Quantification of molten salt components for nonproliferation and material accountancy purposes

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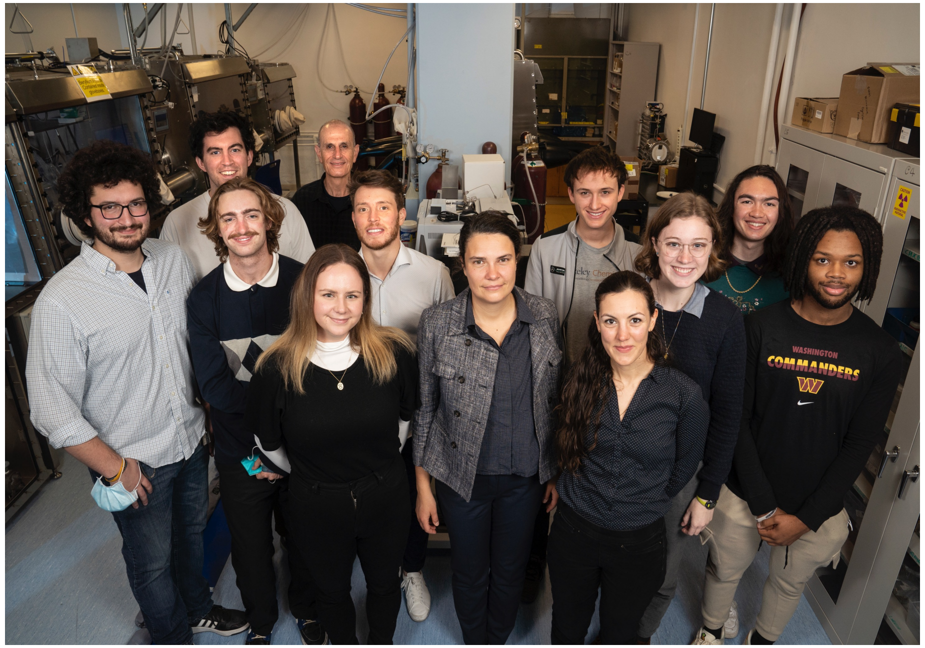
Introduction



Department and University: Nuclear Engineering at University of California Berkeley
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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)**

Background

- 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[2]
  - 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)

