



Optical techniques for advanced salt systems

Prepared for
US Department of Energy

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Pacific Northwest National Laboratory

September 2024
PNNL-36705

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for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

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SUMMARY

Molten salt reactors are receiving significant interest worldwide as a Gen IV nuclear reactor design that can safely and efficiently deliver reliable green energy. However, the means by which material will be accounted for within these systems still needs to be determined. This report covers recent advancements in the exploration of optical spectroscopy for the use in online monitoring of molten salts. Online monitoring tools can provide in situ and real-time insight into process conditions. Utilizing optical tools such as ultraviolet-visible (UV-Vis) absorbance and Raman spectroscopy can provide highly detailed information on the chemical composition, not only quantifying analytes such as uranium (U) or plutonium (Pu) but determining oxidation states and speciation. While traditionally this type of information has been less valuable to material control and accounting than the isotopic information gained from radiometric techniques, within molten salt systems, the added insight into chemistry is essential. Potential inhomogeneities as well as operational trends can provide necessary information to better understand how to accurately account for nuclear materials.

Work accomplished in fiscal year (FY) 24 built upon previous advancements by pushing forward online monitoring capabilities in two key areas: improving the small-scale salt characterization system to better approximate materials/behaviors anticipated in deployed sensors and expanding demonstration of applications to Pu bearing salts. These will be discussed in detail here, but it is worth emphasizing the importance of the Pu characterization work. Obtaining Pu materials, processing them to be in the correct chemical state for addition into salts, and then completing work at even a small-scale with Pu in a molten salt are major accomplishments. Not only did these efforts provide valuable insight into system needs for monitoring Pu, but they were invaluable opportunities in building capability and awareness for the safe handling and processing of Pu to support any future endeavors on characterizing molten salts containing transuranics (TRU).

The next needed steps to fully understand the potential role of UV-Vis and Raman-based online monitoring for material control and accounting include expanding optical collection into the near infrared (NIR) which could provide a unique avenue to resolve optical fingerprints of target species whose concentrations extend beyond the linear range into the UV-Vis range. This will involve the investigation of more robust optical materials and testing of TRU chemical targets in the presence of mixed analyte media in order to calculate uncertainty of target quantification.

This report meets milestone M3RS-24PN0401063: "Support Advancement of Optical Sensor Testing."

CONTENTS

SUMMARY	4
CONTENTS	5
FIGURES	6
ACRONYMS AND ABBREVIATIONS	7
1. INTRODUCTION	1
2. Chemical Materials and Preparation.....	2
2.1. Reagents and Materials	2
2.2. Inert Box Setup	2
2.3. Plutonium Chloride Synthesis and Handling	2
3. ADVANCING THE SMALL SCALE SETUP	3
4. RESULTS AND DISCUSSION	5
4.1. Testing of new optical cell	5
4.2. Proof of concept testing of Pu in molten chloride	7
5. CONCLUSION AND RECOMMENDATIONS	9
5. ACKNOWLEDGMENTS	11
6. REFERENCES	12

FIGURES

Figure 2-1. Photographs of Pu synthesis.	3
Figure 3-1. (A) Schematic of small-scale furnace system showing vessel inside a clam-shell furnace with both Raman and UV-Vis optics connected via fiber optics to the spectroscopic instruments. (B) Photograph of updated small-scale sample holder.	4
Figure 3-2. Photograph of optically transparent sapphire cell.	5
Figure 4-1. U and Nd in LiCl-KCl at 550 °C in a sapphire cell. Photographs of (A) Empty cell at room temperature. (B) LiCl-KCl; (C) 0.301 wt% U(III); (D) 0.198 wt% U and 0.036 wt% Nd immediately after Nd addition; (E) 0.198 wt% U and 0.036 wt% Nd ~24 hours after (D); (F) 0.174 wt% U(III), 0.136 wt% Nd(III).	6
Figure 4-2. Absorbance of U and Nd in LiCl-KCl at 550 °C in a sapphire cuvette.	7
Figure 4-3. 0.75 wt% Pu in NaCl-MgCl ₂ collected at 550 °C. Photographs of (A) optical cell containing solid sample and (B) Pu in molten NaCl-MgCl ₂ at 550 °C. (C) optical fingerprint of Pu(III) in NaCl-MgCl ₂	8
Figure 4-4. Pu with added analytes in NaCl-MgCl ₂ , 550 °C.	8

ACRONYMS AND ABBREVIATIONS

ARDP	Advanced Reactor Demonstration Program
ARSS	Advanced reactor safeguards and security
DOE	US Department of Energy
FY	fiscal year
GAIN	Gateway for Accelerated Innovation in Nuclear
IP	intellectual property
LOD	limit of detection
MC&A	material control and accounting
MSR	molten salt reactor
NIR	near infrared
NTD	national technical director
PNNL	Pacific Northwest National Laboratory
Pu	plutonium
TRU	transuranics
UV-Vis	ultraviolet-visible
U	uranium

1. INTRODUCTION

MSRs represent a key opportunity to efficiently meet growing green energy needs. As one of the key advanced reactor designs within the United States, designs proposed by various vendors have received media attention and financial support from the Department of Energy (DOE) and through Advanced Reactor Demonstration Program (ARDP) and Gateway for Accelerated Innovation in Nuclear (GAIN) awards. Numerous technological advancements and demonstrations/deployments are currently being completed. Focusing on the liquid fuel reactors, it is important to note that each design represents a major change in how radioactive inventory is spread throughout a facility. This can be further complicated by designs that include online refueling, processing, or salt clean up. Overall, traditional material control and accounting (MC&A) approaches used for light water reactors may be difficult to translate to MSR systems.

Online monitoring may offer a key opportunity to follow these more complex molten salt systems. This not only enables highly representative in situ characterization but can provide the unique benefit of continuous monitoring as compared to the discreet and infrequent MC&A completed via grab sample analysis (e.g. inductively couple plasma analysis, mass spectrometry, etc.). Furthermore, careful monitoring of system design may also offer a method to catch precipitation or precursors to precipitation that may otherwise impact accurate MC&A. The challenge here is converting monitoring technology for the application to the molten salt systems since the temperatures and corrosive environments of MSRs challenge many current system designs.

