Quantification of molten salt composition for molten salt reactors using elemental analysis and optical spectroscopy

Alexandra Kennedy[1], Sara Mastromarino[1], Raluca Scarlat[1], Marisa Monreal[2]

[1]University of California- Berkeley [2]Los Alamos National Laboratory

Nuclear Science & Security Consortium

Introduction

Molten Salt Reactors (MSRs) are a category of nuclear reactors that fall under the Generation IV class of nuclear reactor designs. MSRs utilize the thermal properties of molten salts allowing the reactors to operate under high temperature and low pressure. The molten salts used as coolant (FLiBe, FLiNaK, and NaCl) provide high efficiency and safety a level that all Generation IV reactors aim for. Some of these reactors, breeder MSRs, differ from many existing and pre-existing reactors as they are designed to be continuously refueled through liquid or pebble fuel and small size batches; this makes existing safeguards approaches difficult to use to adequately perform material accounting, let alone allow for the detection in a timely manner. Therefore, the development and deployment of advanced nuclear reactors and the advanced fuel cycle introduces challenges to detect, secure, dispose of nuclear and radiological material, and monitor the materials. Therefore, the research presented here addresses the safeguards in MSRs through optical spectroscopy and elemental analysis methods, specifically with the quantification of elements in both clean and corroded FLiNaK salt.

Elemental Analysis Digestion

The goals of the elemental analysis research is to identify the a digestion method to dissolve fluoride salt to identify main constituent concentrations. For the elemental analysis we use ICP-OES (Inductively coupled plasma - optical emission spectrometry). For ICP-OES the salts must be dissolved to a liquid. Three digestion methods are investigated on FLiNaK salt:

- The first digestion method is a two-part process developed by the microwave digester company, CEM, and uses a combination of 10ml of concentrated HNO_3, 1g H_3BO_3, 5ml of deionized H_2O, and 2ml of H_3PO_4. In this process, first HNO_3, H_3BO_3, and DI-H_2O are added to the FLiNaK sample and run on the microwave digester following the parameters outlined in Table 1 below. Once, the sample is run through the digester once, H_3PO_4 is added to the microwave vessel and run through the digester again following the same parameters in Table 1.

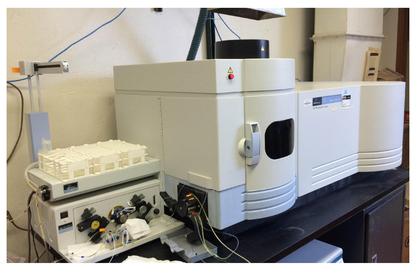
Table 1: CEM Microwave Digester Parameters

Temperature (ºC)	Ramp (min)	Hold (min)	Pressure (psi)	Power (W)	Stirring
210	5:00	5:00	400	300	Med

- The second digestion method also uses a two-part digestion procedure. This method utilizes 8ml of HNO_3 and 2ml of HCl to dissolve the solid sample. First, the 8ml of HNO_3 is added to the salt and run on the digester. Then, after the first digestion, HCl is added and the sample is run through the microwave digester again. Both digestions follow the parameters outlined in Table 1.
- The third digestion method uses only HNO_3 to dissolve the sample. 8ml of HNO_3 is added to the salt and run on the digester following the parameters in Table 1.

Total fluoride recovery and individual analyte concentration will demonstrate how much of the sample was digested when comparing the three digestion methods.

CEM Microwave Digester in the SALT Lab Glovebox



Perkin Elmer 5300 DV optical emission ICP with auto samples

Elemental Analysis Analysis

For the ICP-OES, a standard calibration curve is produced with a high, medium and low concentration standards containing all the elements (in Table 2). The aqueous digestates of the samples from all methods are diluted for their concentration to fall with in the standard range (in Table 3). The dilution factors range from 120 to 160. The diluted samples are then run on the ICP-OES at UC Berkeley. A calibration curves is produced for each ICP-OES run: two runs were performed for this study and two calibration curves are showed (Table 3).

Table 2: Standards used for elemental analysis by ICP-OES*

Standard	Elements in standard (mg/L)
Standard A	Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, In, K, La, Li, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, Re, Sc Se, Sm, Sr, Tb, Th, Tl, Tm, U, V, Y, Yb, Zn
Standard B	Ag, Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, Zr
Standard C	Au, Ir, Os, Pd, Pt, Rh, Ru

*standards obtained from High Purity Standards

Table 3: Sample calibration curve ranges

Standard	Highest Concentration Standard	Medium Concentration Standard	Lowest Concentration Standard
Standard A	1.2 (mg/L)	0.12 (mg/L)	0.0025 (mg/L)
Standard B	1.2 (mg/L)	0.11 (mg/L)	0.0024 (mg/L)
Standard C	1.2 (mg/L)	0.12 (mg/L)	0.0024 (mg/L)

After running on the ICP-OES and performing data analysis, the concentration of elements found in the two different FLiNaK samples are obtained. The results of the different FLiNaK digestions are shown in Table 4.