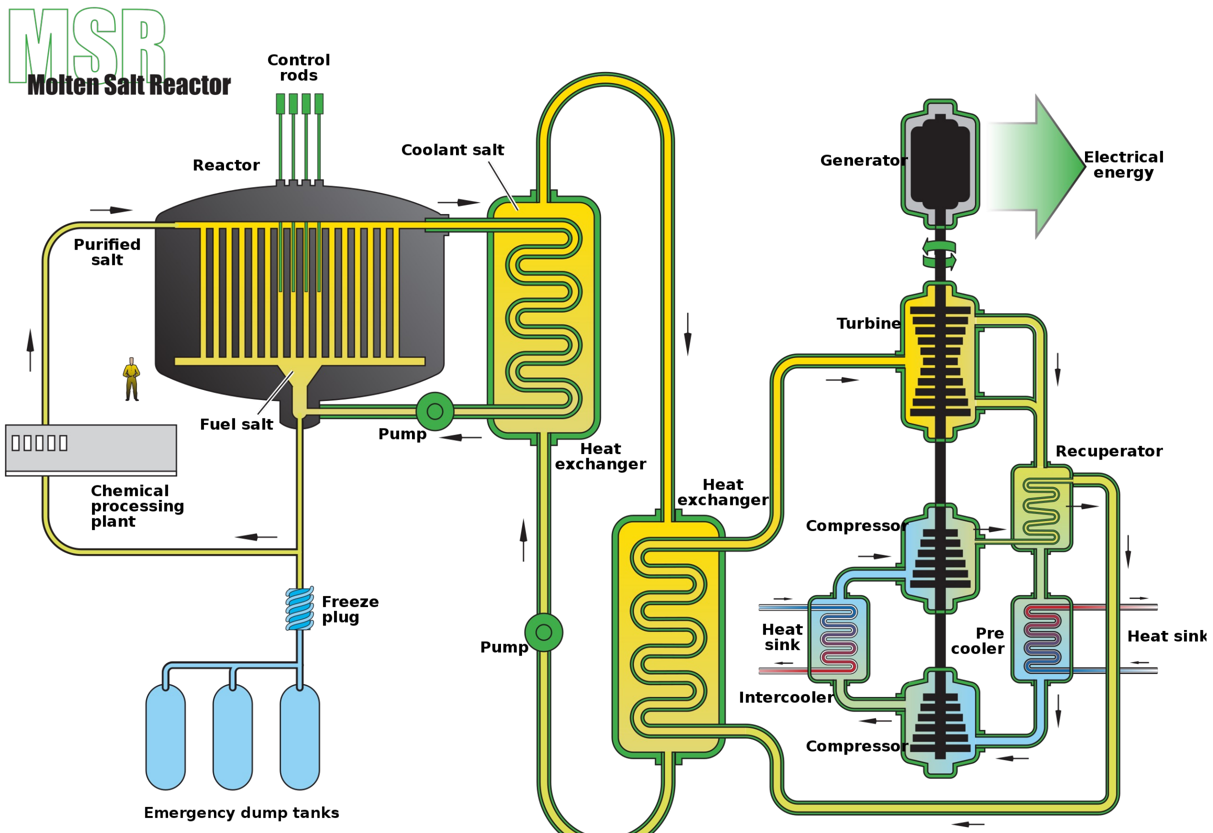

Figure 1: Molten salt reactor schematic[1]

[1]GIF-IV, A. (2002). Technology roadmap for generation IV nuclear energy systems. Technical report, GIF-002-00. US DOE Nuclear Energy Research Advisory Committee and the Generation IV International Forum
[2]Committee on Merits and Viability of Different Nuclear Fuel Cycles and Technology Options and the Waste Aspects of Advanced Nuclear Reactors et. al. Merits and Viability of Different Nuclear Fuel Cycles and Technology Options and the Waste Aspects of Advanced Nuclear Reactors. Washington, D.C.: National Academies Press, 2022. https://doi.org/10.17226/26500.

Previous Literature

- No standardized method for elemental analysis of molten salts[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[5]: **0.93(15) wt% 600°C and 3.9(3) wt% 800°C**
- ORNL 2157 Report[6]: **0.47(7) wt% 600°C and 7.5(1.3) wt% 800°C**

		Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
GDMS	Salt #1	6.1	Matrix	48	< 0.05	24	< 0.0[illegible]	3.6	0.7	1	< 1	1.9	< 1	< 1
	Salt #2	87	Matrix	21	< 0.05	3.1	< 0.0[illegible]	24	7.6	66	3.5	230	< 1	< 1
ICPMS	Salt #1	-	Matrix	81.4	0.43	62	0.01[illegible]	4.56	0.94	6.5	0.01	7.49	0.02	0.08
	Salt #2	-	Matrix	39.4	0.03	4.6	0.09[illegible]	14.94	5.04	65	0.26	207	0.12	0.29

Table 1: Elemental analysis results showing discrepancy in Cr values[3]

[3]Sulejmanovic, Dino, J. Matthew Kurley, Kevin Robb, and Stephen Raiman. "Validating Modern Methods for Impurity Analysis in Fluoride Salts." *Journal of Nuclear Materials* 553 (September 2021): 152972. https://doi.org/10.1016/j.jnucmat.2021.152972.
[4]Scott, Sean R., Francesco Carotti, Alan Kruizenga, Raluca O. Scarlat, Sara Mastromarino, and Martin M. Shafer. "Simultaneous Measurement of Lithium Isotope and Lithium/Beryllium Ratios in FLiBe Salts Using MC-ICP-MS." Journal of Analytical Atomic Spectrometry 37, no. 6 (2022): 1193–1202. https://doi.org/10.1039/D2JA00097K.
[5]J.D. Redman, C.F. Weaver, ORNL Report No. 1816, Oak Ridge, Tennessee, US, (1955).
[6]J.D. Redman, ORNL Report No. 2157, Oak Ridge, Tennessee, US, (1956).

