Evaluation of optical techniques for molten salt reactor materials control and accounting

Nuclear Technology Research and Development

Prepared for
U.S. Department of Energy
MRWFD Campaign
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September 11, 2020
PNNL-30360

SUMMARY

Next generation reactors offer an opportunity to advance nuclear energy efficiency and safety, but in many cases represent a change in paradigm regarding safeguarding or materials control and accountancy (MC&A) approaches. Molten salt reactors (MSRs) are an example of this, where high temperatures (>500°C), highly corrosive environments, the need to isolate systems within an inert atmosphere, and designs that rely on liquid fuel, can make it very difficult to apply traditional MC&A technologies. MSRs are a promising avenue for nuclear energy, with several designers actively advancing the technology and pursuing licensing pathways. Because of this growing interest and reactor technology advancement, concurrent development of technology to support effective MC&A of MSR systems is essential.

While multiple techniques will eventually need to be leveraged to gain a comprehensive understanding of MSR system conditions, optical spectroscopy based on-line monitoring represents a powerful first step. Optical spectroscopy can be utilized to selectively identify and quantify target chemical species within salt melts. Combining optical techniques with chemometric analysis to enable real-time analysis further enables accurate translation of optical data into systems information. Optical approaches are particularly valuable within molten salt systems due to their ability to provide complex chemical information, including concentrations, redox ratios, and speciation; making these techniques valuable to MSR designers and operators as a means to control processes, monitor corrosion, and potentially safeguard materials. However, technology development is needed to advance optical approaches into viable on-line monitoring tools for MC&A applications.

This report discusses the current state of the art of optical based monitoring of molten salt systems, covering literature on optical approaches applied to molten salts and observed signatures of actinides or other target species. Technology gaps are also discussed along with a road map for developing on-line monitoring tools for molten salt systems. Phases of development of optical spectroscopy-based monitoring includes the following steps:

- Laboratory Testing and Development: Tasks to focus on utilization of a small-scale molten salt interrogation system to complete scoping studies and identify key fingerprints of target molten salt analytes and interfering species as well as simultaneous development and testing of a probe for interrogation of large scale molten salt systems of interest to MSR developers and operators.

- Collect Training Set and Model Building: Tasks support systematic collection and spectroscopic measurement of molten salt samples to be utilized in building the chemometric models for quantitative measurement of metallic elements within molten salt systems, followed by validation of the chemometric models developed.

- Large Scale Testing: This phase will require an industry partner/collaboration to explore options in larger scale systems mimicking deployment conditions using the optimized design and models.

- Development Preparation: This stage will identify and assign QA requirements, assess technology transfer options, and explore approved pathways to integrate probes.

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ABBREVIATIONS AND ACRONYMS

An	actinoids (or actinides) (i.e., ${}_{89}$Ac → ${}_{103}$Lr)
CV	cyclic voltammogram (voltammetry)
DOE	Department of Energy
FLiBe	LiF-BeF$_2$ salt (i.e., typically 2 ^{7}LiF•1 BeF$_2$)
MC&A	material control and accounting
MSR	molten salt reactor
NRC	Nuclear Regulatory Commission
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
SEC	Spectroelectrochemistry
TRL	technology readiness level
UV	ultraviolet (light)
Vis	visible (light)

1. INTRODUCTION

Next generation nuclear reactors are gaining interest as reliable green energy options both in the United States and abroad. Several designs are being considered, some representing large shifts away from existing reactor designs. Molten salt reactors (MSRs) are an example of this, where proposed designs operate at temperatures in the range of 500°C and potentially utilize liquid fuel, among other major design differences. However, designs suggest MSRs can meet growing energy needs while also improving safety and operational efficiency as compared to older generation reactors.[1, 2] Multiple designs are currently under development, with at least one designer working with the NRC on licensing pre-application.

MSRs can offer a variety of advancements over existing fleet designs, but there are technical challenges remaining to be addressed before these reactors can be licensed or deployed. A significant challenge is developing tool kits for nuclear material control and accounting (MC&A). A variety of approaches are available to meet MC&A needs within existing fleet designs, though the high temperatures and corrosivity of the molten salt systems make it challenging to translate those technologies and approaches to MSRs.

Of the available technologies that can be adapted to the molten salt environment, one of the most promising is optical spectroscopy. This mature technology has already been utilized to interrogate molten salts *in situ*.[3-9] Optical spectroscopy is capable of providing information that not only supports MC&A, but reactor operation and control as well. This technology has the potential to enable the identification and quantification of fuel components (assuming a molten fuel MSR), fission products, and corrosion products. It can also provide insight into speciation and oxidation state, which is of significant interest to reactor operators seeking to control vessel corrosion. Furthermore, on-line monitoring applications utilizing optical spectroscopy indicate this approach can successfully be applied to the complex systems anticipated in used nuclear fuel or wastes[10, 11], to provide real-time identification and quantification of targets such as uranium and plutonium. [12-14] A significant component of on-line monitoring systems that enables the application of mature optical techniques to accurate, real-time analysis of complex processes is the integration of chemometric modeling. This multivariate analysis approach is integral to systems development and can be utilized to overcome many of the challenges that traditionally hamper applications of optical spectroscopy, including band overlap, baseline effects, and non-linear matrix impacts to system signatures.[3, 15-18] Overall, optical on-line monitoring approaches paired with chemometric analysis for real-time monitoring would be of value to MSR designers and operators on multiple levels.

While it is not the goal of this report to outline the policy needs and therefore the specific targets and target concentration ranges, this report will describe a key technology that could greatly advance MC&A technology options for MSRs. This report will cover the current state of the art regarding optical interrogation of molten salts, key technology gaps, and a road map for developing spectroscopy-based on-line monitoring technology for MC&A of MSRs.

2. OPTICAL TOOLS FOR MOLTEN SALT CHARACTERIZATION

Optical spectroscopy techniques are a common and generally mature technology. While lacking the limits of detection of techniques like mass spectrometry, optical spectroscopy can provide information that few other techniques supply. Specifically, optical techniques can be utilized to identify and quantify unique species or oxidation states as well as overall elemental content of a given sample. Furthermore, several forms of optical spectroscopy are well suited to stand off detection and *in situ* analysis within harsh environments. Because these techniques typically rely on fiber optics to transport light to and from a sample, instrumentation and operators can often be located far away from the sample measurement location. It should also be noted that initial testing of radiation hardness of optical probes and probe materials has been conducted. Published results indicate materials can continue to perform well up to at least 10^7 rad.[11] Overall, optical approaches are ideal for providing complex chemical information within hazardous or difficult to access processes.

A primary weakness of optical approaches is a lack of selectivity for target analytes. In complex samples or processes containing multiple chemical species, interfering optical signatures can make accurate and timely data analysis difficult. However, a variety of recent advancements in data analysis tools can enable highly selective and accurate identification and quantification of targets in complex systems. An example is chemometric analysis, which has been coupled with optical techniques in numerous demonstrations for accurate analysis of complex processes for application to real-time process control. [11, 12, 14-16]

In short, the maturity, ability to handle harsh environments, and capacity to pair with advanced data analysis tools makes optical spectroscopy an ideal technology to apply to molten salt systems. In particular, the capability to provide insight into oxidation state (key for corrosion control and monitoring) as well as total elemental concentration (essential to process control and MC&A) makes optical spectroscopy a potentially valuable tool to MSR designers and operators. The following sections will discuss how optical approaches have been applied to molten salt systems previously, where the current state of the art is, and what steps are needed to advance optical approaches to provide on-line monitoring capability for MC&A of MSR systems.

2.1 Applications to Molten Salts in the Literature

Application of optical spectroscopy to molten salt systems has been explored in the literature and has been demonstrated as a powerful tool for gaining insight into the chemical composition and behavior of molten salts. These applications have been investigated for various species that would be anticipated in MSR salts, including lanthanides, corrosion products, and most valuable to this report, actinides. Interestingly, many of these studies are paired with electrochemistry or otherwise utilize chemical additives to control redox states of species present. The resulting data and analytical tools are valuable to MSR designers and operators both as a means to optimize their designs and to control salt conditions. These capabilities also have the potential to be utilized for MC&A.