Table 4: Elements measured in FLiNaK

	FLiNaK (one digestion just HNO3)		FLiNaK (two digestions with HNO3 and HCl)		FLiNaK (two digestions with (HNO3, boric acid, H3PO4)	
	Conc (mg/kg)	Std dev %	Conc (mg/kg)	Std dev %	Conc (mg/kg)	Std dev %
Total fluorides	74.84%	19%	92.17%	1.7%	60%	0.1%
K	336164	12	359139	1.1	251291	6
Li	59589	10	88282	0.8	47666	3
Na	13817	12	31056	1.1	23810	1.2
Au	211	8	216	6.6		
Zr	101	7				
Be	33	10				
Cr					125	3
Ca					628	10
Ge					670	5

The results from the digestion methods are found in Table 4. Better recovery of main constitutes is observed after two digestions with two acids than just one. This gives preliminary data on the effectiveness of theses digestion methods.

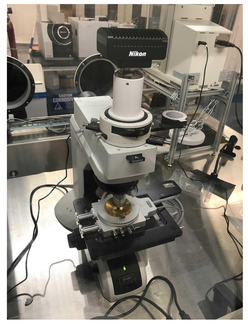
Further investigations and experimentation must be done in order to verify the CEM digestion methods such as verifying that the method given dissolves >90% of the FLiNaK. This data demonstrates preliminary data that uncovers a direction to take for molten salt elemental quantification.

Optical Spectroscopy

Optical spectroscopy analysis aims to use the color of the sample to understand what is in it, specifically, the determination of oxidation states in elements with the optical spectroscopy technique of UV-Vis. No experiments have taken place, but this section will highlight the capabilities that the SALT lab has procured and will utilize in the future.

The SALT lab has been working on testing with molten fluorides a high temperature optical cell from Linkam Scientific instruments that allows for high temperature optical and electrochemical experiments. Linkam built a custom cell called Linkam TS1000EV 17/3 with 4 BNC probes. This instrument will be used for quantification of elemental composition, specifically the quantification of relative concentration of metal species in different oxidation states (e.g. U3+ vs U4+, Cr2+ vs Cr3+).

This quarter, the SALT lab has specified and procured a Cary 60 UV-Vis that is compatible with the Linkam stage which will allow for in situ optical spectroscopy analysis of molten salts. Additionally, the use of the Raman Instrument at LBNL xwill use the Linkam stage to obtain more optical measurements.



Left: Linkam Stage for high-temperature optical spectrocopy on optical microscope in SALT lab glovebox

Top: Cary 60 UV-Vis Spectrophotometer (to be delivered April 2022).

Conclusions and Future Directions

In conclusion, the research done is used to quantify elemental compositions and the oxidation states of solutes in the molten salt samples. There digestion methods for elemental analysis were tested: first, a mixture of nitric acid, boric acid, phosphoric acid, and water; second, a mixture of nitric and hydrochloric acid; third only nitric acid to digest the salt sample. Further investigations are required to quantify uncertainty in elemental analysis due to salt sampling, digestion and ICP-OES sample analysis. Preliminary ICP-OES results reported here demonstrate sensitivity of results to digestion protocol. Optical spectroscopy through UV-Vis is another method that is being developed to further quantify elements in molten salts with the help of a high temperature optical cell. UV-Vis analysis will allow for quantification of the solutes in molten salt, and in-situ identification of their oxidation state.

Future directions are aimed towards the quantification of actinides through elemental analysis and optical spectroscopy. Specifically, developing a method to quantify elements through optical spectroscopy is a near future goal. After, another future direction is the quantification of actinide elements in fluoride and chloride salts, as actinide verification is an imperative contribution to the NSSC mission of safeguards and nonproliferation.

Acknowledgements

I would like to acknowledge and thank the support shown from the UC Berkeley SALT laboratory group. I would also like to thank Dr. Wenbo Yang for his training on the ICP-OES and undergraduate Reese Carlton for his code to process the elemental analysis ICP-OES data.

THE SALT RESEARCH GROUP
Berkeley UNIVERSITY OF CALIFORNIA Nuclear Engineering

This material is based upon work supported in part by the Department of Energy National Nuclear Security Administration through the Nuclear Science and Security Consortium under Award Number DE-NA0003996.

National Nuclear Security Administration