Goals and Objectives

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

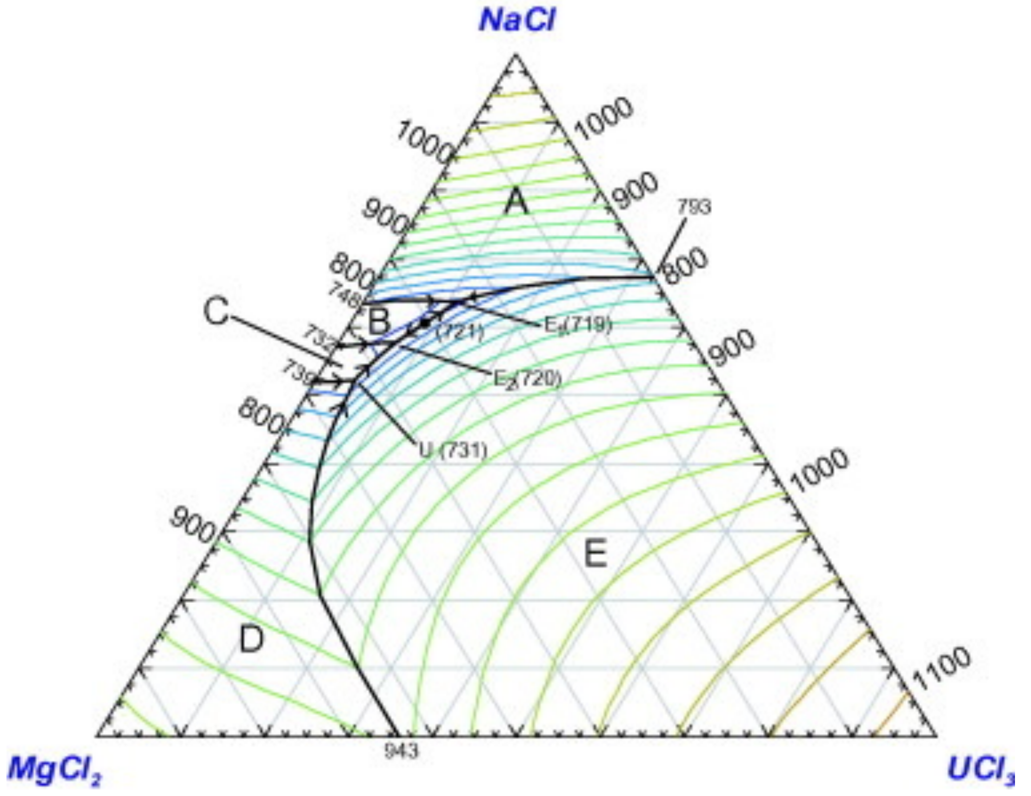

Figure 2: Modeled ternary phase diagram to validate experimentally[7]

Determining solubility and composition important for material accountancy and nonproliferation

[7] O. Beneš, R.J.M. Konings. Thermodynamic evaluation of the NaCl-MgCl2-UCl3-PuCl3 system. Journal of Nuclear Materials, 375 (2008), pp. 202-208, 10.1016/j.jnucmat.2008.01.007

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

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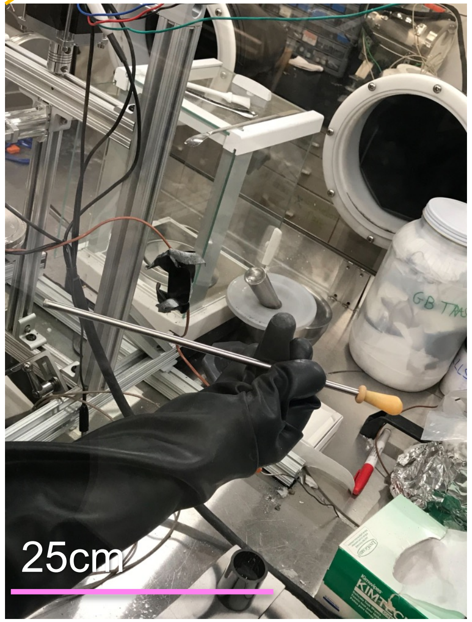