Fortunately, several technologies can provide highly useful MC&A information and can be adapted to the molten salt environment. A technology of interest here is optical spectroscopy, which can provide unparalleled insight into chemical speciation, redox states, and concentrations in molten salt systems.¹⁻⁷ This information can be highly valuable in accurately accounting for actinides that display complex chemistry under molten salt conditions. Furthermore, optical monitoring approaches can be combined with advanced analysis techniques such as chemometric modeling for the real-time and accurate analysis of optical data.⁸⁻¹⁴ However, transitioning these technologies to molten salt systems requires key technology advances, which were identified and outlined in previous reports,¹⁴⁻¹⁶ including a roadmap released by this campaign.

Project work in FY24 was focused on preparing optical techniques for transition to and demonstrations on real industry salt loops. This included developing materials for small-scale laboratory testing as models for scaling up sensor performance for extended monitoring in an industry scale environment. This will allow for more advanced testing of configurations that are representative of real deployment conditions. Work also includes exploring more complex chemical systems that include TRU targets, e.g., Pu.

2. Chemical Materials and Preparation

2.1. Reagents and Materials

Plutonium chloride was synthesized in-house as described in Section 2.3. Uranium (III) chloride and NaCl-MgCl₂ salts were acquired from TerraPower. Lithium chloride (Sigma Aldrich, 99.998%), potassium chloride (Sigma Aldrich, 99.999%), magnesium chloride (Alfa Aesar, 99.99%), and neodymium (III) chloride (Thermo Scientific, 99.9%) were purchased and used without further purification. Cobalt (II) chloride (Sigma Aldrich, 98%) was heated in a vacuum oven at >150 °C for ≥3 days in order to drive off water before being immediately placed in an inert atmosphere glovebox.

2.2. Inert Box Setup

All molten salt experiments were conducted in an inert atmosphere glovebox. The atmosphere in the glovebox is maintained at <0.2 ppm O₂ and <5 ppm moisture. The box pressure is maintained at -1.1" w.c. (water column). The inert atmosphere was provided by ultra-high purity argon. Sample holders were thoroughly acid cleaned and dried at >150 °C prior to being placed into the glovebox.

A fairly unique aspect of this inert glove box is that it is approved as safety significant to allow for the safe handling of fissionable materials as well as handling high temperature systems such as molten salts. This is a powerful and highly valuable capability that was leveraged under this work to allow for characterization of molten salts containing Pu.

2.3. Plutonium Chloride Synthesis and Handling

Evaluation of the ability of optical monitoring tools to provide information on Pu within a molten salt was a key piece of FY24 efforts. Though an important component of MSR fuel, plutonium chloride is less studied due to safeguards and critically concerns and scarcity. Gaining access to Pu samples, processing them to be in the proper chemical form for addition to the molten salt, and then completing molten salt experiments requires a significant effort. This section will provide insight into this aspect of FY24 efforts.

The Pu sample was provided by collaborating teams at Pacific Northwest National Laboratory (PNNL). The Pu sample was obtained as a Pu(IV/VI) mixture in nitric acid and required purification and processing to produce the PuCl₄ that would be added into the molten salt matrixes (Figure 2-1). The sample was treated with hydrogen peroxide and sodium nitrite to convert all of the Pu to Pu (IV) (Figure 2-1A). The Pu sample, a dark green solution, was then loaded onto a 4 mL ion exchange (IX) column (Bio-Rad AG 1-X8 resin, 100 – 200 mesh) (Figure 2-1B) until the green band (indicating Pu) filled ~1 inch above the column bottom. The Pu was then stripped from the IX column with 2 M hydrochloric acid (HCl) until the green band was no longer observed on the column. Stripping with HCl took ~5 bed volumes, resulting in a reddish-brown solution (Figure 2-1C), indicating conversion to the plutonium chloride form.

Following elution with HCl, the plutonium chloride sample was reduced in volume over slight heating then reconstituted with sodium hydroxide, forming a fluffy green $\text{Pu}(\text{OH})_4$ precipitate (Figure 2-1D). The clear, colorless supernatant was decanted, The remaining $\text{Pu}(\text{OH})_4$ was rinsed with de-ionized water, then redissolved in 10 M HCl (Figure 2-1E), resulting in a clear, red solution. UV-Vis spectroscopy was used to estimate oxidation state at ~95% Pu (IV).¹⁷

Solid plutonium chloride was recovered by coprecipitation with sodium chloride (NaCl). NaCl was chosen to easily incorporate the recovered solid into the NaCl- MgCl_2 eutectic chosen for optical studies this FY. The plutonium chloride solution was evaporated down to dryness over gentle heating. Precipitation occurred in stages, as observed in Figure 2-1F. The lighter brown solids consist primarily of NaCl salt, and the darker brown solids consist mostly of PuCl_4 . The solids were separated and recovered by color intensity in order to subaliquot small amounts for analysis requested by collaborators that provided the Pu (Figure 2-1G). The remaining solids were ground into a homogeneous mixture, then submitted for gamma energy analysis, confirming a mass concentration of 3.33 wt% Pu in NaCl. Spectroscopic analysis of the heterogenous mixture confirmed 80 – 85% PuCl_4 and 15 – 20% PuCl_3 . The formation of PuCl_3 is likely due to alpha radiolysis.¹⁸