As an initial example to demonstrate the level of characterization that can be achieved, non-radioactive systems characterizations are highly valuable. Work by Schroll et al. demonstrates both fundamental characterization,[4-6] and demonstration of the ability to quantify analytes in complex matrices.[3] Figure 2-1 below presents figures taken from various papers by Schroll et al. which focus on the fundamental characterization aspects of analysis. In these manuscripts, spectroelectrochemistry (SEC), a combination of optical spectroscopy and electrochemistry, was utilized to characterize europium within various chloride-based eutectics. Analyses included identifying the optical fingerprints of Eu in the 3+ and 2+ oxidation states, as well as characterizing redox behavior as a function of eutectic composition and temperature. The diffusion coefficient of Eu was also determined experimentally and is a valuable metric when determining how products migrate through reactor melts.

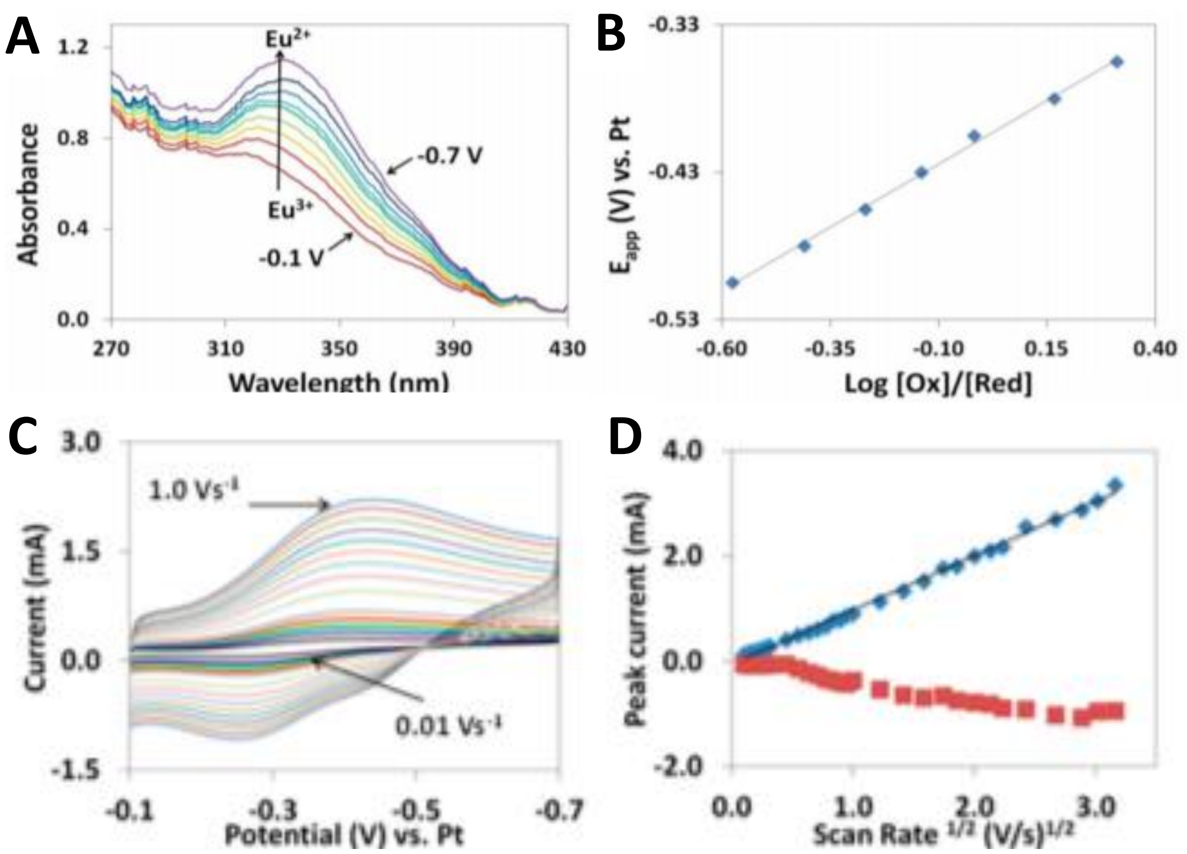

Figure 2-1. (A,B) Figure demonstrating the use of spectroelectrochemistry to characterize the formal reduction potential and optical fingerprints of Eu in chloride based eutectic[4]; (C,D) Figure demonstrating use of spectroelectrochemistry to calculate diffusion coefficients of Eu in chloride based eutectic. From Schroll et al. [5]

Schroll et al. also provided valuable demonstrations of the ability to quantify target analytes within complex melts.[3] Figure 2-2 presents figures taken from this article where melts containing up to six lanthanides with interfering signatures were optically interrogated. In this work, chemometric models were built to quantify the lanthanides within the melt. Figure 2-2A presents the UV-vis absorbance fingerprints of the six lanthanides studied. An example of how the fingerprint intensity correlates to lanthanide concentration in the melt is shown in Figure 2-2B. Noticeable overlap is observed between signatures. Despite this, chemometric models could accurately quantify melts containing 1 to 6 lanthanides across a range of concentrations. Figure 2-2C and D present parity plots demonstrating quantification accuracy for the most sensitive (Nd) and one of the least sensitive (Sm) lanthanides. This proof of principle demonstration of *in situ* quantification suggests this approach could successfully be applied to other key analytes within molten salt systems.

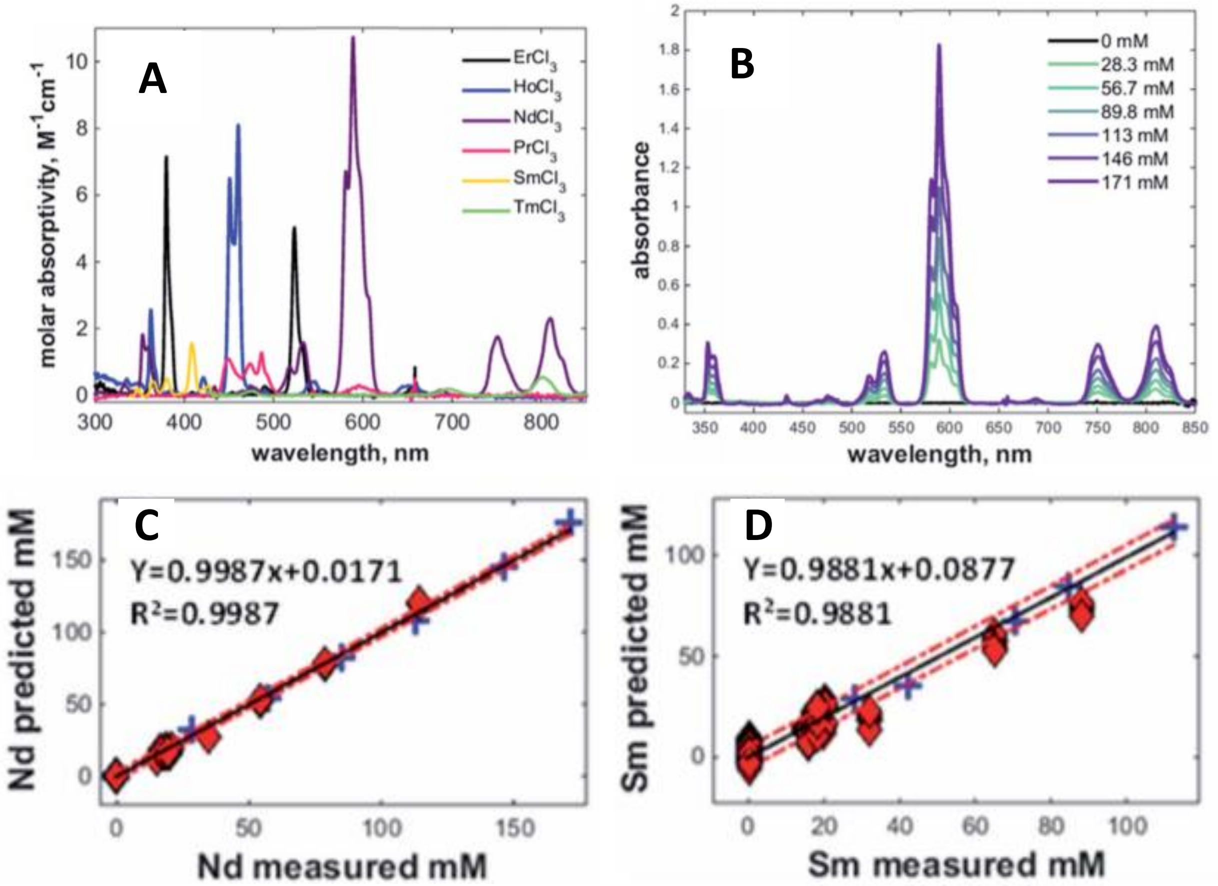

Figure 2-2. (A) UV-vis absorbance fingerprints of 6 lanthanides within LiCl-KCl eutectic and example (B) of how UV-vis fingerprints vary with lanthanide concentration within the salt melt. These data were used to build chemometric models to quantify the lanthanides in the melt where the resulting parity plots are shown for two lanthanides, (C) Nd and (D) Sm. From Scroll et al.[3]