Figure 3: Pipette made from Cu straw and rubber bulb

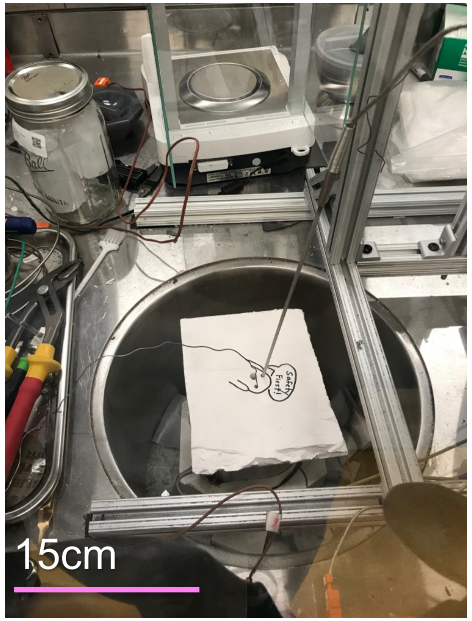


Figure 4: Sampling the salt while molten

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

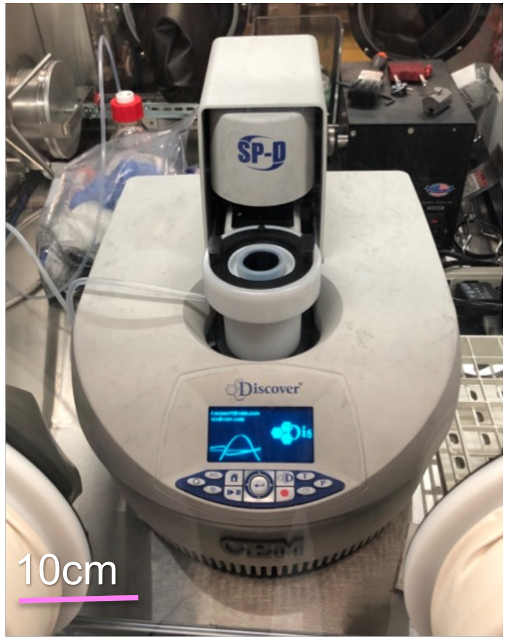


Figure 6: Microwave Digester in SALT lab at Berkeley

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

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

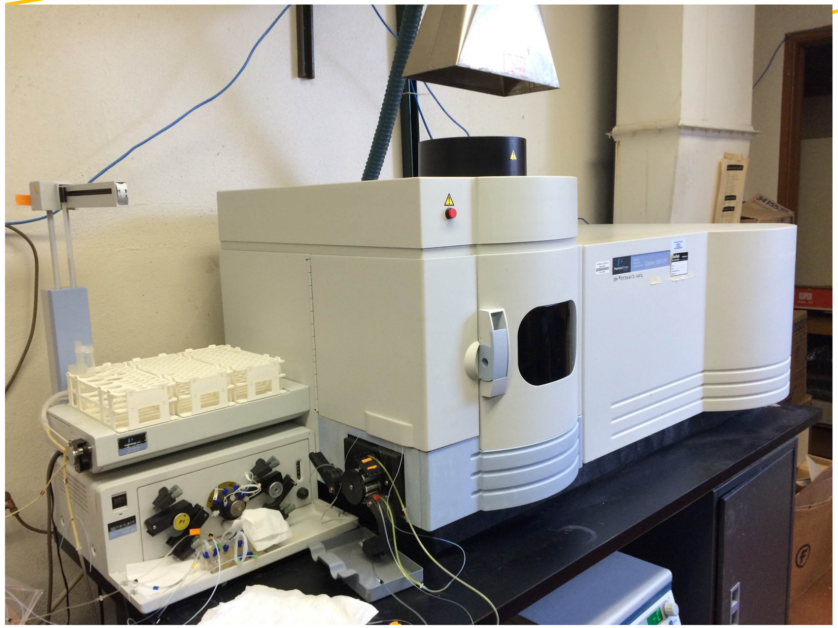


Figure 8: ICPOES at UC-Berkeley

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 600ºC** 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 850ºC and then lowered to 800ºC. Sampled with Cu straw exact temp: 799ºC. Transferred to glassy carbon crucible to cool
- Lowered to 600ºC. Sampled with Cu straw exact temperature at 596ºC. 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_2O was added and digested
- Digestates removed and diluted to 35ml with DIH_2O
- Analyzed on UV-Vis