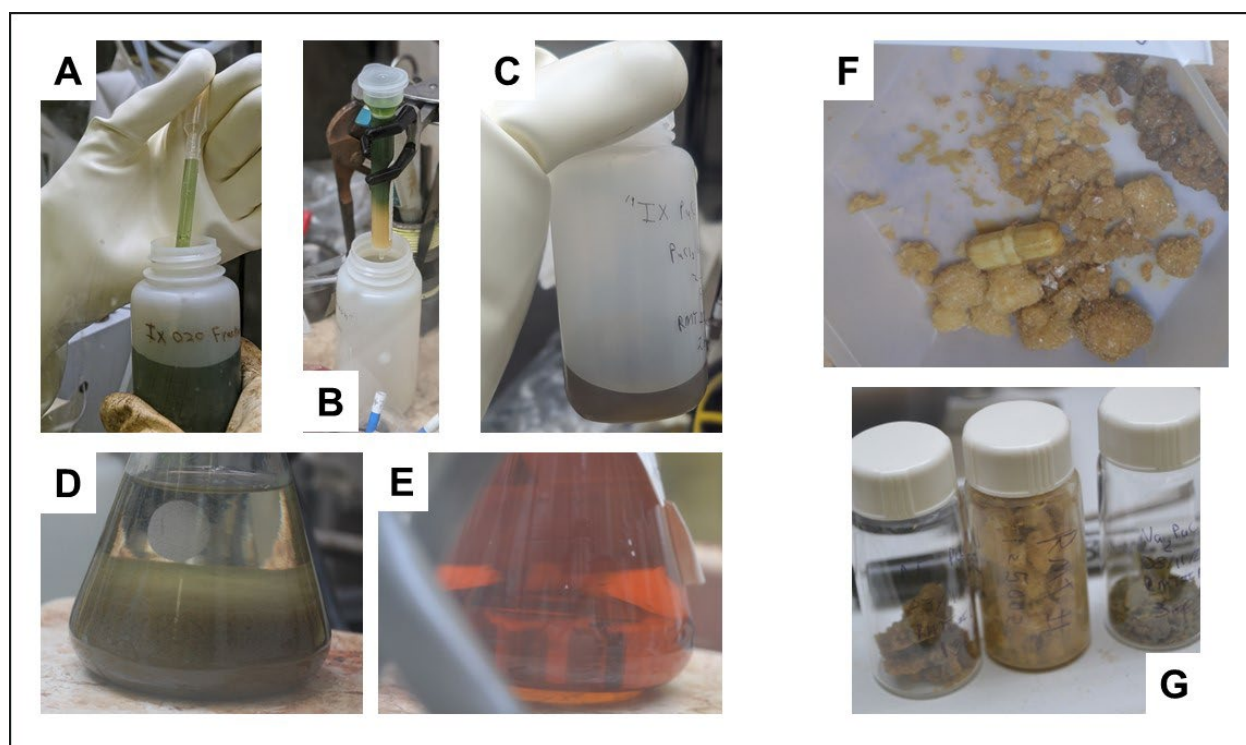


Figure 2-1. Photographs of Pu synthesis.

3. ADVANCING THE SMALL-SCALE SETUP

PNNL originally developed a unique, small-scale system for characterizing the optical fingerprints of molten salts several years ago.^{1, 19} This system was later advanced to

include Raman spectroscopy in support of efforts under the Advanced reactor safeguards and security (ARSS) and related campaigns. However, the system was not ideal or optimized for applications to the various chemical systems of the greatest interest to MC&A and did not provide an avenue to explore fingerprints using the optical materials most likely to be deployed as probes in larger-scale molten salt systems. This section covers the advancements made to the small-scale system to address these limitations.

A small-scale furnace system was utilized for this work. The system was based on preexisting setups³ and modified to allow for better temperature and optical control. Figure 3-1 shows a schematic of the furnace system. The system is designed to hold an optically transparent sample holder (cuvette). In this design, the sample holder has a very long neck to provide a cold finger in order to prevent the molten salt from creeping out of the vessel. Both Raman and UV-Vis spectroscopy can be measured simultaneously.

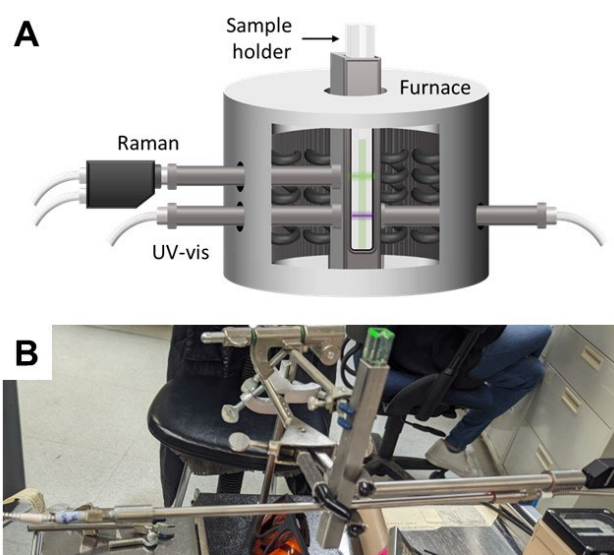


Figure 3-1. (A) Schematic of small-scale furnace system showing vessel inside a clam-shell furnace with both Raman and UV-Vis optics connected via fiber optics to the spectroscopic instruments. (B) Photograph of updated small-scale sample holder.

Raman and UV-Vis spectroscopic instruments were acquired from Spectra Solutions Inc., and each utilized a high throughput volume phase holographic grating spectrograph with a thermoelectrically-cooled two-dimensional charge-coupled device detector. The UV-Vis instrument had a functional wavelength range of approximately 450 – 850 nm. The Raman instrument utilized a 532 nm excitation laser with a fiber optic Raman probe with a backscattering (180°) optical design. The wavenumber axis was calibrated using naphthalene and the resolution was $<5\text{ cm}^{-1}$. The wavenumber range is 140 – 4500 cm^{-1} .

One of the goals for FY24 was to work with a manufacturer to develop a prototype optical cell made of robust optical material. This year, the PNNL team procured and tested a sapphire cuvette (Figure 3-2) for small-scale optical spectroscopy. Further details for the testing of this optical cell are discussed in Section 4.1.



Figure 3-2. Photograph of optically transparent sapphire cell.

