ANL/CFCT-23/50

Report for the US Department of Energy, Office of Nuclear Energy

Molten Salt Reactor Fuel Cycle Chemistry Workshop

September 19-21, 2023
Hosted by Argonne National Laboratory

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Abbreviations, Acronyms and Initialisms

ART	Advanced Reactor Technology
DOE NE	Department of Energy Office of Nuclear Energy
DSC	Differential Scanning Calorimetry
FRD	Future Research Direction
FSF	Fundamental Safety Function
GAIN	Gateway for Accelerated Innovation in Nuclear
HALEU	High Assay Low Enriched Uranium
IAEA	International Atomic Energy Agency
INL	Idaho National Laboratory
LEU	Low-Enriched Uranium
LLFP	Long-Lived Fission Product
LWR	Light Water Reactor
MBA	Material Balance Area
MC&A	Materials Control and Accountancy
MCRE	Molten Chloride Reactor Experiment
MOX	Mixed Oxide
MSR	Molten Salt Reactor
NA-22	Office of Defense Nuclear Nonproliferation Research and Development
NDA	Non-Destructive Analysis
NEAMS	Nuclear Energy Advanced Modeling and Simulation
NE-43	Office of Materials and Chemical Technology
NE-4	Office of Nuclear Fuel Cycle and Supply Chain
NE-5	Office of Reactor Fleet and Advanced Reactor Deployment
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
TRL	Technological Readiness Level
UKNNL	United Kingdom National Nuclear Laboratory
UNF	Used Nuclear Fuel

Executive Summary

Deploying commercial molten salt reactors (MSRs) requires closing technological gaps associated with supplying fuel salt, maintaining fuel salt, and dispositioning used fuel salt at the end of a reactor campaign and operation. A workshop was held to identify the technological gaps in synthesizing, purifying, and supplying fuel salts and recovering and recycling resource materials from used fuel. Issues addressed during the workshop included:

- *Conversion of a variety of fuel sources to salt:* Fuel sources for MSRs may include uranium, thorium, or plutonium as fresh or used fuels and may come in metal or oxide forms. Synthesis processes for producing salts from a variety of materials were discussed.

- *Fresh fuel salt purification technology:* Molten salt is readily contaminated during synthesis by corrosion and exposure to oxygen or water, and this contamination can impact its performance as a fuel. Technologies for removing oxygen, water, and trace metal impurities from molten chloride and fluoride fuels were discussed.

- *Scale-up of fuel synthesis, packaging, and delivery:* Large quantities of salt must be synthesized, packaged, and delivered to deployed MSRs. Efforts to scale salt synthesis and packaging requirements to ensure that delivered salt has not become contaminated were discussed.

- *Fuel salt characterization and qualification:* Reactor fuels must be characterized, and properties must be demonstrated to satisfy safety functions before use in a reactor. Acceptable levels of contamination and qualification requirements remain to be determined. Methods for characterizing molten salt for the purposes of material accountancy and fuel qualification were discussed.

- *Technologies for recovering actinides:* A significant portion of the actinide inventory of a molten salt fuel will remain unreacted as fission products build up in the fuel. Electrochemical, chemical, and physical methods of recovering fissile actinides from used molten salt fuel were discussed.

- *Used fuel salt purification for recycle:* Contaminants, including fission products, corrosion products, oxygen, and moisture, will accumulate in molten salt during use in a reactor. Removing these contaminants will extend the lifetime of the fuel and may be done on-line, in-line, at-line, or off-line. Recycling purified base salt back to the reactor would significantly decrease waste volumes relative to direct disposal. Methods for removing fission products and other impurities from molten salts were discussed.

- *Recovery and transmutation of long-lived isotopes:* Long-lived isotopes in used nuclear fuel extend the time used fuel will be more radioactive than background levels. Technologies for recovering long-lived isotopes from used molten salt fuels and the use of MSRs to transmute long-lived fission products were discussed.

- *Noble metal and insoluble fission product recovery:* Noble metals and insoluble fission products form precipitates in the molten salt fuel during its use in an MSR. The anticipated behavior of these elements and technologies for the removal of these insoluble species from molten salt fuel were discussed.

- *Safeguarding liquid fuels and fuel cycle facilities:* Molten salt fuels are potentially more vulnerable to diversion than other fuel types while in use due to the fluid nature of the fuels. This presents unique challenges for safeguarding the radionuclide inventory of a reactor. Approaches to safeguarding the production, storage, and shipment of fresh MSR fuel salt, as well as the recycle and treatment of used MSR fuel salt, were discussed, including issues related to on-site and/or on-line fuel purification that is planned by many MSR developers.

The above issues formed the basis for nine workshop sessions. Salt waste forms and corrosion and material selections for reactors were considered outside the scope of this workshop. Sessions consisted of presentations on the current state of technology by experts in each area, a question and answer period, and an extended open discussion during which research needs were identified. These research needs were collected into the future research directions (FRDs) listed here:

FRD 1: Develop and Demonstrate Efficient and Scalable Synthesis Processes

FRD 2: Understand the Impact of Impurities on Molten Salts

FRD 3: Optimize and Demonstrate Separation Technologies for Removing Impurities from Molten Salts

FRD 4: Develop Salt Chemistry Monitoring and Control Technologies

FRD 5: Adapt and Optimize Actinide Separation Technologies to Chloride and Fluoride Salts

FRD 6: Develop Technologies to Remove Fission Products from Chloride and Fluoride Salts

FRD 7: Understand the Behavior of Insoluble Fission Products in Molten Salts

These FRDs encompass research necessary to successfully deploy MSRs and support fuel cycle facilities. Some FRDs address fuel salt issues relevant during reactor operation, such as FRDs 2 and 7, and some address fuel cycle issues, such as FRDs 1, 3, 5, and 6. FRD 4 addresses safeguarding challenges that will be relevant both in a reactor and at fuel cycle facilities. Investigations addressing fuel behavior relevant to reactor operation are being conducted under the US Department of Energy Office of Nuclear Energy's Advanced Reactor Technology Program's MSR campaign. Based on presentations and discussions held during this workshop, it is recommended that research addressing molten salt fuel cycle chemistry and technologies that is described as parts of FRDs 1, 3, 5, and 6 be initiated and the impactful research addressing issues described in FRDs 2 and 7 that is underway be continued to enable deployment of MSRs.

1. Introduction

1.1. Workshop Introduction

As MSRs move from concept to design and on to pilot scale demonstrations, there is a need to establish a supply chain for molten salt fuels and develop a recycle or disposition pathway for used molten salt fuels. Recent examples of this shift from concept to pilot scale facilities include Kairos Power's Hermes Test Reactor and TerraPower's Molten Chloride Reactor Experiment (MCRE) project. The US Department of Energy (DOE) Office of Nuclear Energy currently supports the deployment of these reactor concepts through the Advanced Reactor Technology (ART) campaign, providing measurements of fundamental data on molten salts and materials, and through the Nuclear Energy Advanced Modeling and Simulation (NEAMS) campaign, providing modeling and simulation tools to support reactor design and licensing. There is a need to support the development of a fuel cycle for MSRs, including a fuel supply chain, recycling or separations technologies and a disposition path for molten salt fuels.

The DOE Office of Materials and Chemical Technology (NE-43) currently supports the development of fuel cycle technologies for several fuel types, including oxide, metal, and coated fuels. NE-43 seeks to support the MSR industry in developing MSR fuel cycle technologies by adapting existing technologies to molten salt fuels and supporting the development of any necessary new technologies. A three-day DOE-sponsored workshop, the *Molten Salt Reactor Fuel Cycle Chemistry Workshop*, was held to identify technological gaps in synthesizing, purifying, and supplying molten salt fuels and in recovering and recycling resource materials from used fuel. The overall goal of the workshop was to identify technological gaps, specific research needs, and future research directions to close those gaps. The goal of NE-43 is to develop a set of separation technologies that MSR developers can draw upon to build their fuel cycle strategies. In addition, an ambition for the workshop was to identify existing fuel cycle-related technologies that could be applied to molten salts and increase collaboration between the DOE Office of Nuclear Fuel Cycle and Supply Chain (NE-4) and the DOE Office of Reactor Fleet and Advanced Reactor Development (NE-5) such that ongoing and future work would be complementary and not redundant.

1.2 Background

Deploying commercial MSRs requires closing technological gaps associated with supplying fuel salt, maintaining fuel salt, and dispositioning used fuel salt at the end of a reactor campaign and operation. Molten salt reactors will require qualified fuels to operate, but sources of MSR fuel salts have not yet been identified. Scalable technologies for chlorination and fluorination of metallic and oxide fuel sources to generate fuel salt are needed. Small amounts of pure fuel salts are currently produced at the laboratory scale in specialized facilities such as gloveboxes for use in salt property measurements or feasibility tests, but there is no commercial capability to produce the large quantities of salt required for fueling an MSR.