Many of the actinide analyses in melts have been more focused on fundamental characterization as opposed to on-line monitoring tool development. Much of the focus falls around the need to control the U(III)/U(IV) ratio within the salt melt; a key factor in controlling the extent of corrosion of the structural materials. This oxidation state control can be accomplished or effectively characterized using electrochemistry as well as optical spectroscopy. [19-21] By modulating the potential across the electrodes in the salt, the uranium oxidation state can be changed. Species such as U^{3+}, U^{4+}, UO_2^+, and UO_2^{2+} each have unique UV-vis signatures (Figure 2-3) which can be used to identify the species present in the system.[7, 8] By following the change in optical signature with applied electrochemical potential, the change in oxidation state can be monitored. For example, the in-growth of the higher intensity U^{3+} UV-vis signature can be followed as U^{4+} is reduced to U^{3+}.[8, 9, 22] The reduction of UO_2^{2+} to UO_2^+ has also been monitored using UV-vis spectroelectrochemistry in a NaCl-2CsCl eutectic.[23] UV-vis has also been used to monitor chemical reactions resulting in oxidation state changes. Lambert et al. followed the oxidation of U metal to U(IV) by reaction with $BiCl_3$ in a LiCl-KCl eutectic.[24] Cho et al. followed the decrease in UV-vis signature of U(III) as it reacted with Li_2O and precipitated as UO_2 in a LiCl-KCl eutectic.[25]

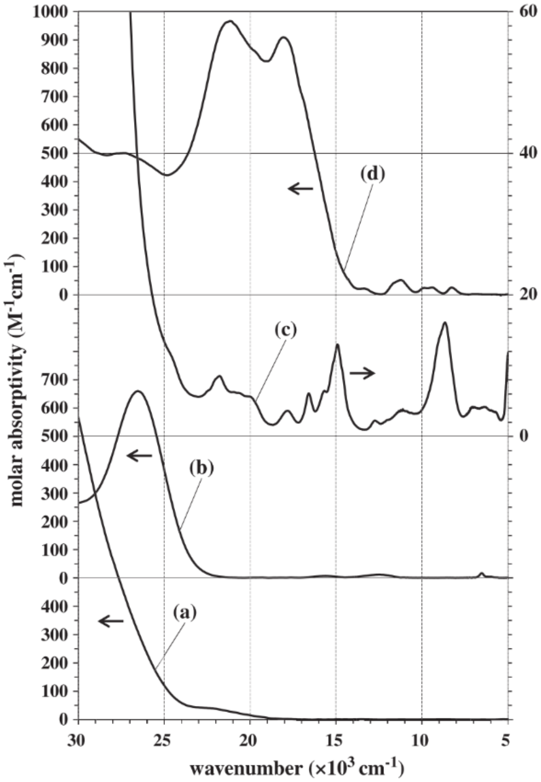

Figure 2-3. The absorption spectra of (a) UO_2^{2+}, (b) UO_2^{+}, (c) U^{4+}, (d) U^{3+} in LiCl-RbCl eutectic melt at 400°C. From Nagai et al.[7]

Additional optical techniques are potentially applicable to U within molten salt systems. An example is Raman spectroscopy, where UO_2^{2+} has a Raman signal from the uranyl O=U=O symmetric stretch. This band is typically observed at around 880 cm^{-1} in aqueous solution and shifts to between 830-870 cm^{-1} in molten chloride systems depending on the salt composition.[8, 26] Figure 2-4 presents examples of the Raman fingerprints of U within various salt melt types. This Raman signature could be a useful tool in confirming that U has not oxidized beyond ideal speciation and ratio between U^{3+} and U^{4+} in the melt, or otherwise providing an accurate total content analysis of U by accounting for any material that has oxidized and no longer has a strong UV-vis signature. Raman is also a valuable tool for monitoring corrosion products or the interaction of key actinides with corrosion products. Interactions of U in its various oxidation states with species such as Cr can impact optical fingerprints (UV-vis and Raman). Utilizing a vibrational approach such as Raman allows operators to build a comprehensive understanding of total U (or potentially other actinide targets) content within a salt melt.

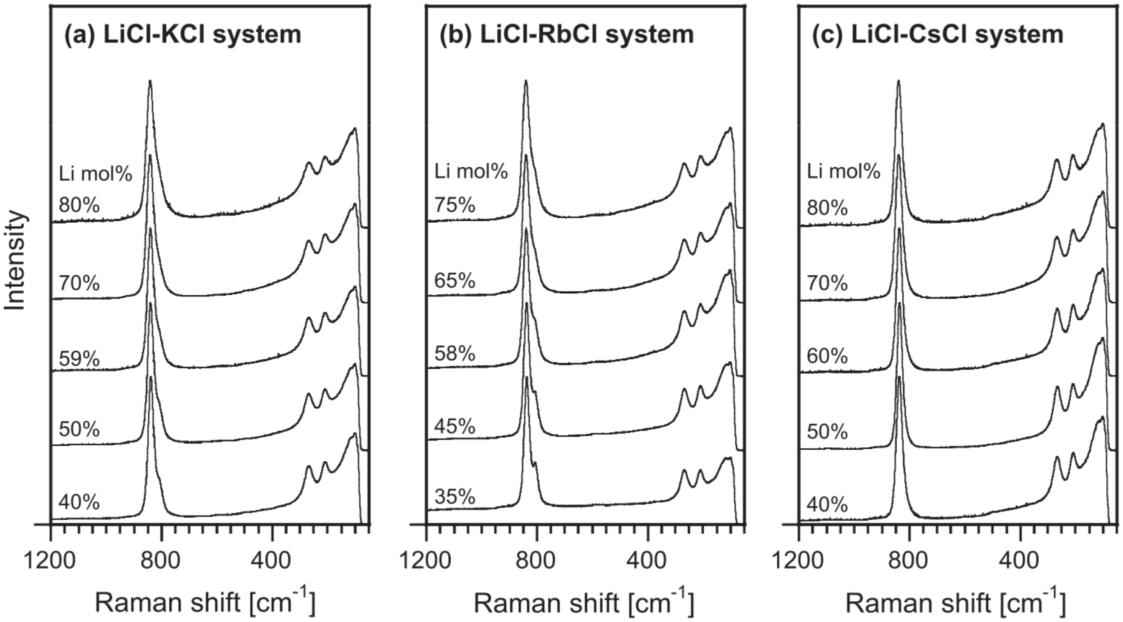

Figure 2-4. Raman spectra of alkali chorides including 3 mol% U(VI) at 823 K. (a) LiCl-KCl system. (b) LiCl-RbCl system. (c) LiCl-CsCl system. From Fujii et al.[27]

Other optical techniques such as florescence spectroscopy could also be valuable within molten salt systems, giving the potential to increase selectivity for targets by controlling excitation wavelength. Applications of florescence to molten salt systems have been limited, but recent literature suggests beneficial opportunities. The signature of UCl_3 has been noted by Im et al.[28] In addition to common species such as U^{3+} and U^{4+}, some works indicate less common targets could be also be followed by florescence. In a recent article, Liu et. al. dissolved U_3O_8 in a LiCl-KCl eutectic in the presence of NH_4Cl at 450 °C and measured the fluorescence of the quenched salt at room temperature (Figure 2-5). [29] The peaks at 500 nm, 524 nm, 549 nm, and 572 nm correspond with previous findings for U(VI) in aqueous systems. [30, 31] This fluorescence signature for uranium could be used to determine the chemical form of U present in molten salts.