4. RESULTS AND DISCUSSION

4.1. Testing of new optical cell

For optical spectroscopy to support MC&A within MSRs, the ability to interrogate the molten salt media holds significant importance to long-lived monitoring of these complex chemical systems. The standard window for optical spectroscopic interrogation is fused silica. This material has shown to lose integrity over time when exposed to harsh conditions, such as that of molten salts. Optical ceramics have a lot of features that make them good candidates for interrogation of molten salts, such as high hardness, chemical (corrosion) resistance, wide transmission spectrum, and low thermal expansion.²⁰⁻²⁴ Among the optical ceramics, alumina oxide (sapphire) stands out as the most promising candidate for molten salt interrogation. Some challenges that have been identified in the literature are the ability to integrate sapphire windows into configurations that vendors need to allow for optical interrogation of harsh environment equipment.^{25, 26} Given the challenges of working sapphire into unique configurations, many manufacturers use organic adhesives to build custom sapphire cells, which will not hold a seal when exposed to harsh molten salt environments.

One of the goals for FY24 was to work with a vendor to explore pathways for unique sapphire window configurations that could withstand these environments. The prototype optical cell received was composed of bonded sapphire plates (bonding technique is proprietary to vendor) with a small area of the plates being polished for optical transparency. The inner dimensions of the cell are 2 × 10 mm at the polished section and 10 × 10 mm at the non-frosted section.

Initial testing of the cell focused on leak testing under molten salt conditions. The cell showed some residue on the inside and outside of the optically transparent portion of the

cell (Figure 4-1A) and persisted after acid cleaning and drying in the lab. The cell was brought into the glovebox and exposed to a molten LiCl-KCl (Figure 4-1B). Some initial cracking was observed at the bottom of the cell and darkening of the adhesive was observed around the bonded seals. After about 12 hours when no leaking was observed, 0.301 wt% U(III) was added, showing its characteristic dark red color (Figure 4-1C). The concentration of U(III) was decreased to 0.198 wt% with LiCl-KCl and 0.036 wt% Nd(III) was added to the cell (Figure 4-1D). Immediately after adding Nd(III) to the cell, some precipitates were observed in the melt media. The cell was left to equilibrate for about 24 hours and the dark red color characteristic with U(III) has significantly decreased in intensity (Figure 4-1E). More Nd(III) was added – final content: 0.174 wt% U(III), 0.136 wt% Nd(III) – and left to equilibrate. After another 24 hours, the melt media is nearly colorless.

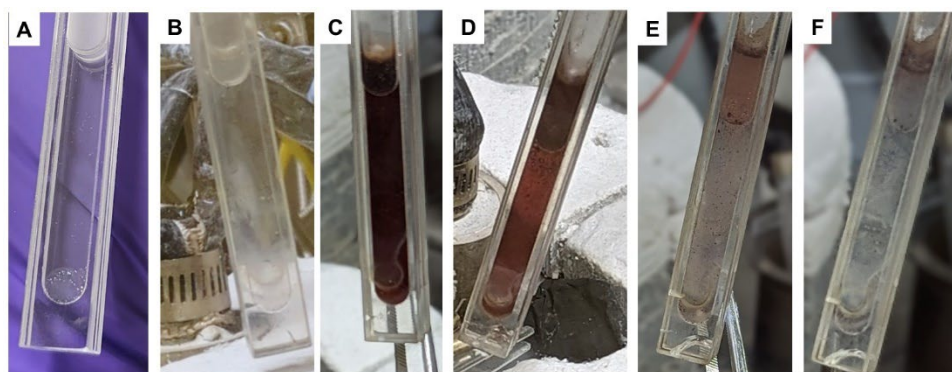


Figure 4-1. U and Nd in LiCl-KCl at 550 °C in a sapphire cell. Photographs of (A) Empty cell at room temperature. (B) LiCl-KCl; (C) 0.301 wt% U(III); (D) 0.198 wt% U and 0.036 wt% Nd immediately after Nd addition; (E) 0.198 wt% U and 0.036 wt% Nd ~24 hours after (D); (F) 0.174 wt% U(III), 0.136 wt% Nd(III).

One possibility for the depletion of U(III) is that the addition of Nd(III) could be carrying some other contaminant within the carrier salt (e.g., water, oxide, hydroxide, etc.) that interacts with U(III) causing the oxidation to U(IV). It is worth noting that the Nd(III) reagent was received from the manufacturer at 99.9% purity and used without further purification. This is supported by the reduction in absorbance intensity observed for U(III) (Figure 4-2). U(III) has a very high molar extinction coefficient at its max absorbance.²⁷ One of the challenges identified during this experiment was the transmission wavelength range of the light source with the spectrometer available for this measurement. Presence of U(III) is observed qualitatively by the near saturation of the detector. As the amount of U(III) is depleted after addition of Nd(III), the overall light absorbance decreases, and an optical fingerprint characteristic of N(III) is observed at 590 nm.²⁸ A small shoulder also appears around 670 nm that is consistent with U(IV)²⁷, which could be reasonably inferred given that the molar extinction coefficient of U(IV) is a factor of ten less than that of U(III) (Figure 4-2).

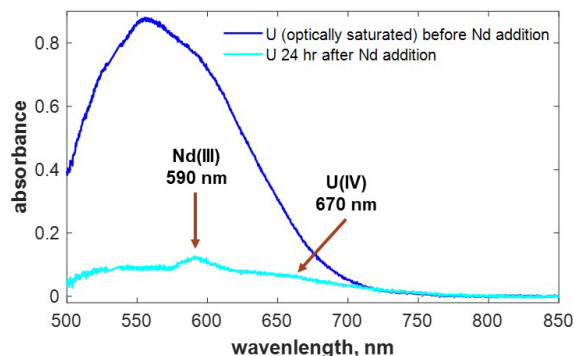


Figure 4-2. Absorbance of U and Nd in LiCl-KCl at 550 °C in a sapphire cuvette.

The results of this testing show the robustness of this optical cell when containing a molten chloride after ~100 hours. These testing results were also shared the manufacturer which led to discussions about a new iteration of this cell, which is expected to arrive in FY25. This demonstration also sets a good precedence for testing in more high-risk molten chloride media (e.g., Pu) as well as initial testing in molten fluoride. The testing of this cell provides insight for vendors to explore the machinability of sapphire for other configurations, such as windows or fibers for robust, long-lived optical interrogation of MSR process streams.