Chloride salts for fast spectrum reactors may require the use of ^{37}Cl to avoid generating ^{36}Cl during reactor operation, which is a strong neutron absorber and would reduce the efficiency of the fuel. Likewise, fuel compositions with LiCl or LiF may require the use of reagents made with the stable isotope ^{7}Li instead of neutron-absorbing ^{6}Li to mitigate the generation of tritium. Scalable methods for producing mass quantities of salts with desired isotopes are needed to supply MSRs with fuel.

Molten salt can be readily contaminated by corrosion of containment and production equipment and exposure to atmospheric oxygen or water during synthesis, which can impact operations and fuel performance. Technologies for removing oxygen, water, and trace metal impurities from chloride and fluoride salts are experimental in nature and must be scaled up to purify the quantities of salt needed for the growing MSR industry. After pure salt has been synthesized and purified, it must be properly packaged for delivery to a reactor. Packaging must be compatible with the salt, protect the salt from contamination, and be compatible with the equipment used at the reactor site to load salt into reactor vessels or piping without contamination.

Prior to use in a reactor, reactor fuels must be characterized and demonstrated to meet qualification requirements to be suitable as part of licensing. Acceptable levels of contamination and qualification requirements remain to be determined for molten salt fuels. Methods for characterizing molten salt for purposes of material accountancy and fuel qualification are experimental and should be developed into standard procedures.

In order to license an MSR, there must be a plan in place to disposition used fuel salt. Some developers are targeting a once-through fuel cycle in which used salt fuel is disposed of in a geologic repository. Others plan to reuse the salt, but an end-of-life plan for the disposal of salt must still be developed. Salts are highly reactive to oxygen and water and rapidly convert to highly corrosive oxyfluoride or oxychloride species when contacted by air and are water-soluble. The used fuel salt will need to be stabilized prior to containerization and disposal to limit corrosion. These salt-bearing waste forms must be developed and shown to be effective prior to MSR deployment, as even interim storage is problematic.

Used salt fuels contain activation products, corrosion products, fission products, reusable actinides, and stable radioisotopes such as ^{37}Cl and ^{7}Li. Some developers are proposing limited conditioning of used salt fuels to recover noble gases, noble metals, and rare earth elements. Other developers are considering fully recycling molten salt fuels to include actinide recovery, rare earth element extraction, recycling of the ^{37}Cl or ^{7}Li, and repurification and reuse of the base salt. Technological gaps in these disposition or recycling strategies include efficient separation methods, equipment development, process monitoring and control technologies, and material monitoring technologies.

2. Workshop Organization

The *Molten Salt Reactor Fuel Cycle Chemistry Workshop* was held at Argonne National Laboratory on September 19-21, 2023. Representatives from the US Department of Energy, the Electric Power Research Institute, the US Nuclear Regulatory Commission, and experts from industry, universities, and national laboratories attended. The list of participants is provided in Appendix A.

To ensure good coordination between existing programs, national technical directors for the Molten Salt Reactor campaign, Dr. Patricia Paviet, and the Material Recovery and Waste Form Development campaign, Dr. Ken Marsden, as well as the federal manager for the Material Recovery and Waste Form Development campaign, Dr. James Willit, were in attendance.

The workshop sessions were planned to address both the front and back end of the MSR fuel cycle. The titles of the workshop sessions are listed below and span topics ranging from supplying and qualifying fuel to recovering and recycling fuel. Waste forms and disposal were not addressed in this workshop.

Session 1: Conversion of fuel sources to salt

Session 2: Fresh fuel salt purification technology

Session 3: Scale-up of fuel synthesis, packaging, and delivery

Session 4: Fuel salt characterization and qualification

Session 5: Technologies for recovering actinides

Session 6: Used fuel salt purification for recycle

Session 7: Recovery and transmutation of long-lived isotopes

Session 8: Noble metal and insoluble fission product recovery

Session 9: Safeguarding approaches for liquid fuels and fuel cycle facilities

Workshop sessions consisted of two invited talks followed by a question-and-answer period with the speakers and extended discussions among the participants. The presentations, discussions, and identified technology gaps from each session are described in the session reports in Chapter 3.

Each session report consists of an introduction to the topic, a summary of the current state of research, and the challenges and research needs identified during the session discussions. The specific identified research needs are in bold for emphasis. The identified research needs are also gathered into Table 1 in this chapter. Each session report concludes with a summary and identification of any future research directions, which are indicated in bold italic text.

Future research directions and their potential impact on the deployment of MSRs and MSR fuel cycle facilities are collected in the conclusion of this report. The workshop agenda is provided in Appendix B. Extended abstracts provided by workshop speakers are included in Appendix C.

Table 1: Summary of Issues and Identified Research Needs and Their Impact on MSR Deployment Collected from Session Reports

Session 1: Conversion of Fuel Sources to Salt (From Session Report in Chapter 3.1)		
Issues	**Research Needs**	**Impact**
Fission products and cladding species dissolve into the fuel during the halogenation of used nuclear fuel (UNF). If these species impact the performance of the fuel in the reactor, they need to be removed during synthesis.	Determine the impact of fission products and dissolved cladding material on fuel synthesis and product quality to determine which elements must be removed. Develop processes for removing and capturing gaseous fission products from halogenated UNF.	Using UNF to supply MSR fuel salt will enable rapid deployment of MSRs and a reduction of the national inventory of UNF.
MSR developers need to know the impact of impurities on salt properties to define fuel purity specifications.	Quantify the impact of oxygen, water, and corrosion products on fuel salt performance to establish required composition controls.	Quantifying the impact of contaminants on fuel performance will allow fuel specifications to be defined. Purity specifications determine the required separation efficiency of purification processes.
Strong halogenating agents used to synthesize fuel from metallic sources pose risks to human and environmental safety.	Develop synthesis processes that minimize the number of steps and mitigate the safety hazards of working with strong halogenating species. Optimize liquid-solid exchange reactions to ensure contamination levels are low and high concentrations of actinides can be achieved in the salt flux.	Reducing the risk associated with and complexity of fuel synthesis will lower costs.
It is necessary to control the corrosivity of fuel salts during synthesis. Monitoring and adjusting the ratios of different valence states of actinides can provide this control of redox state.	Demonstrate electrochemical and chemical methods of measuring and adjusting the ratios of different valence species in the salt in both chloride and fluoride salts. Develop a chloride sensor to measure the concentrations of free Cl^- and a fluoride sensor to measure the concentrations of free F^- in the salt.	Controlling the corrosivity of the salt will protect process vessels and reactor materials. Measuring the halobasicity of salts will inform atomic-level models of molten salt behavior, improving predictions of salt properties.

Session 2: Fresh Fuel Salt Purification Technology (From Session Report in Chapter 3.2)

Issues	Research Needs	Impact
Fuel specifications must be defined to ensure salt will function properly as a fuel and coolant.	Quantify the impact of a variety of impurities on fuel performance to determine purity requirements. Determine the solubility of halogenating agents and their byproducts in molten salt.	Understanding the impact of contaminants on fuel performance will allow fuel synthesis processes to be optimized to meet these purity requirements.
Methods for removing fission products, corrosion products, and synthesis byproducts are needed to purify salts.	Demonstrate volatility-based separations in both chlorides and fluorides across a wider range of impurities.	Purification technologies will enable the production of high-purity salts for synthesizing fuel salts.
	Assess the feasibility of precipitation and filtration of fission products from salts produced from UNF for both chloride and fluoride fuels.	Efficient removal processes for fission product species will enable the production of molten salt fuels from UNF.
Moisture and oxygen are known to alter the redox of the system and cause enhanced corrosion of reactor components.	Engineering-scale halogenation should be conducted to develop solutions to engineering challenges to minimize maintenance and mitigate safety risks.	Scalable, safe, and efficient purification technologies will mitigate the corrosion of reactor components.

Session 3: Scale-Up of Fuel Synthesis, Packaging, and Delivery (Chapter 3.3)

Issues	Research Needs	Impact
Actinide halides are not commercially available at quantities and purities needed for deployment.	Resolve engineering challenges associated with the use of strong halogenating agents to halogenate actinide metals at the 10–100 kg scale. Optimize the current process for producing high-purity UF_4 with a defined UF_3:UF_4 ratio.	The availability of high-purity actinide halides for producing fuel salt will enable rapid deployment of MSRs.
Packaging for salts must prevent contamination and be compatible with salts and reactor equipment.	Develop packaging with input from salt suppliers, MSR developers, and other end users.	Proper salt packaging ensures high-purity salt can be delivered and loaded into the reactor, enabling deployment.