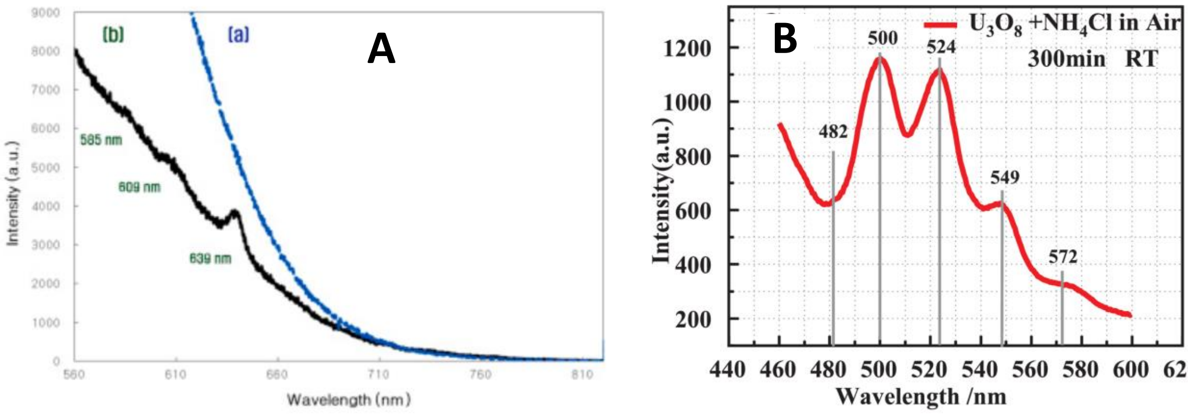

Figure 2-5. Florescence spectra of (A) UCl_3 in LiCl eutectic melt (black line) mixed in HMICl (1-hexyl-3-methyl-imidazolium chloride) ionic liquid (λ_{ex}=504 nm) from Im et al. [28]; and (B) dissolved U_3O_8 in a quenched LiCl-KCl eutectic in the presence of NH_4Cl. The concentration of U in the quenched salt was 0.47 wt. %. From Liu et al. [29]

Other key actinides including Pu have been discussed to a limited extent within molten salt systems. Electrochemical studies of Pu have been performed in molten salts looking at the $Pu^{0/3+}$ redox reaction.[21, 32, 33] These initial studies have provided some necessary characterization of the electrochemical behavior of Pu in molten salts. Optical interrogation of Pu within molten salts is limited in the literature. However, optical and spectroelectrochemical techniques have been applied to Pu in other systems. An example being aqueous HNO_3 solutions where UV-vis based-spectroelectrochemistry was used to characterize optical fingerprints and redox behavior of Pu.[34, 35] The UV-vis signature was found to change as the oxidation state was electrochemically modulated between the +3, +4, and +6 oxidation states. This result in aqueous systems is a promising indication that Pu SEC can be applied to molten salt systems.

Another actinide of interest is Np, which has been studied in molten salts using spectroelectrochemical methods and its UV-vis optical signature.[36-38] Figure 2-6. from Polovov et al. shows the changes in the UV-vis spectrum as Np(IV) was electrochemically reduced to Np(III) in a LiCl-KCl eutectic melt.[36] These optical fingerprints can be used to detect Np in the molten salt system and determine its oxidation state.

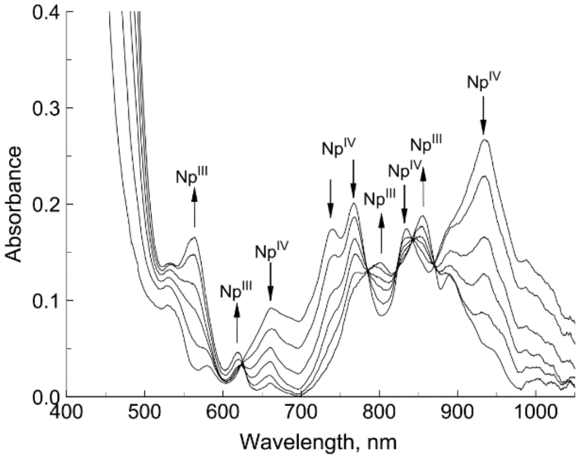

Figure 2-6. Spectra recorded during electrochemical reduction of Np(IV) to Np(III) in 3LiCl-2KCl eutectic melt at 450 °C. Initial concentration of neptunium(IV) - ca. 0.015 mol/L. Total time of reduction - 1280 sec, current - 5 mA. From Polovov et al. [36]

2.2 Technology Gaps and PNNL Steps Towards Developing On-line Monitoring Tools

A variety of technology gaps will need to be addressed to support the development of on-line monitoring technology for MSR systems. As noted in the previous section, application of optical approaches to molten salt systems has been limited, both in terms of optical approaches utilized and target analytes that were characterized. Fortunately, optical instrumentation is generally a mature technology, where most of the needed development falls on the probes or systems utilized to hold/interrogate salt melts. It should be noted that interrogation tools need to be developed at multiple scales. Small-scale systems enable the efficient scoping and characterization of optical fingerprints and chemical behavior. Small-scale systems are especially important for probing the behavior of the highly radiotoxic transuranic elements (Np, Pu, Am, and Cm). Larger scale probes and sensors support monitoring of salt loops or systems built and utilized by MSR designers and operators.

Initial focus on small scale systems will allow for optimized testing and development of optical spectroscopy-based monitoring tools. The PNNL team has been pursuing this, first developing a spectroelectrochemical setup for *in situ* molten salt characterization to characterize lanthanides. Figure 2-7 presents pictures from the related Schroll et al.[5] paper depicting the original setup. This system utilized UV-vis absorption spectroscopy to interrogate chloride-based melts within a thin layer spectroelectrochemical cell. The figure includes pictures of the cells containing salts. These provide a good example of the size of the salt sample interrogated and also show how the salt is colored by the presence of different dissolved metal species. This system was a significant first step, but lacked flexibility in several areas, including the ability to interrogate salts via multiple optical techniques.

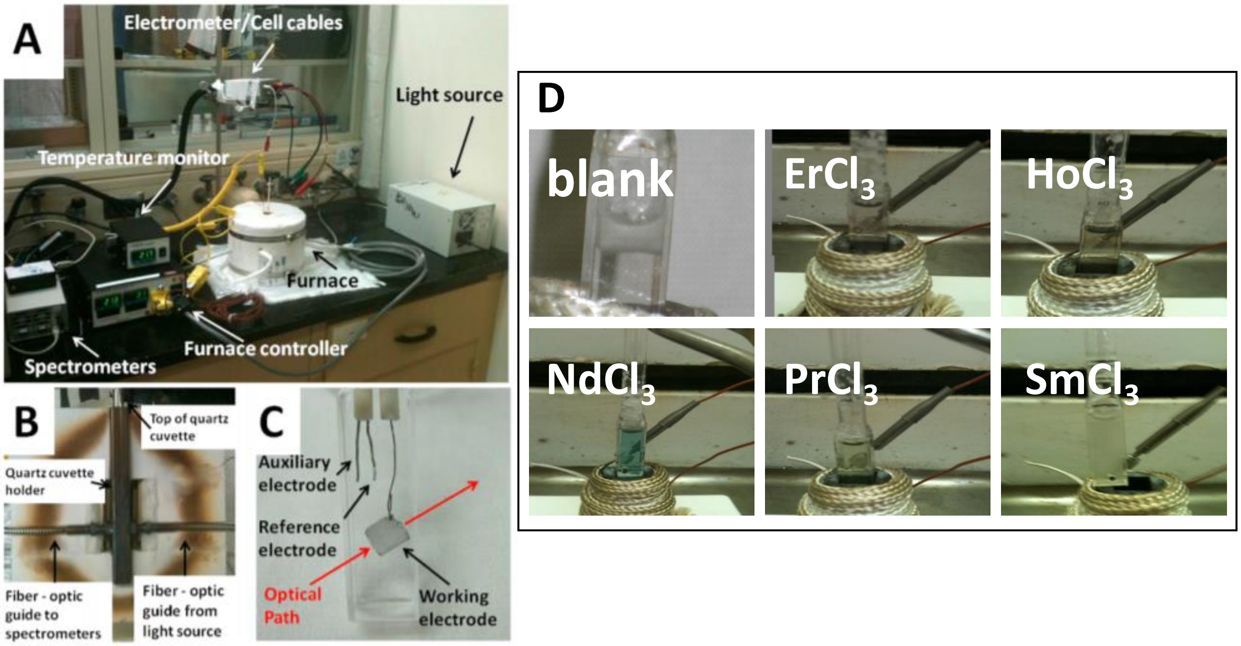

Figure 2-7. The spectroelectrochemistry setup design, relying on UV-vis absorbance spectroscopy (A), with a picture of the cross section of the furnace/cell holder (B), and molten salt cell with electrodes in place (C), along with pictures of melts containing lanthanides (D). From Schroll et al. [5]