4.2. Proof of concept testing of Pu in molten chloride

In addition to the materials synthesis required to prepare Pu for molten salt testing, significant work was required to prepare the inert atmosphere glovebox to handle and accept safety significant amounts of Pu. Laboratory protocols, and technical working documents were generated, approved, and utilized for all work involving Pu. This allowed the team to effectively and safely work with Pu while ensuring any collaborating teams sharing lab space understood neighboring hazards and how to appropriately interact with them. This initial development of the safety approach is highly valuable because it can be translated to other transuranic systems under future work and efforts. Because of criticality safety constraints with the inert atmosphere glovebox, the plutonium chloride was synthesized in a negative glovebox then transferred in smaller quantities to the inert atmosphere glovebox.

The proof-of-concept demonstration of Pu in molten chloride is shown in Figure 4-2. The Pu was prepared in a fused silica optical cell with NaCl-MgCl₂. In order to accommodate the correct molar ratio needed for the NaCl-MgCl₂ eutectic, additional MgCl₂ was added to accommodate the NaCl present in the plutonium chloride sample (Figure 4-2A). A photograph of the melted sample is shown in Figure 4-2B. The max absorbance is observed at 568 nm, with minor peaks at 604 nm, 672 nm, and 798 nm (Figure 4-2C). These signatures are very consistent with what is reported for Pu(III) in LiCl-KCl²⁹ and similar to what is shown for Pu(III) in molten NaCl-CsCl^{30, 31} and a molten fluoride.³²

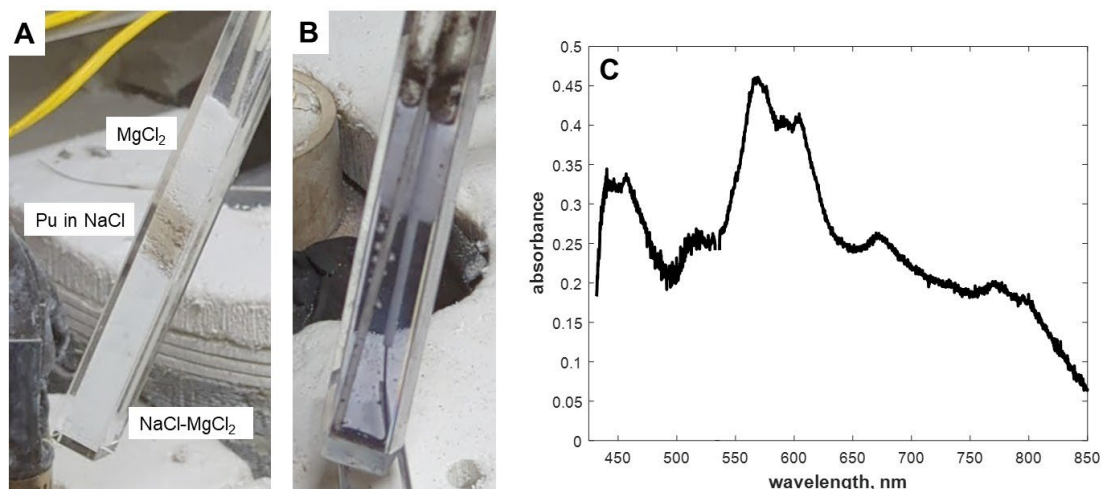


Figure 4-3. 0.75 wt% Pu in $NaCl-MgCl_2$ collected at $550\text{ }^\circ C$. Photographs of (A) optical cell containing solid sample and (B) Pu in molten $NaCl-MgCl_2$ at $550\text{ }^\circ C$. (C) optical fingerprint of $Pu(III)$ in $NaCl-MgCl_2$.

The same Pu sample was saved and recovered for initial testing to measure Pu in the presence of mixed analytes, including $U(III)$, $Nd(III)$, and $Co(II)$. Some challenges were observed almost immediately, namely the presence of precipitates distributed throughout the sample upon addition of $U(III)$ to the Pu sample, making collection of optical spectra difficult.

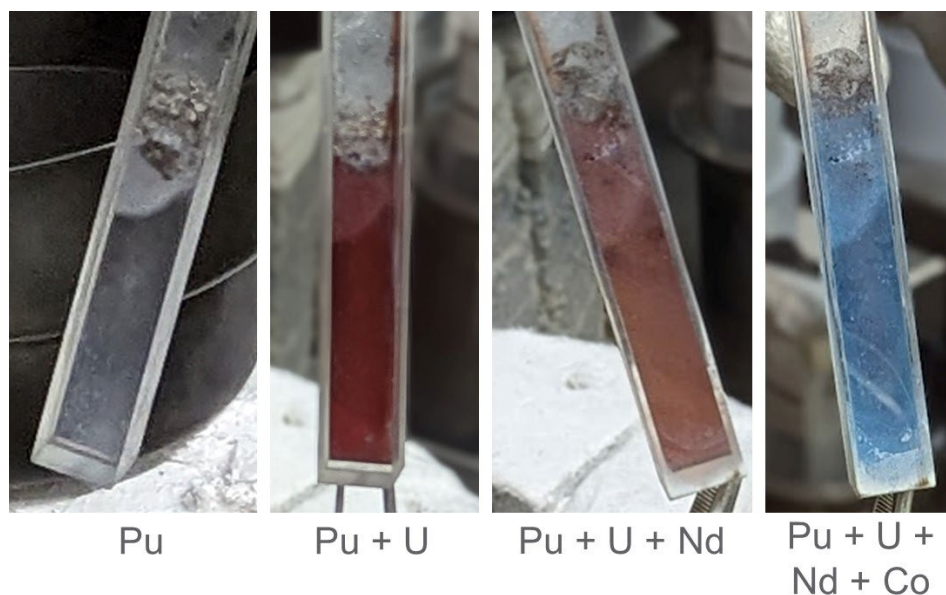


Figure 4-4. Pu with added analytes in $NaCl-MgCl_2$, $550\text{ }^\circ C$

This observation, along with the results of the sapphire experiment, highlighted possible paths forward for expanding the capability of optical collection. These possibilities include using multiple light sources and detectors to capture transmissions from the UV to NIR range ($\sim 200\text{ nm}$ up to $\sim 2000\text{ nm}$). While fuel species of interest (e.g., U and Pu)

have unique fingerprints in the visible, the fingerprints can overlap and their molar extinction coefficients are high.^{27, 29, 32} These species, however, also have unique fingerprints in the NIR range.³²⁻³⁴ While fission surrogates and corrosion products can also have overlapping fingerprints in the visible range,^{1, 3, 35, 36} these interferents also have unique fingerprints in the UV³⁷ and NIR^{38, 39} range. Preliminary investigations were conducted with additional funding received from this ARSS campaign and is detailed a separate memo sent to the campaign NTD.