<table>
<tr><th colspan="3">Session 3: Scale-Up of Fuel Synthesis, Packaging, and Delivery (From Session Report in Chapter 3.3) Cont.</th></tr>
<tr><th>Issues</th><th>Research Needs</th><th>Impact</th></tr>
<tr><td>^{37}Cl will be needed for fast reactors to prevent neutron absorption by ^{35}Cl and to avoid generating long-lived ^{36}Cl, which will be a disposal challenge.</td><td>Develop processes for producing 10–100 kilogram quantities of ^{37}Cl, such as liquid-liquid extraction or microchannel distillation.</td><td>10–100 kilogram-scale quantities of stable isotopes will enable the synthesis of molten salt fuels at scales required for deployment.</td></tr>
<tr><td>If pure unary actinide halide species are not available, developers may decide to synthesize and purify mixtures of binary or ternary halide salts directly.</td><td>Optimize liquid-solid exchange reactions to ensure contamination levels are low and that high concentrations of actinides can be achieved in the salt flux.</td><td>Reducing the risk associated with fuel synthesis at scale will lower cost.</td></tr>
<tr><th colspan="3">Session 4: Fuel Salt Characterization and Qualification (From Session Report in Chapter 3.4)</th></tr>
<tr><th>Issues</th><th>Research Needs</th><th>Impact</th></tr>
<tr><td>Developers must demonstrate that fuel salt properties are adequate to ensure safe operations. Operational windows must be established across concentrations, temperatures, and redox states to ensure that fuel salt properties can be controlled sufficiently to meet the safety criteria throughout the fuel lifetime.</td><td>Quantify the effect of ingrowth of oxygen, water, and trace metal contamination on molten salt properties.
Measuring property values for a wide range of molten salt mixtures will provide validation data and lead to improved models for molten salt properties. If measured values are not available, the uncertainty of modeled values should be quantified.</td><td>The definition of operational windows for molten salt fuels will enable developers to demonstrate how fuel salt will achieve the safety functions for both fuel and coolant.
Understanding the uncertainty in property models will determine the required accuracy of monitoring technologies and safety margins associated with the operational window.</td></tr>
<tr><td>Fuel salt composition and the resultant fuel properties will change due to fission and ingress of oxygen and water. Developers must ensure that fuel salt properties remain adequate.</td><td>Develop accurate techniques for measuring oxygen and water content on-line and in situ.</td><td>Control of salt chemistry will ensure fuel properties remain adequate throughout the anticipated fuel lifetime.</td></tr>
<tr><td>Salt properties depend on temperature, concentration, and speciation of elements in the salt. These properties should be monitored during use to ensure fuel properties remain adequate.</td><td>Develop standard or reference measurement methods and demonstrate monitoring technologies at pilot-scale facilities.</td><td>Monitoring salt composition and redox state will demonstrate that fuel remains qualified during use.</td></tr>
</table>

Session 5: Technologies for Recovering Actinides (From Session Report in Chapter 3.5)		
Issues	**Research Needs**	**Impact**
Recovering actinides from the molten salt fuel is typically required prior to the removal of fission products due to their relative equilibrium potentials. Technologies for recovering actinides from light water reactor (LWR) fuel and metal fuels, developed under the US DOE Office of Materials Recovery and Waste Forms (NE 43), can be adapted and optimized for molten salt fuels.	Develop robust filters for removing particulates, including actinide oxides, from the harsh molten salt environment. Demonstrate electrolysis of high actinide concentration salts for co-recovery of actinides in both fluorides and chlorides. Measure the activity of actinides in a variety of liquid metal electrodes to enable the optimization of electrolysis for the recovery of actinides. Demonstrate volatility-based separation of actinides from a complex salt containing fission product salts at the lab scale.	Recovery of actinides from used molten salts will allow the reuse of the fuel elements, enable the drawdown of fission products, and minimize salt waste.
Valuable ^{37}Cl may be released as actinides are recovered from molten salt fuels.	Develop chlorine capture technologies that allow for the reuse of the chlorine in rehalogenation of the actinides.	Recovery and reuse of the ^{37}Cl will reduce cost in fuel synthesis and minimize waste.

Session 6: Used Fuel Salt Purification for Recycle (From Session Report in Chapter 3.6)		
Issues	**Research Needs**	**Impact**
Salt purification methods have been developed in NE-43 to support pyroprocessing; these will need to be adapted for processing and recycling molten salt fuels.	Determine if Cs, Sr, and Ba must be removed for fuel salt to be reused. Measure the activity of lanthanides in a variety of liquid metals to enable optimization of electrolysis for fission product removal. Determine the achievable separation efficiency of crystallization methods for purifying molten salt fuels.	If some fission product elements can remain in the salt indefinitely, this will reduce the number of operations needed to recycle salt fuels. Removal of lanthanides would enable salt recycle and minimize salt waste. If a high separation efficiency can be achieved, pure salts could be recycled, reducing the need for fresh fuel salt.
Actinides are typically removed from used fuels prior to removing lanthanides to prevent the loss of actinides in lanthanide waste forms.	Identify technologies for removing lanthanides while leaving actinides in the molten salt.	Minimizing the number of steps associated with recycling molten salt fuel will reduce costs.

Session 7: Recovery and Transmutation of Long-Lived Isotopes (From Session Report in Chapter 3.7)		
Issues	**Research Needs**	**Impact**
The assessment of transmutation strategies relies upon accurate nuclear data.	Measure nuclear data for transmutation of long-lived isotopes through neutron, photon, and charged particle irradiations.	Improved nuclear data will enable the robust evaluation of transmutation strategies.
Methods for recovering long-lived isotopes from used MSR fuel have not been developed.	Develop separation technologies for the recovery of long-lived isotopes from MSR fuel sources.	The recovery of long-lived isotopes from MSR fuel could reduce high-level waste volumes.
Session 8: Noble Metal and Insoluble Fission Product Recovery (From Session Report in Chapter 3.8)		
Issues	**Research Needs**	**Impact**
Insoluble fission products may build up in disadvantageous locations either in-reactor or during off-line salt processing.	Design and demonstrate the effectiveness of filters made of salt-compatible materials such as ceramic foams or intermetallic structures.	Filtering insoluble species will reduce fouling of reactor piping and a reduction in piping diameter due to plate out.
Insoluble fission products form atom by atom in MSR fuel salt, and it is unknown if these atoms will stay suspended, form agglomerates, or plate out on surfaces.	Determine the behavior of insoluble fission product species by performing irradiation testing of molten salt fuel.	Understanding the behavior of insoluble species in MSR fuels will inform fuel qualification, reactor design, and licensing activities.
Some isotopes produced in MSR fuel salt may be valuable for medical uses in imaging and diagnostics (e.g., ^{99}Mo, ^{131}I, ^{133}Xe).	Identify selective media that can be used to collect targeted high-value isotopes, such as those relevant to medical applications.	Recovery of medically relevant isotopes from MSR fuels will support a domestic supply of these important materials.
Session 9: Safeguarding Approaches for Liquid Fuels and Fuel Cycle Facilities (From Session Report in Chapter 3.9)		
Issues	**Research Needs**	**Impact**
The inventory of radionuclides in the fuel will change in an MSR, especially as fission products are removed, makeup fuel is added, or redox state is adjusted, as some developers plan to do.	Develop and validate reactor physics models to simulate depletion of molten salt fuel during use in a reactor with on-line or at-line removal of fission products and additions of makeup fuel salt.	Understanding the evolution of the fissile and fertile inventory in the salt during use is essential to safeguarding that material.
It is expected that many of the technologies currently used for safeguarding LWR reactors will not be applicable to molten salt reactors.	Develop non-destructive analysis (NDA) detection technologies for fissile material in molten salt.	NDA detection methods will provide flexible methods of safeguarding MSRs and their fuel cycle facilities.

3. Session Reports

3.1. Conversion of Fuel Sources to Salt

3.1.1. Introduction

MSR developers are considering the use of a wide variety of materials for synthesizing fuel salts: used nuclear fuel, uranium from high-assay low-enriched uranium (HALEU), and low-enriched uranium (LEU) materials, stockpiled materials, and mined materials in oxide and metallic forms. These are being considered as source materials for the uranium, thorium, and plutonium in MSR fuels. Chloride fuels are commonly synthesized for use in fast reactors, and fluoride fuels are commonly synthesized for use in thermal reactors. The status of current technologies for converting these source materials to halide salts is summarized in the following section.

3.1.2. Current State of Conversion Technologies

Current technologies for converting metal and oxide fuel materials to salts include voloxidation, reactions with strong halogenating gases, and liquid-solid exchange reactions. Voloxidation is often the first step in halogenating oxide materials. In this process, UO_2 is heated in a dry atmosphere with oxygen gas to convert it to U_3O_8 and break up the sintered pellets into a fine powder with a high specific surface area. This powder is then halogenated.