Following this demonstration, the PNNL team modified the spectroelectrochemical setup to allow for simultaneous UV-vis and Raman interrogation of the salt. Additional flexibility was incorporated around electrode setup, integrating new micro-reference electrodes for added stability during electrochemical oxidation state control. For the purposes of actinide characterization, UV-vis can provide invaluable insight into the presence of species such as U^{3+} and U^{4+} while Raman can support any characterization of polyatomic species (e.g. UO_2 or potentially complexes with corrosion or fission products) that could form under non-ideal conditions. Figure 2-8 presents schematics of the modified system. This system is being further modified by the PNNL team to enhance efficiency, safety, and control of molten salt characterization experiments. Additionally, the system is being transferred to an inert box. These modifications and location change will allow for the collection of optical fingerprints that accurately capture the conditions anticipated within molten salt systems.

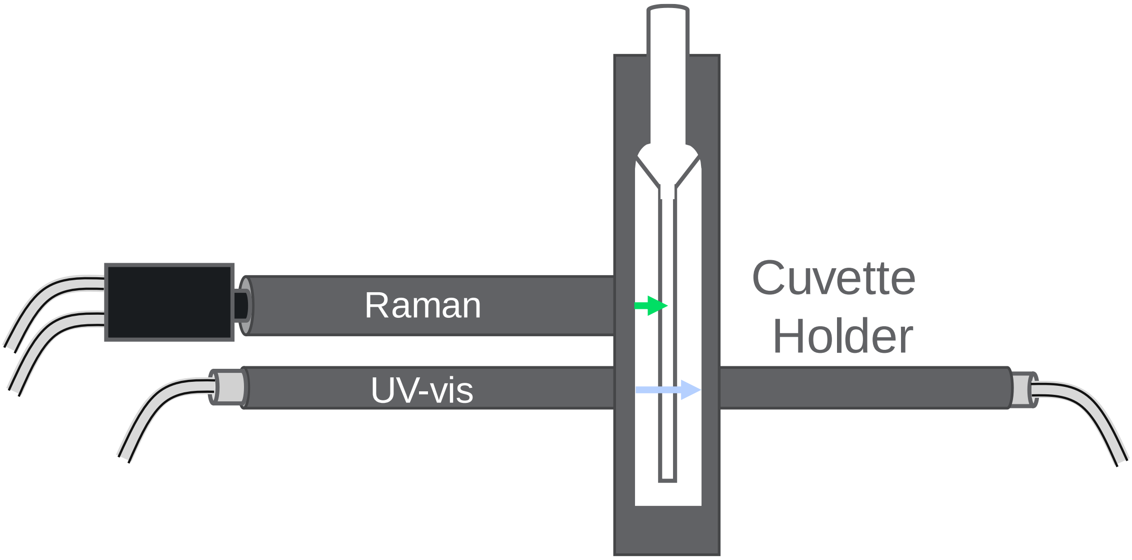

Figure 2-8. Schematic of modified cell characterization setup, allowing for both UV-vis absorbance and Raman spectral interrogation

These small-scale systems allow for *in situ* characterization of 2-4 g of salt, where salt is housed in a fused silica cell. The utilization of the fused silica cell limits studies to chloride-based salt melts. Cells that can support characterization of fluoride-based systems are needed, where PNNL is exploring design options. A key limiting feature is optical window material choice. The fluoride and chloride-based salt melts exhibit different corrosive properties, where fused silica is an example of a material that can work for Cl but not F systems. Literature suggests a variety of optical window materials could be utilized to effectively enable interrogation of both fluoride and chloride-based salts. Table 2-1 below includes a list of potential materials. Under previous studies, the PNNL team has tested compatibility of several of these window materials, including sapphire and diamond. Enabling small-scale system characterization can greatly enhance the ability to complete scoping studies and characterize optical fingerprints of target analytes on shorter time scales with limited salt waste generation.

Note, while PNNL investigations to date have primarily focused on small scale studies utilizing the systems pictured in the figures above, methods to engineer probes into MSR systems are needed. Again, materials considerations are key, with window materials and sealing mechanisms representing some of the largest challenges. These engineering challenges vary with integration method, with immersion probes providing possibly the most diverse application options. Engineering, testing, and deploying these probes is a technology gap currently being addressed by the PNNL team.

Table 2-1. Important properties of some common glasses ranked by glass transition temperature (T_g), annealing temperature (T_a), working temperature (T_w), or melting temperature (T_m), denoted by the letter in parenthesis next to the temperature [denoting subscript of label, e.g., (g) is used for T_g]. This table was taken from [39].

Material	**$T_g/T_a/T_w/T_m$ (°C)**	**Rupture Modulus (MPa)(a)**	**Transmission Range (µm)**	**Potential Coolant Compatibility Issues(b)**	**References**
CVD Diamond	4,027 (m)	200–1000	0.225–200		[40]; [41]; [42]
Magnesium Oxide (MgO)	2,800 (m)	105	0.3–6		[43]
ALON ($Al_{23}O_{27}N_5$)	2,150 (m)	379	0.22–5		[44]
Spinel ($MgAl_2O_4$)	2,135 (m)	170	0.25–6.5	MS?	[45]
Sapphire (Al_2O_3)	2,040 (m)	448	0.17–5	SCW	[46]; [47]
YAG ($Y_3Al_5O_{12}$)	1,940 (m)	350	0.25-5		[48]; [43]
Zinc Sulfide Cleartran	1,827 (m)	69	0.4–12		[49]
Zinc Selenide (ZnSe)	1,520 (m)	55	0.55–18		[49]
Calcium Fluoride (CaF_2)	1,418 (m)	37	0.13–10		[50]; [49]
Silicon (Si)	1,412 (m)	124	1.2–10	Na, MS, SCW	[49]
Barium Fluoride (BaF_2)	1,354 (m)	26	0.15–12.5		[50]; [51]; [49]
Magnesium Fluoride (MgF_2)	1,255 (m)	49	0.11–7.5		[49]
Gallium Arsenide (GaAs)	1,238 (m)	72	1–15		[50]; [49]
Fused Silica(c)	1,185 (g)_	49	0.25–3.5	SCW, Na	[49]
Cadmium Telluride (CdTe)	1,092 (m)	22	1–25		[50]; [49]
Vycor Glassware	1,020 (a)	41	0.2–2.6		[52]; [42]
Germanium (Ge)	937 (m)	104	2–17		[49]
Lithium Fluoride (LiF)	870 (m)	11	0.12–8.5		[49]
Aluminosilicate	721 (a)	11	0.25–2.8		[53]
Cesium Iodide (CsI)	632 (m)	6	0.25–55		[50]; [49]
ZERODUR	600 (w)	43	0.4–2.5		[54]; [50]; [55]
Pyrex 7740	560 (g)	69	0.28–2.7		[56]
BK7 Schott	557 (g)	17	0.35–2		[57]
AFO Fabry-Pérot -35	527 (g)		0.40–0.85, 1.10–2.50		[58]
Borofloat 33	525 (g)	25	0.28–2.75		[59]
ZBLAN	260 (g)	>600	0.32–4.0		[60]; [61]
Chalcogenides	185–368 (g)	17–19	0.7–12.5		[62]; Schott (2013b); [63]

(a)Rupture modulus is also commonly known as flexure or bending strength. Not specified for all materials.

(b)Known chemical incompatibility with AdvSMR coolants and chemistries. Listed categories include supercritical water = SCW, high temperature gas = He, molten sodium = Na, molten lead = Pb, molten salt = MS.