5. CONCLUSION AND RECOMMENDATIONS

Optical spectroscopy tools continue to demonstrate valuable applicability to online monitoring of key MC&A targets within molten salts. In FY24, the PNNL team applied optical online monitoring using UV-Vis absorbance and Raman spectroscopy to characterize molten chloride salts containing Pu and other key interferents. While Pu data ultimately was limited, this provided a valuable opportunity to better understand the monitoring needs for Pu, how to handle Pu, and how Pu can be expected to behave within molten chloride salts. Ultimately Pu (and other metal species) behavior will be dependent on many factors in the salt, and this is a key first step to building the understanding necessary to support effective MC&A of molten salt systems. This was a key opportunity to expand data sets and characterization of additional dissolved metal species in the molten salts. It is important to highlight the role, not only of online monitoring to trend analysis to support more accurate MC&A, but the role of advanced data analysis to enable real-time data analysis. FY24 work highlighted these benefits, and it is expected this will continue to be demonstrated in follow-on efforts.

The PNNL team also advanced their small-scale molten salt system design to allow for optimized testing and characterization of molten salts while testing and using materials that would be expected for use in sensors in larger-scale salt systems. This included improving furnace design, improving optics integration, and utilizing cell materials that correspond to sensor window materials. It is recommended that the system be further improved and tested in follow-on efforts to include updates such as excitation sources with wider output profiles.

Additionally, the PNNL team continues to look for opportunities to collaborate with industry partners to better understand monitoring needs and limitations while exploring options to test or validate sensors on relevant systems. PNNL has had a long-standing interaction with TerraPower that resulted in the sharing of salts in previous FYs. More recently, the PNNL team has begun discussing collaboration opportunities with Curio. The team is also considering opportunities to extend efforts into molten fluoride salts, which tend to be denser and may require modifications to approach. This may lead to considerations of using multiple fiber bundles to support measurement of multiple pathlengths, including the development of sensors for very short pathlengths, or possibly for recommendations of sampling loop configurations.

Ultimately, to support safe and effective deployment of MSRs, tools to enable MC&A are needed. Sensors capable of online monitoring can provide unique benefits for trend monitoring. Where on-line tools cannot provide the uncertainties typical of off-line methods,

they can provide unique and continuous insight into reactor operation. Furthermore, using sensors that provide detailed chemical information (e.g., speciation, oxidation state, etc.) but not isotopics can be highly valuable for accounting for material in molten salt systems where chemical species can be heterogeneously distributed through the salt.

In FY25, tasks will continue to advance and modify the existing small-scale setup for optical interrogation of molten salts. This will push the system to both better represent the materials and components anticipated in an operating loop as well as expand applicable modalities to salt characterization. A significant goal of FY25 will include expanding optical spectroscopic collection into the NIR which may provide a unique avenue to resolve optical fingerprints of target species whose concentrations extend beyond the linear range in the UV-Vis range. Scope will also include expanding small-scale characterization to include TRU chemical targets, e.g., Pu in complex salt mixtures.

5. ACKNOWLEDGMENTS

This work was funded by the Department of Energy Office of Nuclear Energy's Advanced Reactor Safeguards Campaign. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830.

The team would like to acknowledge and thank TerraPower for providing a variety of salt samples allowing the team to explore applications to representative salt systems. The team would also like to acknowledge and thank Richard Clark and team from PNNL for providing the Pu for plutonium chloride synthesis and testing.