[8]Yin, Huiqin, Peng Zhang, Xuehui An, Jinhui Cheng, Xiang Li, Shuang Wu, Xijun Wu, Wenguan Liu, and Leidong Xie. “Thermodynamic Modeling of LiF-NaF-KF-CrF3 System.” *Journal of Fluorine Chemistry* 209 (May 2018): 6–13. https://doi.org/10.1016/j.jfluchem.2018.02.005.

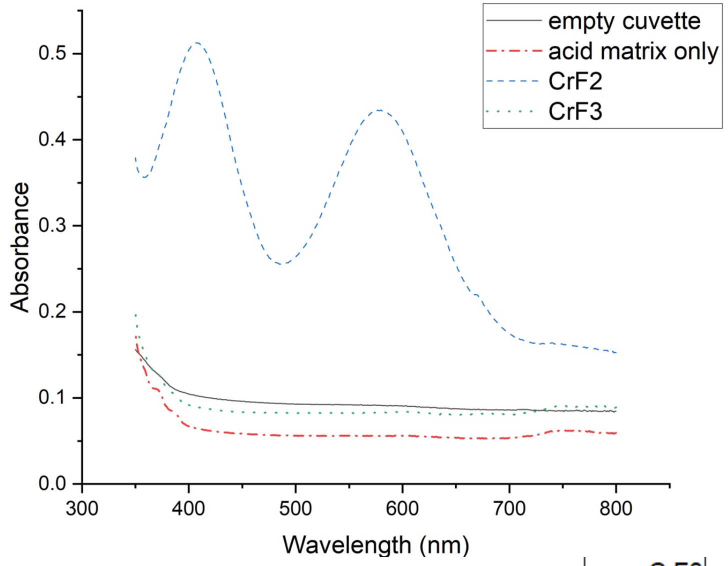
[9]Chan, Ho Lun, Elena Romanovskaia, Jie Qiu, Peter Hosemann, and John R. Scully. “Insights on the Corrosion Thermodynamics of Chromium in Molten LiF-NaF-KF Eutectic Salts.” Npj Materials Degradation 6, no. 1 (June 9, 2022): 46. https://doi.org/10.1038/s41529-022-00251-3.

Preliminary Results- Pure Cr digestion

Table 2: CrF_2 and CrF_3 were digested and analyzed via ICPOES to verify full digestion

Percent CrF_2 digested and detected by ICPOES	Percent CrF_3 digested and detected by ICPOES
93(2)%	0.23(5)%

- Could see solid at the bottom of digestion tube after digestion
- No CrF_3 absorbance- like acids (matrix it is in)