Processes for fluorinating materials were established during the development of enrichment technology (Iwaski 1968; Sakurai 1974) but are designed to fluorinate to UF_6 for use in gas centrifuge technology rather than to UF_4, which is anticipated for use in MSR fuels. Fluorination processes for uranium enrichment produce gaseous rather than solid products. Converting the material to the UF_6 gas phase purifies the material. Source UF_4 purchased from current suppliers is generally a byproduct from enrichment fluorination processes as material that failed to generate UF_6 and, thus, has not been purified. Attendees at the workshop shared their experience that these materials are often contaminated with 10–50 wt.% UO_2. If the same fluorination processes are to be used to fluorinate oxide or metallic feedstock for use in molten salt reactors, these processes will need to be optimized to produce high-purity UF_4.

Alternative processes using fluorinating agents such as HF, NF_3, and NH_4HF_2 have been explored at the lab scale. The use of HF and NF_3 is considered risky, as both are strong corrosive gases and hazardous to handle (Kim et al. 2002; Souček et al. 2017; Pomiro et al. 2020; Scheele 2012). Ammonium bifluoride can be used to produce HF in situ during a solid-gas reaction for converting UO_2 to UF_4 (Yeamans 2003; Foster 2021), but, as Polke points out in her abstract in Appendix C (Appendix C.2), many design challenges remain as the byproduct ammonium and excess HF can recombine in the gas space to clog piping and interrupt proper gas flow. The use of strong halogenating gases poses significant hazards that must be mitigated during the scale-up of these processes. Alternative processes for fluorinating and chlorinating are summarized in Table 2.

Chlorination of feed materials is an underdeveloped process. Proposed technologies include solid-gas reactions and solid-liquid reactions. Solid-gas reactions include direct chlorination with HCl (Halstenberg et al. 2020), CCl_4 (Gens 1959), Cl_2 (Haas et al. 1991), and NH_4Cl (Eun et al. 2017) gases. These solid-gas reactions are all diffusion-limited and offer poor selectivity control, and the chlorination agents are considered risky to work with.

Liquid-solid reactions include electroreduction, as in classical pyroprocessing, or exchange reactions with halogen source salts, such as with $FeCl_2$ (Yankey et al. 2023) or $ZnCl_2$ (Appendix C.10) in a molten salt flux. Exchange reactions offer superior mass transfer rates and redox control for selectivity but require the use of a molten salt flux to prevent the formation of pure actinide chlorides. The base salt components of the proposed MSR fuel can be used as the flux to mitigate this issue. For example, NaCl could be used as the flux during the chlorination of uranium in a NaCl-UCl_3 fuel salt. One challenge with these methods is the separation of the reduced halogen source metal byproduct from the synthesized fuel salt. An example is the removal of metallic zinc generated when $ZnCl_2$ is used as the halogen source. If the metal is volatile at reasonably low temperatures, it can vaporize and be collected. If it remains as a condensed phase, it may be filterable. These processes are being developed at the lab scale at universities and national labs to generate small amounts of fuel salt. Another limitation of liquid-solid reactions in a salt flux is the limited solubility of the actinide halide in the salt flux.

Table 2: Common Halogenation Agents and Reactions for Synthesizing Actinide Fuel Salts

Halogenation Agent	Process
HF	$UO_{2\,(s)} + 4HF_{(g)} \rightarrow UF_4 + 2H_2O_{(g)}$
NF_3	$3UO_{2\,(s)} + 4NF_3 \rightarrow 3UF_4 + 2N_{2(g)} + 3O_{2(g)}$
NH_4HF_2	$UO_{2\,(s)} + 4NH_4HF_{2\,(s)} \rightarrow UF_4 + 4NH_{3(g)} + 4HF_{(g)} + 2H_2O_{(g)}$
HCl	$UO_{2\,(s)} + 4HCl \rightarrow UCl_4 + 2H_2O$
Cl_2	$UO_{2\,(s)} + 2Cl_{2(g)} + 2C_{(s)} \rightarrow UCl_4 + 2CO_{(g)}$
CCl_4	$UO_{2\,(s)} + CCl_{4\,(g)} \rightarrow UCl_{4\,(s)} + CO_{2\,(g)}$
NH_4Cl	$U + 3NH_4Cl \rightarrow UCl_3 + 3NH_{3(g)} + 1.5H_{2(g)}$
$ZnCl_2$/$FeCl_2$ in flux salt	$2U_{(s)} + 3ZnCl_{2(in\ flux)} \rightarrow 2UCl_{3\,(in\ flux)} + 3Zn$

Mechanochemistry, which was discussed at the workshop during Session 1 by Sheng Dai (Appendix C.1), is a salt synthesis technique in which individual component salts are milled together outside of a glovebox in a sealed container to fuse them. The salts are then heated above the melting point of the individual components and sparged with HCl gas to dehydrate the salts and chlorinate any oxides (Halstenberg et al. 2020). The method has been used to produce high-purity chloride salts at the lab scale and remains to be demonstrated in fluorides. It requires the feed materials to be halides and would not be suitable for metal or oxide source materials.

When synthesizing fuel salts, it is necessary to control their corrosivity. This is typically done by controlling the redox state. For example, a low ratio of UF_3 to UF_4 can be used to control the redox of uranium fluoride salts. Electrochemical and chemical methods of measuring and adjusting the ratio of different valence species in the salt are under development. Additions of metallic zirconium or uranium are often used to lower the salt redox, and cyclic voltammetry can be used to measure the ratios in situ.

3.1.3. Challenges and Opportunities

Halogenation of pure oxide or metallic feeds is under development at the lab scale for chlorides and at the industrial scale for fluorides; however, some MSR developers are planning to synthesize fuel from used fuel sources containing fission products and other contaminants. The use of molten salt fuels presents a unique opportunity to directly utilize UNF as a fuel material with limited processing needed. It is unclear if halogenation of fission products, cladding, or contaminant species complicates these fuel synthesis processes. For example, the addition of large amounts of metallic zirconium during the chlorination of UNF could result in excessive production of $ZrCl_4$ gas or the reduction of UCl_3 to metal. Therefore, developers will need to decide whether to include cladding materials in the synthesis or to add an extra processing step to declad UNF first.

Ed Pheil of Exodys Energy gave a presentation during this session on the UPCYCLE technology under development at Exodys Energy, which utilizes UNF to produce molten salt fuel for its KLOROS reactor. The UPCYCLE technology will involve a combination of decladding, electrolysis, electroreduction, electrorefining, and reductive extraction to synthesize a molten salt fuel from UNF from light water reactors. A demonstration of the conversion of 50 g of used mixed oxide (MOX) fuel was conducted by Idaho National Laboratory in 2018 under a Gateway for Accelerated Innovation in Nuclear (GAIN) voucher in support of Elysium Industries to explore the technology to conduct this conversion (Fredrickson and Hermann 2019).

Once halogenated, UNF must be processed to reduce the neutron poison content of the fuel. During his presentation, Ed Phiel identified the recovery of gaseous fission products, such as xenon and krypton, from UNF during molten salt fuel synthesis as a low technological readiness level (TRL) technology. **The measured impact of fission products and dissolved cladding species on the thermal properties of molten salt fuels will be used to determine which elements must be removed and to below what concentrations.**

Irrespective of fuel source material, specifications must be defined for molten salt fuels so that synthesis processes can be designed and optimized. These specifications should be based on whether the synthesized fuel salt can meet the safety functions of both fuel and coolant in reactor systems. This is governed by the thermal properties of the fuel salt, such as melting point, density, heat capacity, thermal conductivity, and viscosity. The properties of the fuel salt depend on the salt composition, and most vary with temperature. Impurities introduced to fuel salts during synthesis should be identified, and processes should be optimized to minimize impurities that impact fuel performance. Impurities may include oxygen, water, metals from halogen source salts, or vessel materials such as nickel, chromium, and carbon. While it is understood that moisture increases the corrosivity of the salt by generating oxyhalide species, the concentrations of these species that can be tolerated are not well defined. **Quantifying the impact of impurities on fuel performance will assist developers in defining fuel specifications.** These fuel specifications will likely be unique to each reactor and fuel composition but will be determined based on the impact of impurities on fuel performance.