(c)Fused silica, fused quartz, and silica are commonly interchangeable terms.

3. ROAD MAP FOR ON-LINE MONITORING DEVELOPMENT

An online monitoring system to support chemical composition analysis and MC&A within MSRs will require development. Figure 3-1 shows the general strategy for the systematic development and testing of a monitoring system capable of meeting the MC&A needs of molten salt reactor materials. This section describes the various tasks associated with this roadmap, and the specific elements supporting each task. The section below describes the activities and tasks associated with the advancements.

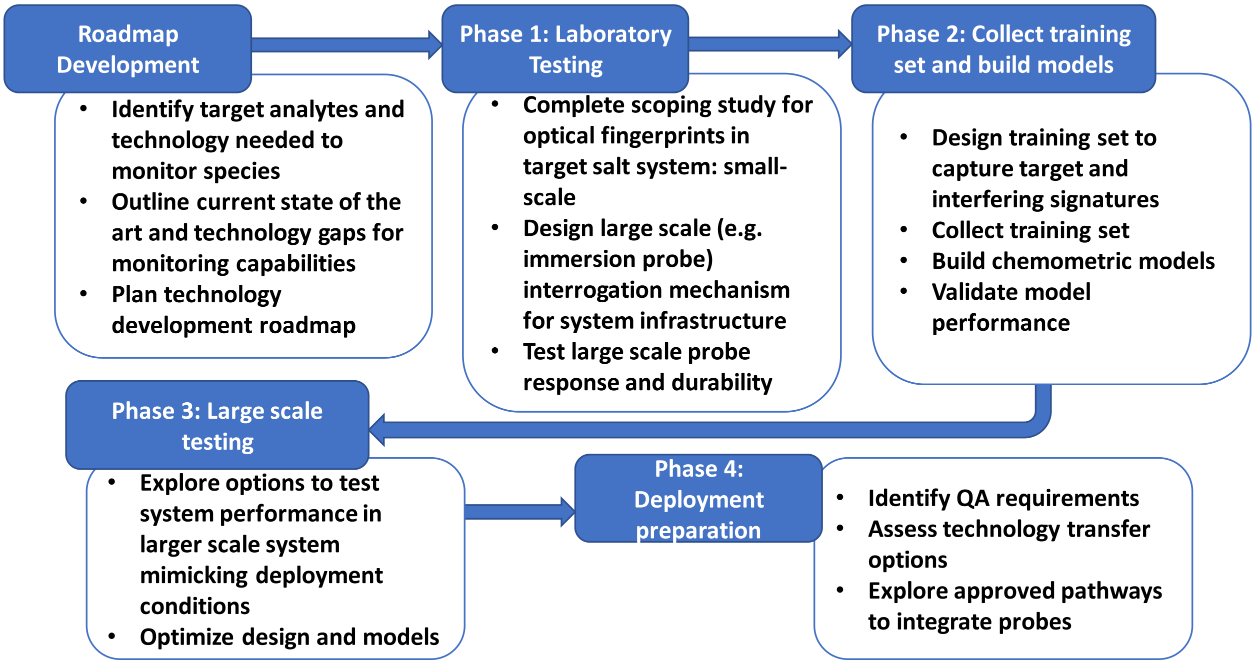

Figure 3-1. Roadmap for on-line monitoring technology development

Roadmap development:

This report summarizes target analytes and technology needed to monitor species and serves as a technology development roadmap. For safeguard concerns, the initial metals considered for MC&A purposes include U, [7] Pu, [21, 32, 33] and Np.[36]

These metals have been measured spectroscopically in their respective various oxidation states, which allows for the direct measurement of the relative contribution of the various redox species present. While all redox species are measurable using optical spectroscopic methods, the relative sensitivity of each of these species differ for each element, requiring effort to determine the level of detection for each analyte, and a combined level of detection for the sum of all redox species.

Technology gaps have been identified and focus primarily on the probes and sensors utilized in contact with the salt systems. In the case of many optical approaches, including UV-vis and Raman spectroscopy, instrumentation such as detectors and lights sources are already commercially available. While some optimization of detector specifications may be required to meet monitoring needs, much of this can be readily completed by vendors.

Phase 1: Laboratory Testing and Development

The first phase of testing and development will involve a scoping study for optical fingerprints in target salt systems on the laboratory scale (small scale). The small-scale testing will utilize methods that have been employed and found successful in past research studies. Initial measurements will establish a database of fingerprints for the various redox state metal signatures within molten salt systems.

Optical probes for large-scale molten salt systems are not currently commercially available and will be a second focus of phase 1 testing and development efforts. It should be noted that a wide variety of probes have been designed for a wide variety of applications within large-scale chemical processes. As an example, immersion probes have been designed for other systems with harsh conditions including high corrosivity or high pressure. These designs can be found commercially but will need to be modified to withstand the molten salt environment. This includes carefully selecting materials including metal body, optical window, and metal-window seal. The PNNL team is already working with a small business partner to design and build molten salt probes.

A final component of phase 1 activities is the testing of the large-scale probe before comprehensive signature collection to ensure the design can provide the needed interrogation capabilities within the salt over extended exposure to the salt conditions.

Phase 2: Collect Training Set and Model Building

Phase 2 testing incorporates the systematic collection and spectroscopic measurement of the training set to be utilized in building the chemometric models for quantitative measurement of metals within molten salt systems. The design of the training set to capture target and interfering signatures is an integral feature to ensure the span of concentrations of key analytes, each of which are represented in their respective redox states, are included. Additionally, interferents or species known or expected to interact with key analytes causing spectral changes, will also be included within the training set matrix.

The analytical analysis packages are possibly the most important aspect of an on-line monitoring system. These are composed of algorithms that enable the real-time transformation of data into information and are key for implementing and effectively utilizing on-line monitoring for MC&A or control purposes. While the technology to develop algorithms is commercially available, significant work is required to collect optical training sets and build associated chemometric models. This activity represents the largest cost and time commitment need for the development of on-line monitoring capabilities for MSRs.

The validation of the chemometric models developed under this phase is extremely important, as it offers an independent verification of the reliability and effectiveness of the models. Validation of models is performed by using independently measured molten salt samples containing the expected complexity in the designed system.

It is also valuable to keep in mind that while instrumentation or even probes can be optimized for multiple salt types (e.g. chloride or fluoride based) analytical analysis tools will be salt specific. Fingerprints of target species such as U or Pu as well as interfering corrosion or fission products will vary with salt matrix. Therefore, unique training sets and chemometric models need to be built for different salt systems and optimized for the anticipated conditions within the given process.

Phase 3: Large Scale Testing

Large scale testing in Phase 3 encompasses methods for integrating probes into salt systems. This step will require an industry partner and integration pathways vary depending on where in the loop/system probes are being placed. This phase will explore options in larger scale systems mimicking deployment conditions using the optimized design and models.

Note this phase will involve demonstrating ability to follow key chemical species on an industrially representative scale. In the case of highly radiotoxic transuranic elements (Np, Pu, Am, and Cm), this will have a significant cost associated with testing.

Phase 4: Deployment Preparation

This phase will identify and assign QA requirements, assess technology transfer options, and explore approved pathways to integrate probes. A high-level example of the development steps required to build an on-line monitoring system for a given salt system is shown in Figure 3-1. Time required for each step will depend on funding levels as well as determined requirements for quality assurance. Note, the assumption is that development will occur under basic science QA levels to advance technical readiness level (TRL) positioning. The determination of needed QA levels and building to meet those levels will occur after initial demonstrations of applicability and value.

4. CONCLUSIONS AND NEXT STEPS

This report summarizes the current state-of-the-art regarding optical interrogation of molten salts, key technology gaps, and outlines a road map for developing spectroscopy-based on-line monitoring technology for MC&A of MSRs. Section 2 describes available technologies that can be adapted for MC&A of the molten salt environment. One of the most promising technologies is optical spectroscopy, which has already been utilized to interrogate molten salts *in situ* and can form the basis for reactor materials control and accountability. Optical spectroscopy can provide information that not only supports MC&A, but reactor operation and control as well. This technology has the potential to enable the identification and quantification of fuel components (assuming a molten fuel MSR), fission products, and corrosion products. Of the optical techniques discussed, absorbance spectroscopy utilizing UV-vis and NIR has been extensively utilized in MSR related systems due to the richness of lanthanide and actinide active bands observed for all oxidation states of the related metal species. Raman spectroscopy is also utilized but is limited to those metal complexes exhibiting Raman active bands, and thus has a more limited utility. Fluorescence spectroscopy has also been demonstrated on a limited scale yet promises to be a useful technique due to its high sensitivity and selectivity.