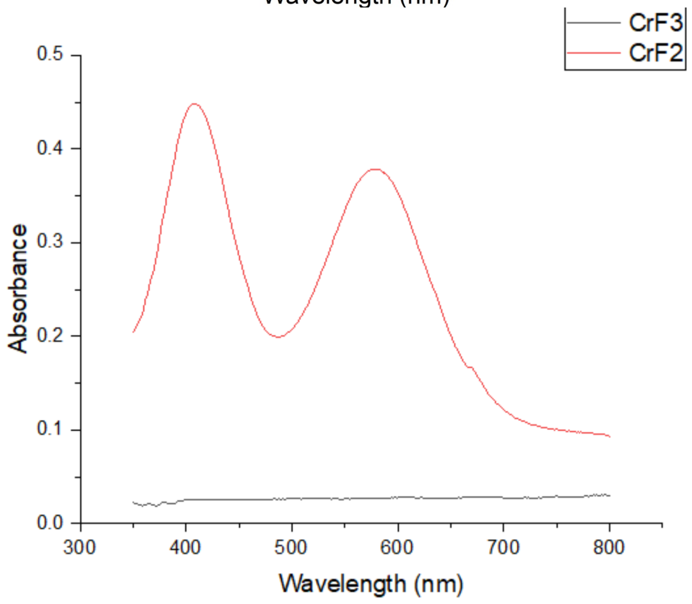


Figure 9 (top): CrF_2 and CrF_3 digestates absorbance spectrum

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

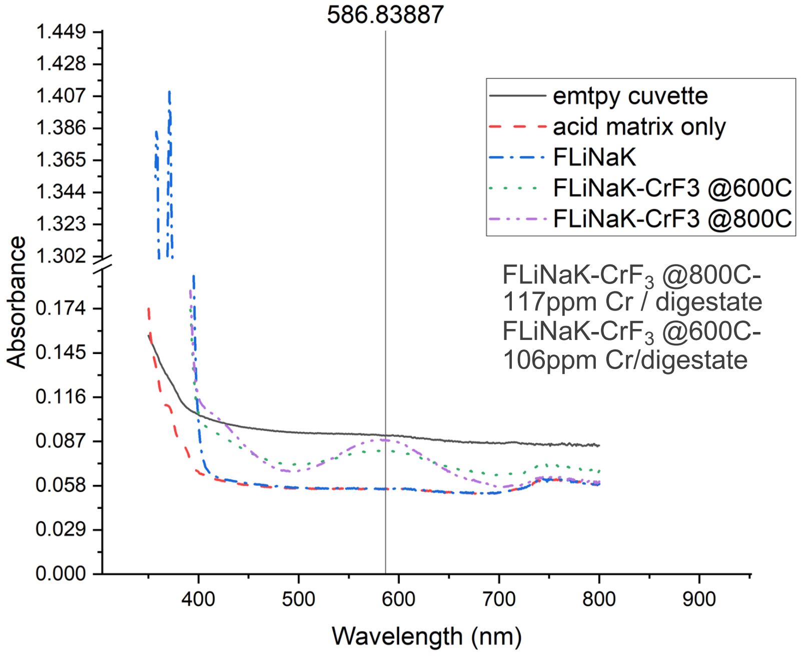


Figure 11 (left): spectra of FLiNaK-CrF_3, FLiNaK, cuvette, and acid matrix

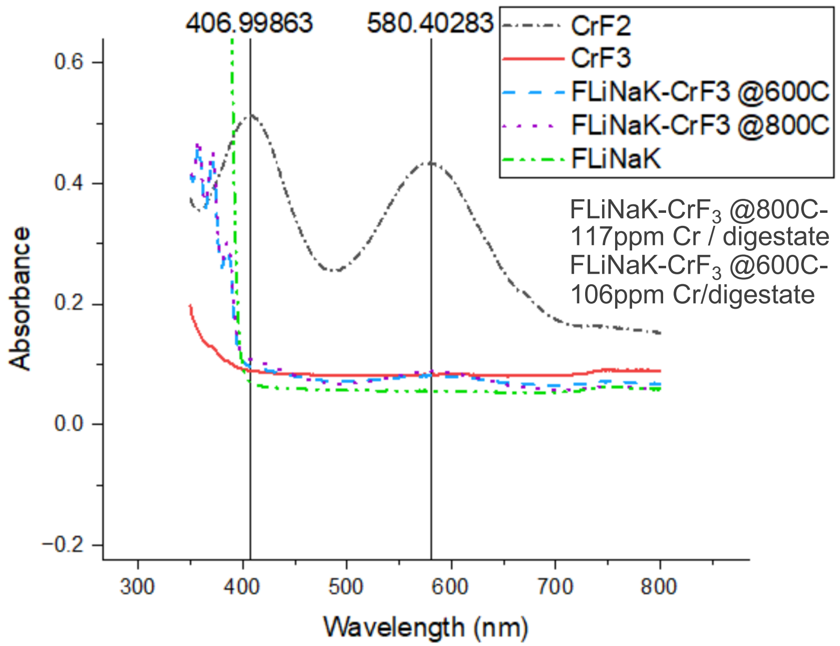


Figure 12 (middle): FLiNaK-CrF_3 spectras compared to CrF2/3 spectra with matrix not numerically subtracted