The use of different feed materials and synthesis processes will require different processing conditions. Some processes may require inert atmosphere glovebox enclosures, while others may require hot cell environments (for example, halogenation of UNF due to its high radiotoxicity). Some processes use strong halogenating agents that require the use of redundant safety systems, frequent maintenance, and replacement of consumable parts. Other processes done in the liquid state pose fewer risks; for example, liquid-solid exchange reactions. **Developing synthesis processes that minimize the number of steps and eliminate or mitigate the safety hazards of working with strong halogenating species will reduce the cost of fuel synthesis.** One promising option is the use of exchange reactions in a molten salt flux that do not require the use of strong halogenating agents. **Optimizing these liquid-solid exchange reactions to minimize contamination levels from residual halogen source metals and maximize the concentration of actinides in the produced fuel salt will offer a safer and simpler option for fuel synthesis.**

It is necessary to control the corrosivity of fuel salts during synthesis. This is typically done by producing a low-concentration buffer species to control the redox state, such as UF_3 in UF_4. Monitoring and adjusting the ratios of different valence states of actinides can provide this control of redox state. **Electrochemical and chemical methods of measuring and adjusting the ratio of different valence species in the salt should be demonstrated in both chloride and fluoride salts**. The formation of complex anions results in non-ideal behavior that affects properties of molten halides. The formation of complex anions is a function of the haloacidity of the solution. **Developing a chloride sensor to measure the concentration of free Cl^- and a fluoride sensor to measure the concentration of free F^- in the salt will provide data that can be used to improve atomic-level models of molten salts and predictions of their properties.**

3.1.4. Summary

While fluorination processes have been used extensively in the uranium enrichment industry, these processes have not been optimized to produce high-purity molten salts. Alternative methods of halogenating various feed materials to produce MSR fuel salts were discussed during this session and are summarized here, including direct halogenation with strong halogenation agents and liquid-solid reactions such as exchange reactions. Fuel specifications to ensure that fuel behavior is adequate for MSRs should be developed so that synthesis processes can be optimized to meet those requirements. The synthesis processes should be designed and optimized to meet these fuel specifications while minimizing the number of steps to reduce cost and mitigate risk when using hazardous materials. A future research direction is therefore defined: ***Develop and demonstrate efficient and scalable synthesis processes***, which encompasses the identified research needs in the area of fuel salt synthesis.

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3.2. Fresh Fuel Salt Purification Technology

3.2.1. Introduction

Once fuel salt is synthesized, it will need to be purified to meet fuel specifications that ensure it can fulfill its functions as both fuel and coolant. Fresh fuel salt can be contaminated by impurities from the atmosphere during preparation and storage, synthesis processes, and interactions with the crucible or container materials. If the fuel were prepared from UNF, additional impurities could include fission product species and other constituents of the UNF. The impurities that affect fuel salt performance in the reactor need to be identified and prioritized so that fuel specifications and processes for removing high-impact impurities can be developed. Fuel salt performance is governed by the thermal properties of the fuel salt, such as melting (freezing) point, density, heat capacity, thermal conductivity, and viscosity. The properties of fuel salt depend on the salt composition, redox state, and temperature. Determining which impurities affect fuel salt properties or impact reactor performance and developing technologies for removing them will support a molten salt fuel supply chain.

3.2.2. Current State of Purification Technology

Impurities in fresh fuel salt can come from a variety of sources. Molten salts are hygroscopic and corrosive, making them prone to contamination from oxygen and moisture in the atmosphere and corrosion products from interactions with container materials. Synthesis processes may introduce contaminants as well, such as Zn, Fe, MgO, and dissolved halogenating agents. The potential sources of impurities and common impurities from those sources are summarized in Table 3.

Table 3: Impurities in Molten Salts

Impurity Source	Impurity
Atmosphere	O_2, H_2O
Crucible or Vessel	Ni, Cr, Fe C
Synthesis Process	Zn, Fe from exchange reactions Dissolved halogenation agents (HF, HCl, etc.)
Used Light Water Reactor Fuel	Fission products (Nd, Cs, Sr, Ba, etc.) Noble metals (Mo) Semi-volatile fission products (I, Te) Gaseous fission products (Xe, Kr)

The effect of impurities on molten salt thermal properties must be quantified to understand the impact of the impurities on fuel performance. This is being done through work conducted under the DOE NE ART MSR campaign. Moisture is known to hydrolyze salts, producing hydroxides, which can alter the redox state of the system and enhance the corrosion of reactor components (Kipouros and Sadoway 1987; Huang et al. 2011). It is unclear if the presence of corrosion products such as iron, chromium, and nickel oxides; excess dissolved halogenation agents; vessel materials; or the fission product species present in halogenated UNF have a significant effect on fuel performance. Argonne National Laboratory recently measured the effect of fission product contamination on the heat capacity and thermal diffusivity of fluoride and chloride salts, finding that the specific concentrations of fission products studied did not measurably affect the properties of the two salts studied (Rose et al. 2023). Further work will be needed on quantifying the many possible impurities and their effects on all molten salt properties relevant to fuel salt performance.

The concentrations of trace impurities in salts must be measured to quantify acceptable levels of impurities. Technologies for measuring the concentration of impurities in salts include spectroscopic methods for trace metals, inert gas fusion devices for dissolved oxygen, electrochemical methods for measuring the redox states of species in the salt, and ion-selective electrodes for measuring the anion content. X-ray diffraction, X-ray photoelectron, and laser-induced breakdown spectroscopic methods can provide information on the speciation of elements in the salts. Calorimetric measurements can monitor shifts in the melting behavior of salts due to impurities. All these methods have uncertainties that limit the ability to quantify the effects of small concentrations of impurities on salt properties.

The strong halogenation agents listed in Table 2 for use in synthesizing salts can also be used to remove water and oxygen from salts. Researchers at Argonne have used NH_4HF_2 to generate HF in situ by breaking down the NH_4HF_2 to NH_3 and HF, which is used to purify UF_4 by removing UO_2 and H_2O at the 200-g scale (Appendix C.2). This method has been used by university researchers to purify UF_4 at the Massachusetts Institute of Technology (Yeamans 2003) and the University of South Carolina (Foster 2021) as well as at Ames Laboratory to purify yttrium fluoride (Walker and Olson 1959). During purification with ammonium bifluoride, excess HF can combine with the NH_3 produced in the off-gas system, clogging pipes and preventing proper gas flow, requiring frequent maintenance and the use of several consumable parts. At a larger scale, the TerraPower MCRE project has demonstrated the purification of NaCl-$MgCl_2$ salt by chlorination with CCl_4 at the 100-kg scale (Appendix C.3).

Volatility-based methods can be used to remove metal fission products, corrosion products, and synthesis byproduct species. Separation by volatility is being demonstrated as part of the TerraPower MCRE project to produce high-purity UCl_4. Crystals of UCl_4 have been collected from a mixture of UO_2, tin, iodine, strontium, cerium, and neodymium using the volatility method at the laboratory scale, where the Ce, Nd, and Sr were left in the crucible, and iodine was collected in a cold zone separate from the UCl_4 product (Fitzgerald et al. 2023).

Sheng Dai proposed the use of an oxygen sparge to form insoluble fission product oxides or oxychlorides that could be removed from a chloride salt. This was demonstrated at the lab scale with $LaCl_3$ in a $MgCl_2$-KCl melt where a white powder suspected to be $LaOCl_3$ was precipitated after 260 minutes of sparging oxygen gas (Maltsev et al. 2022). It is unclear if oxygen sparging will affect the other constituents of the salt or only the impurity species. This process is still under development.

3.2.3. Challenges and Opportunities

A challenge in optimizing purification systems for molten salt fuels is that target purity specifications have not been defined. Purity specifications will be defined based on the impact of impurities on the properties of the fuel salt. Not all impurities will have an impact on fuel salt performance or need to be removed. The purity specifications must ensure fuel salt satisfies its fundamental safety functions as both fuel and coolant. Purity specifications will need to take into account limitations in salt synthesis procedures and uncertainty in concentration measurements. A challenge in defining purity specifications is that the uncertainties of the methods for measuring the thermal properties of the salts that are being developed under the MSR campaign are typically 5–20% (Rose et al. 2021). At this sensitivity, small effects due to impurities are not measurable. The US Nuclear Regulatory Commission will use the properties of the fuel salts as an indicator of fuel performance when qualifying MSR fuels. Developers will need to provide technical justification for impurity limits to make the safety case for their designs. It is of paramount importance that **the impact of all potential impurities on fuel salt performance be measured to determine which impurities must be specified.** Another consideration in developing fuel purity specifications is the ability of state-of-the-art analytical methods to measure the concentrations of relevant impurities. If analytical measurement uncertainty exceeds purity specifications, it cannot be proved that the fuel salt meets the requirements for qualification.

Development of a chemical production industry for high-purity precursors would enable developers to purchase 10–100 kg quantities of high-purity component salts for use in synthesizing their fuel salt mixtures. To support the chemical industry in developing this capability, developers need to determine the purity requirements of their reactor system. Developers need fundamental data on the effect of a variety of impurities on fuel salt properties to determine these purity requirements. Purity specifications must conform to the available purity level of current salt synthesis methods so as not to over-specify the fuel salts. Some developers have established relationships with salt suppliers to secure their supply chain. For example, Terrestrial Energy has formed an agreement with Orano (NEI 2021), and Kairos has formed a cooperative development agreement with Materion (Nuclear Newswire 2022).

