Quantification of molten salt components for nonproliferation and material accountancy purposes

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Structure

- Introduction
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- Goals and Objectives
- Elemental Analysis and Optical Spectroscopy: Method Development
- Elemental Analysis and Optical Spectroscopy: Cr Solubility in fuel and coolant salt
- Preliminary Results
- Conclusions
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- NSSC Experience
- Acknowledgements
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NSSC Research Focus Area(s): Nuclear and Chemical Engineering
Academic Standing: 4th Year PhD Student

Lab Mentor and Partner National Laboratory: Marisa Monreal, Los Alamos National Laboratory

Mission Relevance of Research:

• Molten Salt Reactors (MSRs) amongst the Gen IV reactors being developed where the molten salt mixture can act as either coolant, fuel, or both
• Safeguard Challenges in MSRs:
  • Fuel in fuel salts not contained in assemblies and therefore not possible to perform traditional item accountancy
  • Online fuel reprocessing allows for fraction of salt to be removed while reactor operates
  • High temperature, radiation and corrosive environment introduces challenges for measurement techniques and instrumentation (operating temperatures 400°C-<800°C)
• Generation IV reactors improve safety, sustainability, efficiency, and cost
• Molten Salt Reactors (MSRs): molten chloride or fluoride salt mixture acts as either coolant, fuel, or both
• Fuel salt produces heat; coolant salt transports heat to power plant
• Safeguard Challenges in MSRs
  • Fuel in fuel salts not contained in assemblies and therefore not possible to perform traditional item counting and visual accountability of the salt
  • Online fuel reprocessing allows for fraction of salt to be removed while reactor operates
  • High temperature, radiation and corrosive environment introduces challenges for measurement techniques and instrumentation (operating temperatures 400°C to >800°C)

• No standardized method for elemental analysis of molten salts\textsuperscript{3,4} - see variability in reported values (Table 1) and no uncertainty
• Important for material accountancy and nonproliferation!

• Differing values of CrF$_3$ solubility reported by Oak Ridge National Laboratory Aircraft Nuclear Propulsion Project

• ORNL 1816 Report\textsuperscript{5}: \textbf{0.93(15) wt\% 600\degree C} and \textbf{3.9(3) wt\% 800\degree C}
• ORNL 2157 Report\textsuperscript{6}: \textbf{0.47(7) wt\% 600\degree C} and \textbf{7.5(1.3) wt\% 800\degree C}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
 & Cl & K & Ca & Sc & Ti & V & Cr & Mn & Fe & Co & Ni & Cu & Zn \\
\hline
GDMS Salt #1 & Matrix & 6.1 & 48 & < & 24 & < & 0.5 & 3.6 & 0.7 & < & 1 & 1.9 & < & 1 \\
 & #2 & & & & & & & 0.05 & & & & & & \\
\hline
GDMS Salt #2 & Matrix & 87 & 21 & < & 3.1 & < & 0.5 & 24 & 7.6 & 66 & 3.5 & 230 & < & 1 \\
 & #2 & & & & & & & 0.05 & & & & & & \\
\hline
ICPMS Salt #1 & Matrix & 81.4 & 43 & 62 & 0.05 & 4.56 & 0.94 & 6.5 & 0.01 & 7.49 & 0.02 & 0.08 & & \\
\hline
ICPMS Salt #2 & Matrix & 39.4 & 0.03 & 4.6 & 0.05 & 14.94 & 5.04 & 65 & 0.26 & 207 & 0.12 & 0.29 & & \\
\hline
\end{tabular}
\caption{Elemental analysis results showing discrepancy in Cr values\textsuperscript{3}}
\end{table}
1. Using elemental analysis and optical spectroscopy what is the solubility of CrF$_3$ and CrF$_2$ in FLiNaK and FLiBe?  
   a) Does the digestion method fully digest known amount Cr that is added to FLiNaK?  
   b) How does one sample the salts while molten?  
   c) Can we use UV-Vis to see oxidation states in the digest?  
   d) What is the uncertainty with sample prep and analysis?  

2. Apply to chloride fuel salts (collaboration with LANL)  
   a) Validate phase diagram for fuel ternary phase diagram  
   b) Determine corrosion product solubility in fuel salts and affect with U concentration content- what will happen to U  
   c) Use method for actinide solubility

Determining solubility and composition important for material accountancy and nonproliferation

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Elemental Analysis and Optical Spectroscopy: Method Development for molten salts

Step 1: Salt Sampling while molten

Step 2: Microwave Digestion

Step 3: ICP/UV-Vis Analysis
Elemental Analysis and Optical Spectroscopy: Method Development for molten salts

Step 1: Salt Sampling while molten

Step 2: Microwave Digestion

Step 3: ICP/UV-Vis Analysis

Figure 3: Pipette made from Cu straw and rubber bulb
Figure 4: Sampling the salt while molten
Figure 5: Salt sampled while molten after cooling
Elemental Analysis and Optical Spectroscopy: Method Development for molten salts

Step 1: Salt Sampling while molten

Step 2: Microwave Digestion

Step 3: ICP/UV-Vis Analysis

Get sample to aqueous solution with acid cocktail to analyze by ICP and UV-Vis

Figure 6: Microwave Digester in SALT lab at Berkeley

Figure 7: Microwave digestion vessels used
Elemental Analysis and Optical Spectroscopy: Method Development for molten salts