Specific systems measured includes the quantitative determination of mixtures of lanthanides chloride salts in a molten salt systems using the absorbance spectroscopy technique.[3] This demonstrated the principle of using multivariate chemometric approach for the measurement of multiple species within a molten salt system containing highly overlapping and interfering absorbance bands. Additionally, this was further extended by coupling electrochemistry with the spectroscopic method in the combined spectroelectrochemical approach where fundamental parameters such as diffusion coefficients and formal redox potentials were determined.[4-6]

Many of the measurements of actinides in melts have been more focused on fundamental characterization as opposed to on-line monitoring application development. Much of the focus falls around the need to control the U(III)/U(IV) ratio within the salt melt; a key factor in controlling the extent of corrosion of the structural materials. This oxidation state control can be accomplished or effectively characterized using electrochemistry as well as optical spectroscopy. [19-21] Using spectroelectrochemistry and following the change in spectroscopic signature in a molten salt system containing uranium, the species U^{3+}, U^{4+}, UO_2^{+}, and UO_2^{2+} were each individually observed as unique UV-vis signatures. Other key actinides including Pu and Np have been discussed to a limited extent within molten salt systems. Electrochemical studies of Pu have been performed in molten salts looking at the $Pu^{0/3+}$ redox reaction.[21, 32, 33] Neptunium has been studied in molten salts using spectroelectrochemical methods due to its UV-vis optical signature, [36-38] with the changes in the UV-vis spectrum as Np(IV) is electrochemically reduced to Np(III) in a LiCl-KCl eutectic melt.[36] These optical fingerprints can be used to quantitatively measure Np in the molten salt system and determine its oxidation state.

Raman spectroscopy has been demonstrated on a semi-quantitative basis using the UO_2^{2+} moiety which has a Raman signal based on the uranyl O=U=O symmetric stretch at ~850 cm^{-1} in molten chloride salts, compared to ~880 cm^{-1} in aqueous solution.[26] This band position is variable in molten chloride systems (between 830-870 cm^{-1}) depending on the alkali-chloride salt composition.[8] This Raman signature could be a useful tool in determining the oxidation state of U within the melts as well as subtle compositional changes to the alkali-chloride molten salt environment.

A modified spectroelectrochemical setup containing both UV-vis and Raman probes for the interrogation of molten salt systems has been recently developed at PNNL for the purpose of actinide characterization. UV-vis spectroscopy can provide invaluable information on the presence and concentration of species such as U^{3+} and U^{4+} while the Raman can support the characterization of polyatomic species (e.g. UO_2 or potentially complexes with corrosion or fission products) that could form under non-ideal conditions. These small-scale systems allow for *in situ* characterization of 2-4 g of molten salt materials. The current design utilizes a sample cell composed of fused silica. The fused silica cell limits studies to chloride-based salt melts. It is acknowledged that cells supporting characterization of fluoride-based systems are needed. A key limiting feature is optical window material choice. PNNL is exploring optical material design options for sample cells.

Finally, Section 3 describes a roadmap containing a pathway for developing a molten salt safeguards approach to support chemical composition analysis and MC&A within MSRs. This roadmap contained in Section 3 shows the general strategy for the systematic development and testing of a monitoring system capable of meeting the MC&A needs of molten salt reactor materials. This section describes the various tasks associated with this roadmap, and the specific elements supporting each phase of development.

- Laboratory Testing and Development: The elements of this task include 1) testing and development through scoping studies for optical fingerprints in target salt systems on the laboratory scale (small scale); 2) development of optical probes for large-scale molten salt systems; and 3) the testing of the large-scale probe to ensure the design performs over the extended exposure to the salt conditions.
- Collect Training Set and Model Building: This testing involves 1) the systematic collection and spectroscopic measurement of the training set to be utilized in building the chemometric models for quantitative measurement of metals within molten salt systems; 2) developing the models and algorithms that enable the real-time transformation of data into information, which is essential for implementing and effectively utilizing on-line monitoring for MC&A or control purposes, and 3) validation of the chemometric models developed.
- Large Scale Testing: This phase will require an industry partner/collaboration to explore options in larger scale systems mimicking deployment conditions using the optimized design and models.
- Development Preparation: This stage will identify and assign QA requirements, assess technology transfer options, and explore approved pathways to integrate probes.

REFERENCES

1. Serp, J.; Allibert, M.; Beneš, O.; Delpech, S.; Feynberg, O.; Ghetta, V.; Heuer, D.; Holcomb, D.; Ignatiev, V.; Kloosterman, J. L.; Luzzi, L.; Merle-Lucotte, E.; Uhlíř, J.; Yoshioka, R.; Zhimin, D., The molten salt reactor (MSR) in generation IV: Overview and perspectives. *Progress in Nuclear Energy* **2014,** *77*, 308-319.

2. Delpech, S., 24 - Molten Salts for Nuclear Applications. In *Molten Salts Chemistry*, Lantelme, F.; Groult, H., Eds. Elsevier: Oxford, 2013; pp 497-520.

3. 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. *Anal Methods-Uk* **2016,** *8* (43), 7731-7738.

4. 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. *J Electrochem Soc* **2017,** *164* (8), H5345-H5352.

5. 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.

6. 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

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), 1-6.

8. 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. *Inorganic Chemistry* **2008,** *47* (17), 7474-7482.

9. 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.

10. Bryan, S. A.; Levitskaia, T. 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. *Radiochim Acta* **2011,** *99* (9), 563-571.

11. 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. *Ind Eng Chem Res* **2019,** *58* (47), 21194-21200.

12. Lines, A. M.; Hall, G. B.; Sinkov, S. I.; Levitskaia, T.; Gallagher, N. B.; Lumetta, G. J.; Bryan, S. A., Overcoming oxidation state dependent spectral interferences: On-line monitoring of U(VI) reduction to U(IV) via Raman and UV-vis spectroscopy *Ind. Eng. Chem. Res.* **2020,** *59*, 8894-8901.

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.

14. 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 Sensors* **2020**.

15. Lines, A. M.; Adami, S. R.; Sinkov, S. I.; Lumetta, G. J.; Bryan, S. A., Multivariate Analysis for Quantification of Plutonium(IV) in Nitric Acid Based on Absorption Spectra. *Anal Chem* **2017,** *89* (17), 9354-9359.

16. 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.

17. Nelson, G. L.; Asmussen, S. E.; Lines, A. M.; Casella, A. J.; Bottenus, D. R.; Clark, S. B.; Bryan, S. A., Micro-Raman Technology to Interrogate Two-Phase Extraction on a Microfluidic Device. *Anal Chem* **2018**.

18. Nelson, G. L.; Lines, A. M.; Casella, A. J.; Bello, J. M.; Bryan, S. A., Development and testing of a novel micro-Raman probe and application of calibration method for the quantitative analysis of microfluidic nitric acid streams *submitted* **2017**.

19. Kim, G.-Y.; Yoon, D.; Paek, S.; Kim, S.-H.; Kim, T.-J.; Ahn, D.-H., A study on the electrochemical deposition behavior of uranium ion in a LiCl–KCl molten salt on solid and liquid electrode. *Journal of Electroanalytical Chemistry* **2012,** *682*, 128-135.

20. Prabhakara Reddy, B.; Vandarkuzhali, S.; Subramanian, T.; Venkatesh, P., Electrochemical studies on the redox mechanism of uranium chloride in molten LiCl–KCl eutectic. *Electrochim Acta* **2004,** *49* (15), 2471-2478.

21. Shirai, O.; Iwai, T.; Suzuki, Y.; Sakamura, Y.; Tanaka, H., Electrochemical behavior of actinide ions in LiCl–KCl eutectic melts. *Journal of Alloys and Compounds* **1998,** *271-273*, 685-688.

22. 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. *J Nucl Sci Technol* **2005,** *42* (12), 1025-1031.