Even with the development of a robust chemical industry producing high-purity component salts, it may still be necessary to employ purification technologies at the reactor site due to contamination during shipping or loading into the reactor. Developers may take the approach of purchasing high-purity component salts and mixing them or purchasing lower-quality salts, mixing them, and then purifying the resultant salt mixture. The cost-benefit analysis for each salt purification approach will need to be weighed by each developer.

Removing oxygen and water can be done with strong halogenating agents such as those listed in Table 2. These strong halogenating agents are corrosive and hazardous to handle and present both a safety risk and an engineering challenge. There may be some solubility of these agents in the molten salt mixture, and their impact on fuel properties is unknown. **It is necessary to measure the solubility of halogenating agents in fuel salts and determine their impact on fuel performance when selecting a halogenation agent.** Halogenation for the purification of salts poses significant hazards and engineering challenges that must be mitigated during the scale-up of these processes. In-situ production of a halogenating agent can mitigate safety risks, such as the use of ammonium bifluoride to generate HF in situ during a solid-gas reaction for converting UO_2 to UF_4. **Engineering-scale demonstrations of halogenation should be conducted to develop solutions to these engineering challenges that minimize maintenance and the number of consumable parts to reduce risk and cost.**

Fission product, corrosion product, and synthesis byproduct metals can be removed from molten salts by utilizing the differences in volatility of the metal halides or by precipitation to solids, as in gas sparging to produce fission product oxides followed by filtering. These processes are not well developed. Volatility-based separations have been shown to be effective for a few impurities but have not been demonstrated across all possible impurities found in salts. This method has been tested in chloride salts, and it should be determined if the same advantageous differences in volatility exist for fluoride systems. Therefore, **volatility-based separations should be demonstrated in chlorides and fluoride salts across a wider range of impurities to include fission products, corrosion products, and potential synthesis byproducts.**

Precipitation of oxides or oxyhalides by sparging with oxygen was suggested for removing fission product species and has been demonstrated at the laboratory scale in the absence of actinides. This method will require the development of effective filters that are compatible with molten salts. **The feasibility of precipitation and filtration in complex salts produced from UNF should be assessed for both chloride and fluoride fuels.**

3.2.4. Summary

Fresh fuel salt may be contaminated with impurities from a variety of sources, as listed in Table 3. Fuel composition specifications must be defined to ensure that molten salts will perform safely and effectively in molten salt reactors. Molten salt fuel performance is governed by the thermal properties of the salt, which are affected by its composition. The effects of fuel impurities on the thermal properties of salts must be measured to provide a technical basis for purity specification. This work is taking place under the DOE NE ART MSR campaign but must be expanded to study many more impurity species across a wider range of base salt compositions. The impurities to be removed and their acceptable concentrations must be determined to develop effective purification technologies. Several options for removing impurities were discussed during this session. For oxygen and moisture, halogenation methods were recommended and should be demonstrated at the engineering scale to develop processes that minimize required maintenance and mitigate safety hazards. Methods for removing fission products, corrosion products, and synthesis byproducts included techniques based on volatility and precipitation. Volatility methods need to be demonstrated in both fluorides and chlorides for a wider range of impurities. The feasibility of using precipitation and filtration methods for complex salts produced from UNF needs to be determined. Two future research directions are defined, which encompass the specific research needs identified here for fuel purification: (1) ***Understand the impact of impurities on molten salt properties*** and (2) ***Optimize and demonstrate separation technologies for removing impurities from chloride and fluoride salts***.

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3.3. Scale-Up of Fuel Synthesis, Packaging, and Delivery

3.3.1. Introduction

Once processes for synthesizing and purifying fuel have been demonstrated at the engineering and lab scales, pilot- and industrial-scale facilities can be built to produce the tons of fuel needed to deploy MSRs in the 2030s. No processes for synthesizing industrial-scale quantities of actinide-containing salts have been demonstrated. Packaging for salts must ensure no exposure to ambient air during transport and be compatible with loading salt into a variety of reactor designs. Standard packaging that could be accepted at all proposed reactors would provide economies of scale. Packaging will be required that is compatible with salts without actinides used as coolants, actinide-loaded fuel salts, and salts synthesized from UNF, which have additional radiotoxicity and thermal load and handling requirements for each material type.

3.3.2. Current State of Technology

Scale-up of fuel synthesis processes will require the chemical industry to increase production of high-purity fuel components, including stable isotopes such as ^{7}Li and ^{37}Cl, alkali and alkaline halides, and actinide-bearing halides. ^{7}Li is used in MSRs instead of ^{6}Li to mitigate tritium formation, while ^{37}Cl is needed to avoid neutron absorption by ^{35}Cl which results in the generation of ^{36}Cl. ^{7}Li is produced as a relatively impure byproduct in the manufacture of enriched ^{6}Li, overseen by the DOE Office of Science, by mercury- or laser-based isotopic separations for use in producing tritium. ^{37}Cl can be produced by liquid-liquid extraction or microchannel distillation (Aeschliman and Bottenus 2022). The current capacity for the production of high-purity stable isotopes will not meet the demand for salt production at the tonne scale that will be needed to supply MSR fuels.

The quantities of sufficiently pure actinide halides that will be needed for deployment are not commercially available. UF_4 is available as a byproduct from enrichment processes but must be purified before use in MSR fuel salt. Processes are currently optimized to produce pure UF_6 and do not produce pure UF_4. Alternative processes based on direct halogenation with strong halogenation agents, which were discussed in Chapter 3.1, are under development at laboratory or engineering scales. It will be necessary to synthesize salts at the 10–100 kg scale to support the supply chain for molten salt reactor fuels.

There was a discussion at the workshop regarding the benefits of fuel salt mixtures of two or more unary salts being prepared by the chemical industry and shipped to reactor sites instead of each reactor having a small onsite chemical plant that would perform this function. The approach taken will be decided by individual reactor developers for each concept. Some designs require frequent additions of make-up fuel, necessitating an onsite synthesis. Other reactor concepts plan to load fuel once and make no further additions, and so would be more amenable to a centralized fuel preparation by the chemical industry. TerraPower and Idaho National Laboratory have recently synthesized batches of a binary fuel salt at a 9 kg batch size, converting uranium metal into UCl_3 (Appendix C.5). This is the largest scale at which MSR fuel has been synthesized since the Molten Salt Reactor Experiment at Oak Ridge National Laboratory. A representative of TerraPower indicated that the company does not plan to further scale this fuel production process because 9 kg batches will be sufficient for the limited lifetime of the molten chloride reactor experiment.

Different feed materials and synthesis processes will require the use of different processing conditions at different scales. Some processes may require the use of inert atmosphere glovebox enclosures, while others may require hot cells, such as the halogenation of UNF, due to high radiotoxicity. Some processes use strong halogenating agents that require redundant safety systems, frequent maintenance, and replacement of consumable parts. Other processes pose fewer risks, for example, liquid-solid exchange reactions. As the complexity of the synthesis process increases, so does cost.

Packaging for the transportation of salts should prevent contamination during transport to the reactor from their place of manufacture, whether that is from an onsite chemical plant or a centralized facility. In particular, moisture and oxygen should be excluded from the salt during transport. High-purity salts are currently transported as powders in glass ampoules or double-encapsulated under vacuum and sealed in mylar bags. These methods become impractical at large scales and when interfacing with reactor ports. Packaging requirements will be different for radioactive and non-radioactive salts.

3.3.3. Challenges and Opportunities

Some technologies for producing salts or salt components are mature but require optimization, while others are still being demonstrated at the lab scale and require development. For example, production of ^{7}Li is a mature technology, but optimization is necessary to achieve the purity required for MSRs. **The production of ^{37}Cl is a less mature technology requiring development.** Another example of a mature technology that must be optimized for higher purity is the production of UF_4. Current enrichment processes include uranium fluorination processes that produce high-purity UF_6 and a lower-purity UF_4 byproduct. **Fluorination processes should be optimized for producing high-purity UF_4.** Actinide chlorination technologies are much less mature, having been demonstrated only at the gram and kilogram scales. **Engineering challenges associated with strong chlorination agents must be solved to demonstrate the chlorination of actinide metals at the 100 kg or more scale.**

An increase in the commercial availability of stable isotopes and the halide salts made with them will require engagement between chemical suppliers and MSR developers to establish purity specifications for these materials that meet the needs of MSR systems without undue cost. Some attendees of the workshop felt that the development of a chemical industry focused on producing high-purity salts will be required for MSR deployment. High-purity salts are also needed in much smaller quantities for use in measuring the properties of molten salt fuels for use in designing reactors and setting fuel specifications.