6. REFERENCES

- (1) Schroll, C. A.; Lines, A. M.; Heineman, W. R.; Bryan, S. A. Absorption spectroscopy for the quantitative prediction of lanthanide concentrations in the 3LiCl-2CsCl eutectic at 723 K. *Analytical Methods* **2016**, *8* (43), 7731-7738, 10.1039/C6AY01520D. DOI: 10.1039/c6ay01520d.
- (2) Schroll, C. A.; Chatterjee, S.; Levitskaia, T. G.; Heineman, W. R.; Bryan, S. A. Electrochemistry of Europium(III) Chloride in 3 LiCl - NaCl, 3 LiCl-2 KCl, LiCl - RbCl, and 3 LiCl-2 CsCl Eutectics at Various Temperatures. *Journal of the Electrochemical Society* **2017**, *164* (8), H5345-H5352. DOI: 10.1149/2.0521708jes.
- (3) Schroll, C. A.; Chatterjee, S.; Levitskaia, T. G.; Heineman, W. R.; Bryan, S. A. Electrochemistry and Spectroelectrochemistry of europium(III) chloride in 3LiCl-2KCl from 643 to 1123 K. *Anal Chem* **2013**, *85* (20), 9924-9931. DOI: 10.1021/ac402518p From NLM PubMed-not-MEDLINE.
- (4) Schroll, C. A.; Chatterjee, S.; Levitskaia, T.; Heineman, W. R.; Bryan, S. A. Spectroelectrochemistry of EuCl₃ in Four Molten Salt Eutectics; 3 LiCl-NaCl, 3 LiCl-2 KCl, LiCl-RbCl, and 3 LiCl-2 CsCl; at 873 K. *Electroanalysis* **2016**, *28* (9), 2158-2165. DOI: 10.1002/elan.201600048.
- (5) Polovov, I. B.; Volkovich, V. A.; Charnock, J. M.; Kralj, B.; Lewin, R. G.; Kinoshita, H.; May, I.; Sharrad, C. A. In situ spectroscopy and spectroelectrochemistry of uranium in high-temperature alkali chloride molten salts. *Inorg Chem* **2008**, *47* (17), 7474-7482. DOI: 10.1021/ic701415z.
- (6) Park, Y. J.; Bae, S. E.; Cho, Y. H.; Kim, J. Y.; Song, K. UV-vis absorption spectroscopic study for on-line monitoring of uranium concentration in LiCl-KCl eutectic salt. *Microchemical Journal* **2011**, *99* (2), 170-173. DOI: 10.1016/j.microc.2011.04.013.
- (7) Nagai, T.; Uehara, A.; Fujii, T.; Yamana, H. Reduction behavior of UO₂²⁺ in molten LiCl-RbCl and LiCl-KCl eutectics by using tungsten. *Journal of Nuclear Materials* **2013**, *439* (1-3), 1-6. DOI: 10.1016/j.jnucmat.2013.03.078.
- (8) Bryan, S. A.; Levitskaia Tatiana, G.; Johnsen, A. M.; Orton, C. R.; Peterson, J. M. Spectroscopic monitoring of spent nuclear fuel reprocessing streams: an evaluation of spent fuel solutions via Raman, visible, and near-infrared spectroscopy. In *Radiochimica Acta International journal for chemical aspects of nuclear science and technology*, 2011; Vol. 99, p 563.
- (9) Lines, A. M.; Hall, G. B.; Asmussen, S.; Allred, J.; Sinkov, S.; Heller, F.; Gallagher, N.; Lumetta, G. J.; Bryan, S. A. Sensor Fusion: Comprehensive Real-Time, On-Line Monitoring for Process Control via Visible, Near-Infrared, and Raman Spectroscopy. *ACS Sens* **2020**, *5* (8), 2467-2475. DOI: 10.1021/acssensors.0c00659 From NLM Medline.
- (10) Lines, A. M.; Hall, G. B.; Sinkov, S.; Levitskaia, T.; Gallagher, N. B.; Lumetta, G. J.; Bryan, S. A. Overcoming Oxidation State-Dependent Spectral Interferences: Online Monitoring of U(VI) Reduction to U(IV) via Raman and UV-vis Spectroscopy. *Industrial & Engineering Chemistry Research* **2020**, *59* (19), 8894-8901. DOI: 10.1021/acs.iecr.9b06706.
- (11) Lines, A. M.; Nelson, G. L.; Casella, A. J.; Bello, J. M.; Clark, S. B.; Bryan, S. A. Multivariate Analysis To Quantify Species in the Presence of Direct Interferents: Micro-Raman Analysis of HNO₃ in Microfluidic Devices. *Anal Chem* **2018**, *90* (4), 2548-2554. DOI: 10.1021/acs.analchem.7b03833 From NLM PubMed-not-MEDLINE.
- (12) Lines, A. M.; Tse, P.; Felmy, H. M.; Wilson, J. M.; Shafer, J.; Denslow, K. M.; Still, A. N.; King, C.; Bryan, S. A. Online, Real-Time Analysis of Highly Complex Processing Streams: Quantification of Analytes in Hanford Tank Sample. *Industrial & Engineering Chemistry Research* **2019**, *58* (47), 21194-21200. DOI: 10.1021/acs.iecr.9b03636.