Step 1: Salt Sampling while molten

Step 2: Microwave Digestion

Step 3: ICP/UV-Vis Analysis

Figure 8: ICPOES at UC-Berkeley
Elemental Analysis and Optical Spectroscopy: 
Cr solubility in fuel and coolant salt

- Previously: ORNL Aircraft Nuclear Propulsion Reports demonstrate different CrF\(_3\) solubility values in FLiNaK
- New(er) literature:
  Yin et al\(^8\) reports a calculated solubility limit of CrF\(_3\) in FLiNaK of 0.3wt% at 600\(^\circ\)C and claims that this corresponds to values measured by ORNL. No experimental methods confirmed. H. L. Chan\(^9\) also supports this solubility limit

Method followed to investigate Cr solubility:
- Created a 8.8 wt% FLiNaK-CrF\(_3\) sample (higher than any value reported by ORNL)
- Raised to 850\(^\circ\)C and then lowered to 800\(^\circ\)C. Sampled with Cu straw exact temp: 799\(^\circ\)C. Transferred to glassy carbon crucible to cool
- Lowered to 600\(^\circ\)C. Sampled with Cu straw exact temperature at 596\(^\circ\)C. Transferred to glassy carbon crucible to cool
- After, samples were ground to uniform particle size using a mortar and pestle
- 8ml HNO\(_3\), 4ml HCl, and 3ml H\(_2\)O was added and digested
- Digestates removed and diluted to 35ml with DIH\(_2\)O
- Analyzed on UV-Vis


Preliminary Results- Pure Cr digestion

Table 2: CrF$_2$ and CrF$_3$ were digested and analyzed via ICPOES to verify full digestion

<table>
<thead>
<tr>
<th>Percent CrF$_2$ digested and detected by ICPOES</th>
<th>Percent CrF$_3$ digested and detected by ICPOES</th>
</tr>
</thead>
<tbody>
<tr>
<td>93(2)%</td>
<td>0.23(5)%</td>
</tr>
</tbody>
</table>

- Could see solid at the bottom of digestion tube after digestion
- No CrF$_3$ absorbance- like acids (matrix it is in)

Figure 9 (top): CrF$_2$ and CrF$_3$ digestates absorbance spectrum

Figure 10 (bottom): CrF$_2$ and CrF$_3$ digestates absorbance spectrum. The acid absorbance is removed numerically and result is plotted here
Preliminary Results - FLiNaK-CrF$_3$ sampled at 600°C and 800°C

- See higher absorbance peak for FLiNaK-CrF$_3$ sampled at 800°C
- Spike around ~400nm for FLiNaK containing samples

Absorbance peaks in FLiNaK-CrF$_3$ at ~406 and ~580nm which is similar to CrF$_2$ absorbance spectra
- Due to previous literature, expect to see disproportionation of creation of CrF$_2$
- UV-Vis spectra Figure 12 has the only FLiNaK scan manually subtracted from the FLiNaK-CrF$_3$ values to show what spectra should look like

Figure 11 (left): spectra of FLiNaK-CrF$_3$, FLiNaK, cuvette, and acid matrix
Figure 12 (middle): FLiNaK-CrF$_3$ spectra compared to CrF$_2$/3 spectra with matrix not numerically subtracted
Figure 13: (right): FLiNaK-CrF$_3$ compared to CrF$_2$ and CrF$_3$ spectra
Comparing to previous literature

- Previous literature reports molten FLiNaK-CrF_{2/3} spectras at (exact T not given).
- Two peaks observed in FLiNaK-CrF_{3} spectra similar to peaks observed in this experiment and in pure CrF_{2}—potential oxidation with nitric?
- Broad peaks observed in FLiNaK-CrF_{2} spectra.
- Our FLiNaK-CrF_{3} and CrF_{2} spectra has peaks similar to FLiNaK-CrF_{3} spectra reported by literature.

Figure 14 (left): absorbance spectra FLiNaK-CrF_{2/3} reported by previous literature. 

Figure 15 (top right) and Figure 16 (bottom right): observed absorbance spectra from FLiNaK-CrF_{3} created in this experiment measured at two different temperatures.

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Conclusions

- Higher absorbance peaks in FLiNaK-CrF$_3$ at ~406 and 580nm sampled at 800°C than 600°C - means more Cr?
- New hypothesis: CrF$_2$ was oxidized by nitric acid and created CrF$_3$ so CrF$_2$ spectra might be CrF$_3$ (aligns with literature) – need to test
- Characteristic FLiNaK peak spike starts at ~400nm to UV spectra

Future directions:
- Do ICP on the two FLiNaK-CrF$_3$ samples to confirm Cr content in each
- Obtain CrF$_2$ and CrF$_3$ spectra only digested in HCl
- Digest CrF$_3$ and obtain spectra
- Repeat experiment, but only use HCl as acid for digestion (no HNO$_3$)
The NSSC Experience

Collaborations:
- Conducted summer research at Los Alamos National Laboratory (2022)
- Conduct research every few months still at LANL with my mentor

NSSC Sponsored events:
- Presented at UPR (2022 poster, 2023 oral)
- Presented at NSSC Fall Workshop (2021, 2022)
- NSSC-LANL Keepin Nonproliferation Summer School (2022)
- American Chemical Society Fall Conference (2022 oral)
- Public Policy and Nuclear Threats Summer School (2023)
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