If high-purity unary salts are not commercially available, developers may decide to directly synthesize and purify mixtures of binary and ternary salts. One promising technology applicable to this scenario is synthesis by exchange reactions. For example, LiCl-KCl-UCl_3 can be produced by contacting a mixture of LiCl-KCl-$FeCl_2$ with uranium metal, exchanging the Fe for U, and collecting the iron metal at an electrode or with a magnet (Yankey et al. 2023). **These liquid-solid exchange reactions can be optimized to ensure contamination levels of the exchange metal are low and the concentration of actinides achieved in the salt is high.** Mixed salts could then be purified with methods described in Chapter 3.2.

Salts can be difficult to transfer between containers during preparation and packaging. They often wet crucibles or adhere to container walls as particles of powdered salt due to static forces. Pressing and/or sintering salts into ingots would prevent salt buildup on container walls. Ingots are also less susceptible to hydration than powders due to the smaller exposed surface area. The size of salt containers or ingots for transport may be limited by the actinide content due to criticality concerns or due to high radiotoxicity in the case of fuels made from UNF. Additional considerations that were discussed included the reuse of transport containers, which would require cleaning of the containers. A discussion of who should control packaging requirements or if standard packaging is needed did not result in consensus. The solar and thermal energy storage industries are also planning to use a variety of molten salts and have experience with nitrate salts. It may be valuable to work with those industries on developing salt transport requirements, although they will have fewer requirements for salts without radionuclides. **Packaging should meet the requirements of salt suppliers, MSR developers, and other end users of molten salt materials.**

3.3.4. Summary

Although methods for synthesizing and purifying fuel have been demonstrated at the engineering and lab scales, pilot- and industrial-scale facilities will be required to produce the tons of fuel needed to deploy MSRs in the 2030s. The availability of high-purity stable isotopes and unary halide salts is limited, and processes need to be optimized for purity. Some developers prefer to synthesize complex salt mixtures onsite at their reactors, and exchange reactions show promise for synthesizing mixed salts without the use of strong halogenation agents. Salt packaging must prevent exposure to oxygen and moisture during transport and be compatible with salts with and without actinides and salts synthesized from used fuel having high radiotoxicity and thermal load. MSR developers should work closely with chemical suppliers and thermal storage and solar energy users of molten salts to establish standard salt packaging; therefore, no future research directions are defined for salt packaging requirements. The fuel synthesis issues discussed and the specific research needs identified during this session can be addressed by the future research direction defined in Chapter 3.1: ***Develop and demonstrate efficient and scalable synthesis processes***.

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3.4. Fuel Salt Characterization and Qualification

3.4.1. Introduction

Reactor fuels must be characterized and qualified prior to use in a reactor. The NRC addressed how liquid fuels could be qualified in the recent draft regulation NUREG 7299 (Holcomb et al. 2022). Qualification was defined as ensuring the salt would achieve its fundamental safety functions as either fuel or coolant. Variation in fuel salt properties is expected to impact the achievement of fundamental safety functions. In this way, fuel qualification is the link between properties and facility safety.

3.4.2. Current State of Technology

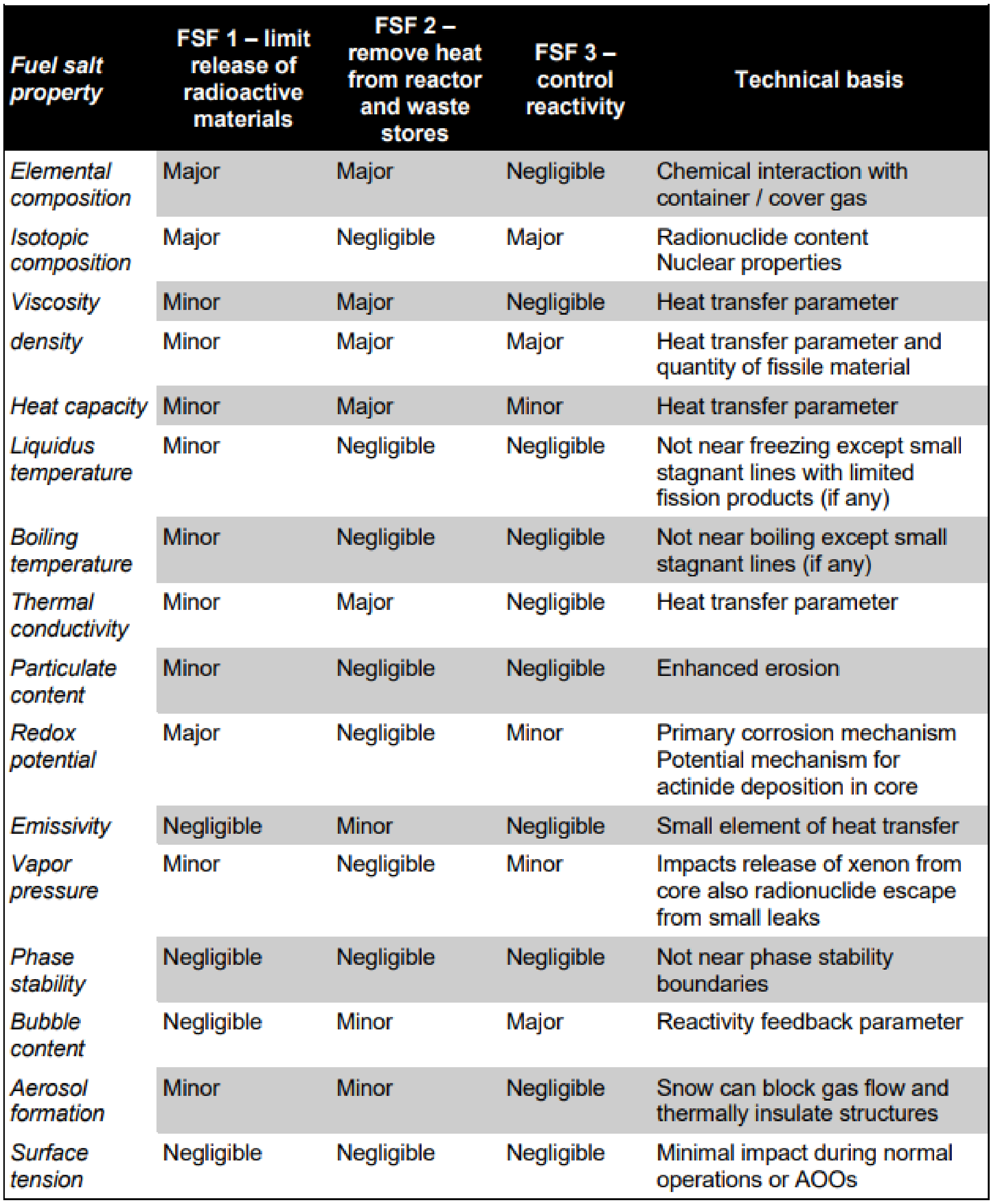
In a public meeting on regulatory process improvements for advanced reactor designs held in 2017, fuel qualification was defined as: “The overall process which provides high confidence that physical and chemical behavior of fuel is sufficiently understood so that it can be adequately modeled for both normal and accident conditions, reflecting the role of the fuel design in the overall safety of the facility. Uncertainties are understood such that any calculated fission product releases include appropriate margin to ensure conservative calculation of radiological dose consequences.” (NRC 2017). This process will depend on the applicant’s ability to demonstrate that a given salt composition will satisfy relevant regulations. Fuel qualification ultimately involves two main tasks: 1) the identification of fuel salt production specifications that ensure fuel salt with known properties is generated and (2) satisfaction of safety criteria by salt manufactured to those specifications.

Fuel qualification will involve demonstrating that fuel salt will maintain acceptable properties during operation under normal and accident conditions. Reactor developers will need to establish operational salt composition windows that maintain acceptable key properties of the fuel salt within the range of operating temperatures, redox states, and oxide activities. These compositional windows will be defined by the expected in-growth of fission products and corrosion products and the ingress of oxygen and moisture. The allowable levels of contaminants will depend on the effect of these species on the molten salt properties.

In NUREG 7299 (Holcomb et al. 2022), a table was published summarizing the effect of a variety of fuel salt properties on three fundamental safety functions (FSFs) that the fuel is required to fulfill in an MSR, shown in Table 4. The effect of each property on each FSF is ranked as either major, minor, or negligible. This table allows researchers to focus on developing measurement capabilities for those properties that will have a significant effect on demonstrating the control of fundamental safety functions.