- (13) Tse, P.; Bryan, S. A.; Bessen, N. P.; Lines, A. M.; Shafer, J. C. Review of on-line and near real-time spectroscopic monitoring of processes relevant to nuclear material management. *Anal Chim Acta* **2020**, *1107*, 1-13. DOI: 10.1016/j.aca.2020.02.008 From NLM PubMed-not-MEDLINE.
- (14) Branch, S. D.; Felmy, H. M.; Schafer Medina, A.; Bryan, S. A.; Lines, A. M. Exploring the Complex Chemistry of Uranium within Molten Chloride Salts. *Ind Eng Chem Res* **2023**. DOI: 10.1021/acs.iecr.3c02005.
- (15) Paviet, P.; Hartmann, T.; Lines, A. M.; Bryan, S. A.; Felmy, H. M.; Glezakou, V.-A.; Nguyen, M.-T.; Medina, A.; Branch, S. D. *Corrosion of Molten Salt Containment Alloys - Fundamental Mechanisms for Corrosion Control and Monitoring*; Pacific Northwest National Laboratory, Richland, Washington, 2020.
- (16) Lines, A. M.; Bryan, S. A.; Felmy, H. M.; Branch, S. D. On-line Monitoring for Molten Salt Reactor MC&A: Optical Spectroscopy-Based Approaches, PNNL-33367. Pacific Northwest National Laboratory: Richland, WA, 2022.
- (17) Lee, M. H.; Park, Y. J.; Kim, W. H. Absorption spectroscopic properties for Pu(III, IV and VI) in nitric and hydrochloric acid media. *Journal of Radioanalytical and Nuclear Chemistry* **2007**, *273* (2), 375-382. DOI: 10.1007/s10967-007-6848-1.
- (18) Kasha, M. S., G. E. . Ionic Equilibria and Reaction Kinetics of Plutonium Ions in Hydrochloric Acid Solution. In *The Transuranium Elements Research Papers*, Glenn T. Seaborg, J. J. K., Winston M. Manning Ed.; 1949; pp 180-226.
- (19) Schroll, C. A.; Chatterjee, S.; Levitskaia, T. G.; Heineman, W. R.; Bryan, S. A. Electrochemistry and Spectroelectrochemistry of Europium(III) Chloride in 3LiCl-2KCl from 643 to 1123 K. *Anal Chem* **2013**, *85* (20), 9924-9931. DOI: 10.1021/ac402518p.
- (20) Wang, G. G.; Zuo, H. B.; Zhang, H. Y.; Wu, Q. B.; Zhang, M. F.; He, X. D.; Hu, Z. H.; Zhu, L. Preparation, quality characterization, service performance evaluation and its modification of sapphire crystal for optical window and dome application. *Materials & Design* **2010**, *31* (2), 706-711. DOI: 10.1016/j.matdes.2009.08.015.
- (21) Brian, G. P.; Richard, D.; Philip, J. G.; Paul, S. K. Development of sapphire windows for use in high-quality IR imaging systems. In *Proc.SPIE*, 1992; Vol. 1760, pp 55-65. DOI: 10.1117/12.130786.
- (22) Passerini, S. Optical and chemical properties of molten salt mixtures for use in high temperature power systems. Massachusetts Institute of Technology, 2010.
- (23) Richard, G.; Edward, M.; Theodore, K.; David, B. V. Comparison Of Large ALON And Sapphire Windows. In *Proc.SPIE*, 1989; Vol. 1112, pp 31-39. DOI: 10.1117/12.960761.
- (24) Tortorelli, P. F.; Bishop, P. S.; DiStefano, J. R. *Selection of corrosion-resistant materials for use in molten nitrate salts*; United States, 1989. <https://www.osti.gov/biblio/5236321>
<https://www.osti.gov/servlets/purl/5236321> DOI: 10.2172/5236321.
- (25) Ockenfels, T.; Vewinger, F.; Weitz, M. Sapphire optical viewport for high pressure and temperature applications. *Review of Scientific Instruments* **2021**, *92* (6), 065109. DOI: 10.1063/5.0047609 (accessed 9/18/2024).
- (26) Bob, H.; Paul, D.; Aric, S.; Marc, T. Recent advances in deterministic low-cost finishing of sapphire windows. In *Proc.SPIE*, 2005; Vol. 5786, pp 154-164. DOI: 10.1117/12.603930.
- (27) Nagai, T.; Uehara, A.; Fujii, T.; Shirai, O.; Sato, N.; Yamana, H. Redox equilibrium of U⁴⁺/U³⁺ in molten NaCl-2CsCl by UV-Vis spectrophotometry and cyclic voltammetry. *Journal of Nuclear Science and Technology* **2005**, *42* (12), 1025-1031. DOI: DOI 10.3327/jnst.42.1025.
- (28) Fukasawa, K.; Uehara, A.; Nagai, T.; Fujii, T.; Yamana, H. Electrochemical and spectrophotometric study on neodymium ions in molten alkali chloride mixtures. *Journal of Alloys and Compounds* **2011**, *509* (16), 5112-5118. DOI: 10.1016/j.jallcom.2011.01.192.
- (29) Lambert, H. Molten salt spectroscopy and electrochemistry for spent nuclear fuel treatment. The University of Manchester (United Kingdom), 2017.

- (30) Nagai, T.; Uehara, A.; Fujii, T.; Shirai, O.; Myochin, M.; Yamana, H. Redox equilibria of Pu⁴⁺/Pu³⁺ and PuO₂²⁺/Pu⁴⁺ couples in molten NaCl-CsCl eutectic as measured by absorption spectrophotometry. *Radiochimica Acta* **2009**, *97* (4-5), 209-212. DOI: 10.1524/ract.2009.1596 (accessed 2023-11-27).
- (31) Shirai, O.; Uehara, A.; Fujii, T.; Yamana, H.; Nagai, T.; Myochin, M. *Absorbance of plutonium in NaCl-2CsCl molten salt*; JAERI-Conf--2005-008; Japan, 2005.
http://inis.iaea.org/search/search.aspx?orig_q=RN:37022141.
- (32) Bamberger, C. E.; Ross, R. G.; Baes, C. F.; Young, J. P. Absence of an effect of oxide on the solubility and the absorption spectra of PuF₃ in molten LiF□BeF₂□ThF₄ and the instability of plutonium(III) oxyfluorides. *Journal of Inorganic and Nuclear Chemistry* **1971**, *33* (10), 3591-3594. DOI: 10.1016/0022-1902(71)80687-5.
- (33) Dai, S.; Toth, L. M.; Delcul, G. D.; Metcalf, D. H. Visible and near-IR Spectroscopic Studies of Uranium(IV) Oxychloride in a MgCl₂-KCl Melt. *Inorganic Chemistry* **1995**, *34* (1), 412-413. DOI: DOI 10.1021/ic00105a066.
- (34) Young, J. P. Spectra of uranium(IV) and uranium(III) in molten fluoride solvents. *Inorganic Chemistry* **1967**, *6* (8), 1486-1488. DOI: 10.1021/ic50054a012.
- (35) Li, J.; Dasgupta, P. K. A simple instrument for ultraviolet-visible absorption spectrophotometry in high temperature molten salt media. *Review of Scientific Instruments* **2000**, *71* (6), 2283-2287. DOI: 10.1063/1.1150442 (accessed 9/19/2024).
- (36) Yoon, S.; Choi, S. Spectroelectrochemical Behavior of Cr, Fe, Co, and Ni in LiCl-KCl Molten Salt for Decontaminating Radioactive Metallic Wastes. *Journal of The Electrochemical Society* **2021**, *168* (1), 013504. DOI: 10.1149/1945-7111/abdc7e.
- (37) Banks, C. V.; Heusinkveld, M. R.; O'Laughlin, J. W. Absorption Spectra of the Lanthanides in Fused Lithium Chloride-Potassium Chloride Eutectic. *Analytical Chemistry* **1961**, *33* (9), 1235-1240. DOI: 10.1021/ac60177a032.
- (38) Moon, J.; Chidambaram, D. Near-infrared spectra and molar absorption coefficients of trivalent lanthanides dissolved in molten LiCl-KCl eutectic. *Progress in Nuclear Energy* **2022**, *152*, 104375. DOI: ARTN 104375
10.1016/j.pnucene.2022.104375.
- (39) Stephanou, S. E.; Nigon, J. P.; Penneman, R. A. The Solution Absorption Spectra of Americium(III), (V), and (VI). *The Journal of Chemical Physics* **1953**, *21* (1), 42-45. DOI: 10.1063/1.1698619 (accessed 2022/08/10).