaporization-temperatures.
- Quaternary system and vapor pressure reduction
- Additives (POCl₃, B₂O₃) to reduce vapor pressure
- Property measurement at high temperatures.

Thank you!
Backup slides for questions and discussions

Gravimetric Method

- Prepare metal surface
- Weigh metal
- Expose metal to molten salt
- Reweigh metal

Gravimetric corrosion rate is weight difference of sample before and after exposure to molten salt

Advantage
- Absolute measurement of corrosion

Disadvantage
- Slow (weeks to months)
- Can only give average corrosion rate (ACR in grams per year, gpy, converted to microns per year, mpy, using density and metal area) over the long intervals of time needed to obtain data so there is a loss of information, that is rate of corrosion due to quick changes in environment
The test cell for obtaining an I/V plot is

- a working electrode (WE) made of the metal in molten salt of interest
- metal potential, \( E_{\text{WE}} \), is obtained by measuring the voltage of the working electrode versus the potential of a silver/silver-chloride reference electrode, \( E_{\text{ref}} \)
- current is passed from working electrode to an inert counter electrode.

Left—High temperature corrosion cell with brown shaded area showing the dimensions of the high temperature furnace.

Right—A blown-up of the cell with working electrode reference electrode in tube terminating with quartz-frit made at Technical Glass Products, Ohio.
Method
The instantaneous corrosion rate (ICR in microns per year) is estimated from interpreting a polarization (current/voltage or I/V) curve. ICR is

\[
ICR = \frac{MB}{(AFz\rho)R_p}
\]

- \(M\) is average molecular weight of the metal or metal alloy (g/mol),
- \(A\) is the surface area (cm²),
- \(F\) is the Faraday constant [96 485 coulomb/(mol e-)],
- \(z\) is the average charge of the metal [(mol e-)/mol],
- \(\rho\) is the density of the metal (g/cm³)
- \(B\) is the Stern-Geary constant (volt)
- polarization resistance, \(R_p\), where \(R_p\) is estimated by measuring:
  - the slope, \(\beta\), of a linear plot of the I/E curve, measured for the anodic (\(\beta_a\)) and cathodic (\(\beta_c\)) branches within 50 mV of the rest potential (\(E_{rest} = E_{corr}\))
  - the \(I_{corr}\), the value extrapolated to the I axis from \(E_{corr}\) at the intersection of the anodic and cathodic linear interpolation of the log I versus V plot

\[
R_p = \frac{\beta_a\beta_c}{[2.303 I_{corr}(\beta_a+\beta_c)]} = \frac{B}{I_{corr}} \quad \text{where } B = \text{the Stern Geary coefficient} = \frac{\beta_a\beta_c}{[2.303(\beta_a+\beta_c)]}
\]

Advantage
Quick (minutes), allows interrogation of changing corrosive environmentals/conditions

Disadvantages
Needs to be normalized by gravimetric data due to uncertainty in \(z\)
Glass cell used for electrochemical determination of corrosion rate of 1008 steel in water
Gravimetric method for corrosion test

Initially, the metal is abraded with 600 grit silicon carbide paper; soaked in 1M aqueous sulfuric acid for 1 minute, rinsed with acetone, dried at room temperature and weighed.

This pre-weighed sample is then exposed to water of known composition and open to the air as shown.

The corroded metal is soaked in acid to remove corrosion products, rinsed with acetone, dried and reweighed to find the net weight loss.

A graphical summary of the gravimetric weight loss results for the steel exposed to water in time.

Plot of weight loss of steel in time for Tucson tap water (TW) and in ultra pure water with 1000ppm sodium sulfate.
The log$_{10}$ of the absolute value of the steady state current, |I|, is plotted versus metal electrode potential.

The Tafel region is the linear region of the I/V curve within 50 mV of $E_{corr}$.
- $\beta_A$ is slope of the of the I/V curve during oxidation of metal
- $\beta_c$ is slope of the curve for oxygen reduction.

$I_{corr}$, the corrosion current, is determined by extrapolating the intersection of the Tafel lines to the current axis at $E_{corr}$. 

Polarization (I/V) curve for steel in aerobic water. With 1000 ppm sodium sulfate. WE=steel, CE=graphite, RE= SCE. $T = 22^\circ C$; $P = 1$ atm in air.
Special handling of eutectics formed from aluminum chloride

Aluminum chloride fumes in moist air forming aluminum-oxides and oxy halides.

An aluminum eutectic (50% AlCl$_3$-15% KCl-35% NaCl) melts at 190°C and appears stable for use as heat transfer fluids, if prepared properly.

Preparation of the eutectic must be done in an inert atmosphere (N$_2$). The AlCl$_3$ is placed in a test tube; then covered by a layer of KCl and then NaCl. When AlCl$_3$ melts all are stirred and heated until this mixture melts at 190°C.

The eutectic cooled to RT (22 °C) is stable in air at RT and when re-heated in air to the highest temperature tested to date, 300°C.

316 stainless steel was added to the molten aluminum eutectic in air. The metal did not disturb the eutectic's stability in air, and no weight change was found for the 316 stainless steel when immersed in the eutectic in air for 100 hours.
Future improvement

– $\text{N}_2$ protection for the current setup (building a home-made enclosure to purge with $\text{N}_2$) in case salts also react with air
– Quartz weight ordered to replace Ni

- **Measure volume expansion directly (alternative way)**

  - Vacuum sealed at the end
  - Take photo of the liquid level through the observation window of the furnace
  - Bulb (volume measured before use)

  Piston dilatometry:
  - The liquid level change here is transferred through a piston to a dial gauge
  - Providing seal also with a piston