23. Nagai, T.; Fujii, T.; Shirai, O.; Yamana, H., Study on Redox Equilibrium of UO2 2+/U2 + in Molten NaCl-2CsCl by UV-Vis Spectrophotometry. *Journal of Nuclear Science and Technology* **2004,** *41* (6), 690-695.

24. Lambert, H.; Kerry, T.; Sharrad, C. A., Preparation of uranium(III) in a molten chloride salt: a redox mechanistic study. *J Radioanal Nucl Ch* **2018,** *317* (2), 925-932.

25. Cho, Y. H.; Kim, T.-J.; Bae, S. E.; Park, Y. J.; Ahn, H. J.; Song, K., Electronic absorption spectra of U (III) ion in a LiCl–KCl eutectic melt at 450°C. *Microchemical Journal* **2010,** *96* (2), 344-347.

26. Lines, A. M.; Hall, G. B.; Sinkov, S.; Levitskaia, T.; Gallagher, N.; 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**.

27. Fujii, T.; Uda, T.; Iwadate, Y.; Nagai, T.; Uehara, A.; Yamana, H., Raman spectroscopic study of uranyl complex in alkali chloride melts. *Journal of Nuclear Materials* **2013,** *440* (1), 575-579.

28. Im, H. J.; Yeon, J. W., Comparison of the spectroscopic characteristics of uranium status when U (III) in LiCl-KCl eutectic melt is leached out with water and ionic liquid. *J Lumin* **2018,** *196*, 302-305.

29. Liu, Y.-C.; Liu, Y.-L.; Wang, L.; Zhong, Y.-K.; Li, M.; Han, W.; Zhao, Y.; Zhou, T.; Zou, Q.; Zeng, X.; Shi, W.-Q., Uranium chemical species in LiCl-KCl eutectic under different conditions for the dissolution of U3O8. *Journal of Nuclear Materials* **2020**, 152475.

30. Sihn, Y.; Yun, J.-I.; Lee, W., Laser spectroscopic characterization and quantification of uranium(VI) under fluorescence quenching by Fe(II). *J Radioanal Nucl Ch* **2016,** *308* (2), 413-423.

31. Lee, J.-Y.; Oh, J. Y.; Putri, K. Y.; Baik, M. H.; Yun, J.-I., Redox behaviors of Fe(II/III) and U(IV/VI) studied in synthetic water and KURT groundwater by potentiometry and spectroscopy. *J Radioanal Nucl Ch* **2017,** *312* (2), 221-231.

32. Serp, J.; Konings, R. J. M.; Malmbeck, R.; Rebizant, J.; Scheppler, C.; Glatz, J. P., Electrochemical behaviour of plutonium ion in LiCl–KCl eutectic melts. *Journal of Electroanalytical Chemistry* **2004,** *561*, 143-148.

33. Bourgès, G.; Lambertin, D.; Rochefort, S.; Delpech, S.; Picard, G., Electrochemical studies on plutonium in molten salts. *Journal of Alloys and Compounds* **2007,** *444-445*, 404-409.

34. Lines, A. M.; Adami, S. R.; Casella, A. J.; Sinkov, S. I.; Lumetta, G. J.; Bryan, S. A., Electrochemistry and Spectroelectrochemistry of the Pu (III/IV) and (IV/VI) Couples in Nitric Acid Systems. *Electroanal* **2017,** *29* (12), 2744-2751.

35. Kim, S. Y.; Asakura, T.; Morita, Y., Electrochemical and spectroscopic studies of Pu(IV) and Pu(III) in nitric acid solutions. *J Radioanal Nucl Ch* **2013,** *295* (2), 937-942.

36. Polovov, I. B.; Sharrad, C. A.; May, I.; Vasin, B. D.; Volkovich, V. A.; Griffiths, T. R., Spectroelectrochemical Study of Uranium and Neptunium in LiCl-KCl Eutectic Melt. *ECS Transactions* **2007,** *3* (35), 503-511.

37. Kim, D.-H.; Park, T.-H.; Bae, S.-E.; Lee, N.; Kim, J.-Y.; Cho, Y.-H.; Yeon, J.-W.; Song, K., Electrochemical preparation and spectroelectrochemical study of neptunium chloride complexes in LiCl–KCl eutectic melts. *J Radioanal Nucl Ch* **2016,** *308* (1), 31-36.

38. Uehara, A.; Nagai, T.; Fujii, T.; Shirai, O.; Yamana, H., Spectrophotometric and electrochemical study of neptunium ions in molten NaCl–CsCl eutectic. *Journal of Nuclear Materials* **2013,** *437* (1), 166-170.

39. Anheier, N.; Suter, J.; Qiao, A.; Andersen, E.; Berglin, E.; Bliss, M.; Cannon, B.; Devanathan, R.; Mendoza, A.; Sheen, D. *Technical Readiness and Gaps Analysis of Commercial Optical Materials and Measurement Systems for Advanced Small Modular Reactors*; PNNL-22622, Rev. 1, SMR/ICHMI/PNNL/TR-2013/04; Pacific Northwest National Laboratory: Richland, WA, 2013.

40. Diamond Materials The CVD Diamond Booklet. http://www.diamond-materials.com/downloads/cvd_diamond_booklet.pdf (accessed May 29).

41. Infrared, I.-V., CVD Diamond Substrates. II-VI Infrared: 2010; p 4.

42. MatWeb MatWeb Material Property Data. http://www.matweb.com/index.aspx (accessed May 29).

43. Crystran CRYSTRAN - UV - Visible - IR Specialist Optics. http://www.crystran.co.uk/ (accessed June 10).

44. Surmet ALON Optical Ceramic. http://www.surmet.com/technology/alon-optical-ceramics/index.php (accessed May 30).

45. Surmet Spinel Optical Ceramic. http://www.surmet.com/technology/spinel/index.php (accessed May 30).

46. Duffey, R.; Leung, L. K. H.; Martin, D.; Sur, B.; Yetisir, M., A Supercritical Water-Cooled Small Modular Reactor. In *Proceedings of the ASME 2011 Small Modular Reactors Symposium*, ASME, New York: Washington, D.C., 2011; pp 243-250.

47. ICL Sapphire (Al_2O_3) Optical Crystals. http://www.internationalcrystal.net/optics_13.htm# (accessed May 30).

48. Koechner, W., Rupture Stress and Modulus of Elasticity for Nd:YAG Crystals. *Applied Physics* **1973,** *2* (5), 279-280.

49. Tosi, J. L. Common Infrared Optical Materials: A Guide to Properties and Applications. http://photonics.com/edu/Handbook.aspx?SID=29&AID=25495 (accessed May 30).

50. ISP, ISP Optics Infrared Catalog. ISP Optics: Irvington, New York., 2002; p 108.

51. Optics, A. Optical Materials. http://www.almazoptics.com (accessed May 30).

52. SGP SGP Specialty Glass Products. http://www.sgpinc.com/materials.htm (accessed May 30).

53. Prazisions Prazisions Glas & Optik. http://www.pgo-online.com/index.html (accessed May 30).

54. Russell, R. *Zerodur*; University of Arizona: Tucson, Arizona, 2011.

55. Lithotec, S. ZERODUR. http://www.sydor.com/pdfs/Schott_zerodur.pdf (accessed May 30).

56. Valley Design Substrates and Wafers. www.valleydesign.com (accessed May 30).

57. Schott *Optical Glass Data Sheets*; Schott North America, Inc.: Duryea, Pennsylvania, 2013.

58. Kigre Leaders in Solid State Laser Components. http://kigre.com/ (accessed June 10).

59. Technologies, A., Specialty Glass Technical Capabilities 11/12. Abrisa Technologies: Santa Paula, California, 2012.

60. FiberLabs Fluoride Fiber (FF). http://www.fiberlabs-inc.com/fluorideFiber.htm (accessed May 30).

61. Zhu, X.; Peyghambarian, N., High-Power ZBLAN Glass Fiber Lasers: Review and Prospect. *Advances in OptoElectronics* **2010**.

62. Schott Infrared Chalcogenide Glasses. http://www.us.schott.com/advanced_optics/english/products/optical-materials/ir-materials/infrared-chalcogenide-glasses/index.html (accessed May 30).

63. Vitron IR Glasses. http://www.vitron.de/english/ (accessed May 30).