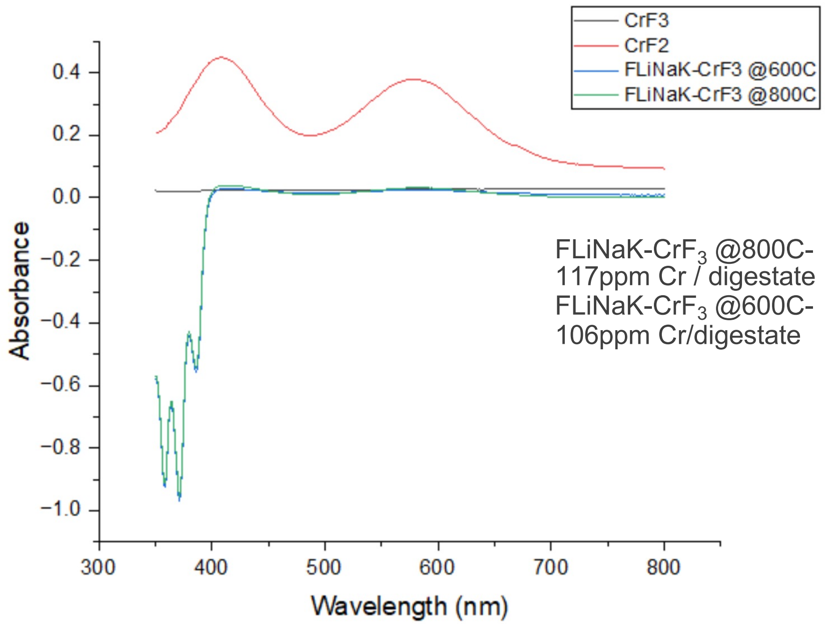


Figure 13: (right): FLiNaK-CrF3 compared to CrF2 and CrF3 spectra

- 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

Comparing to previous literature

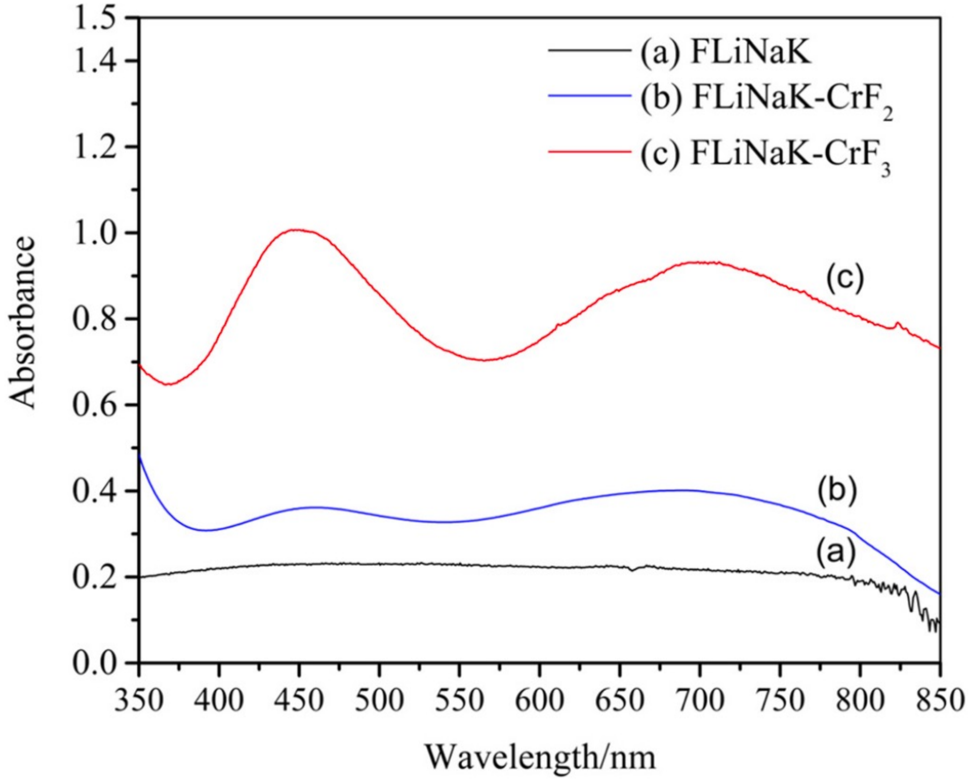
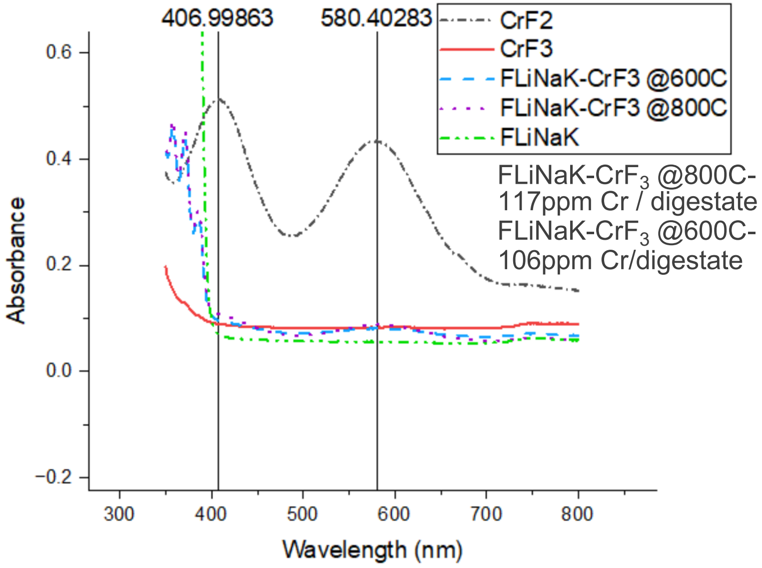
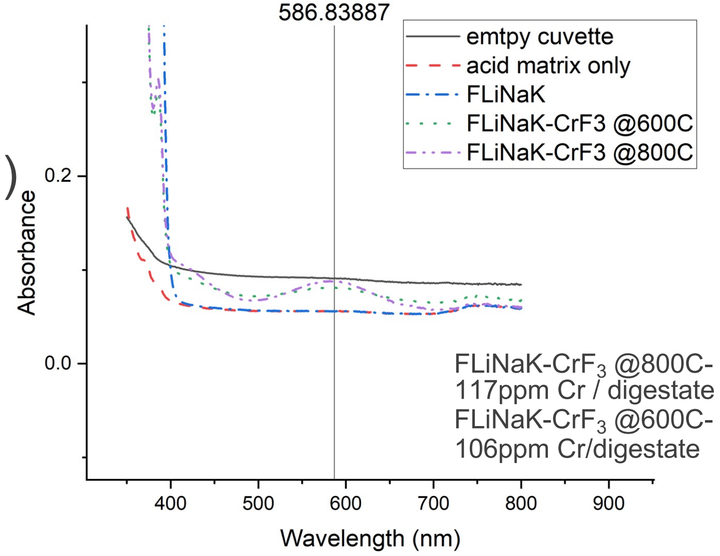


Figure 14 (left): absorbance spectra FLiNaK-$CrF_{2/3}$ reported by previous literature[10]

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





- 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

[10]Liu, Yiyang, Yulong Song, Hua Ai, Miao Shen, Hongtao Liu, Sufang Zhao, Yancheng Liu, Zejie Fei, Xiaobin Fu, and Jinhui Cheng. "Corrosion of Cr in Molten Salts with Different Fluoroacidity in the Presence of CrF3." Corrosion Science 169 (June 2020): 108636. https://doi.org/10.1016/j.corsci.2020.108636.

Conclusions and Future Directions

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)

Acknowledgements

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