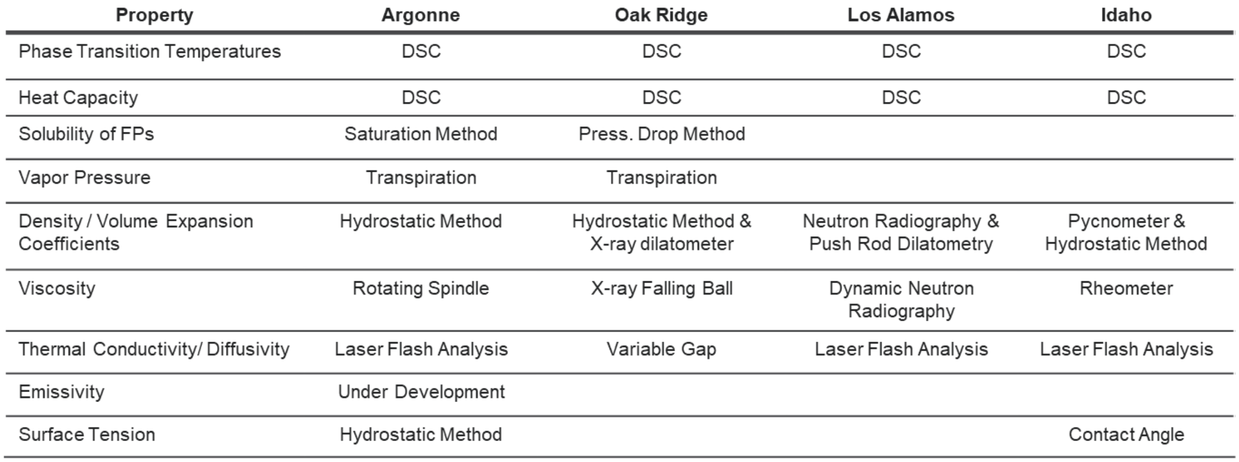
Qualification of fuels relies on verifiable methods of measuring the composition and properties of the fuel. A variety of tools to determine the composition and methods for measuring the properties of salt prior to use and during operation, both in situ and ex situ, are being developed under the ART MSR campaign. For example, differential scanning calorimetry (DSC) is used to measure both the melting point and heat capacity of molten salts. Table 5 summarizes the property measurement methods being used at national laboratories participating in the MSR campaign as of 2021. Capabilities continue to evolve under the MSR campaign; for example, Oak Ridge National Laboratory (ORNL) can now measure the surface tension of salts using both the hydrostatic method and contact angle. Off-line measurements can be used as calibration or benchmarking for on-line measurements. Most of these tools are still at a low TRL, generally due to the complexities of representing the uniquely harsh service environment in MSRs.

Table 4: Molten Salt Preporty Impacts on Fundamental Safety Functions (NUREG 7299)



Fuel salt property	**FSF 1 – limit release of radioactive materials**	**FSF 2 – remove heat from reactor and waste stores**	**FSF 3 – control reactivity**	**Technical basis**
Elemental composition	Major	Major	Negligible	Chemical interaction with container / cover gas
Isotopic composition	Major	Negligible	Major	Radionuclide content Nuclear properties
Viscosity	Minor	Major	Negligible	Heat transfer parameter
density	Minor	Major	Major	Heat transfer parameter and quantity of fissile material
Heat capacity	Minor	Major	Minor	Heat transfer parameter
Liquidus temperature	Minor	Negligible	Negligible	Not near freezing except small stagnant lines with limited fission products (if any)
Boiling temperature	Minor	Negligible	Negligible	Not near boiling except small stagnant lines (if any)
Thermal conductivity	Minor	Major	Negligible	Heat transfer parameter
Particulate content	Minor	Negligible	Negligible	Enhanced erosion
Redox potential	Major	Negligible	Minor	Primary corrosion mechanism Potential mechanism for actinide deposition in core
Emissivity	Negligible	Minor	Negligible	Small element of heat transfer
Vapor pressure	Minor	Negligible	Minor	Impacts release of xenon from core also radionuclide escape from small leaks
Phase stability	Negligible	Negligible	Negligible	Not near phase stability boundaries
Bubble content	Negligible	Minor	Major	Reactivity feedback parameter
Aerosol formation	Minor	Minor	Negligible	Snow can block gas flow and thermally insulate structures
Surface tension	Negligible	Negligible	Negligible	Minimal impact during normal operations or AOOs

Table 5: Summary of Capabilities and Methods of Measuring Molten Salt Properties Available at National Laboratories Participating in the MSR Campaign (Rose 2021).



Property	Argonne	Oak Ridge	Los Alamos	Idaho
Phase Transition Temperatures	DSC	DSC	DSC	DSC
Heat Capacity	DSC	DSC	DSC	DSC
Solubility of FPs	Saturation Method	Press. Drop Method		
Vapor Pressure	Transpiration	Transpiration		
Density / Volume Expansion Coefficients	Hydrostatic Method	Hydrostatic Method & X-ray dilatometer	Neutron Radiography & Push Rod Dilatometry	Pycnometer & Hydrostatic Method
Viscosity	Rotating Spindle	X-ray Falling Ball	Dynamic Neutron Radiography	Rheometer
Thermal Conductivity/ Diffusivity	Laser Flash Analysis	Variable Gap	Laser Flash Analysis	Laser Flash Analysis
Emissivity	Under Development			
Surface Tension	Hydrostatic Method			Contact Angle

The DOE-NE Advanced Reactors Safeguards program produced a comprehensive list of monitoring tools available for MSRs (Moore et al. 2023). These devices include salt samplers for off-line analyses, sensors for particulate monitoring, and electrochemical electrodes/optical tools for composition measurements. Choices about sensor location and monitoring type and frequency will be determined by end users. Developers are encouraged to coordinate with regulators in these design decisions.

While discussing regulatory issues, it was brought up that current NRC rules require that utilities be able to store used fuel onsite indefinitely due to the lack of repositories (NUREG-2157; NEC 2014). There are examples of long-term salt waste storage (e.g., electrorefiner salt at INL, $CsCl/SrF_2$ capsules at Hanford). However, the storage of used fuel salt from commercial plants will be a new challenge because MSR fuel becomes radiolytically unstable once it has frozen. For example, the degradation of chloride salts produces halide gases (e.g., UF_6, Cl_2 including ^{36}Cl). Defueled MSRE salt continues to produce F_2 fifty years after its shutdown. Developers must consider the necessary controls for the safe storage of spent fuel salt or develop a plan to perform post-processing for simpler storage or to recycle it.

3.4.3. Challenges and Opportunities

Developers must demonstrate that the properties of fuel salt compositions will ensure safe operations. Operational windows must be established across concentrations, temperatures, and redox states that ensure safety criteria are met throughout the service lifetime of the salt. The definition of operational windows for MSRs will enable developers to demonstrate that the range of fuel salt compositions will maintain the safety functions associated with both fuel and coolant. It is known that increases in the oxygen or water content of the salt increase the corrosivity of salts. The effects of other impurities, such as fission and corrosion products, on fuel salt properties have not been quantified. The work currently being done by the ART MSR campaign quantifying the effect of fission products on molten salt properties should be extended to **quantify the effect of ingrowth of oxygen, water, and trace metal contamination on molten salt properties.**

Significant uncertainty exists in the measured and modeled properties of pure fuel salts, and very few data are available addressing the properties of complex fuel salts as a function of temperature and redox state. **Generating property values for molten salt mixtures not previously measured will provide validation data and lead to improved models for molten salt properties. Where measured values are not**

available, the uncertainty of models should be quantified. A recent report from the *Molten Salt Thermal Property Uncertainty Workshop* outlines strategies for quantifying uncertainty in property models in the absence of adequate validation data (Rose 2023). Understanding the uncertainty in property models will determine the required accuracy of monitoring technologies to meet fuel qualification requirements.

It will be necessary to verify that fuel salt properties remain acceptable throughout their lifetime due to increasing fission product concentrations and environmental contamination. Salt properties can vary with temperature and the concentrations and speciation of elements in the salt. If an operational window results in acceptable salt properties, adjustments to the fuel salt composition can be made during operation such that the fuel remains in this operational window. Salt composition and redox state should be monitored during use to ensure the properties of the salt are still acceptable. Off-line and on-line monitoring techniques are being developed to monitor salt compositions and redox states. Electrochemical sensors are being developed and tested in salt loops to provide in-situ real-time measurements. **Monitoring technologies with standardized or reference measurement procedures should be developed and demonstrated at pilot-scale facilities.** Monitoring of salt composition and redox state may be used to demonstrate that fuel remains qualified during use. It is unclear if this will be a formal requirement by regulatory bodies.

The oxygen and water contents of salts have a direct impact on the redox conditions in the salt and must be measured in situ in real time to notify operators of any ingress of these materials in a timely manner. **Accurate techniques for measuring oxygen and water content on-line and in situ should be developed.** Direct control of salt chemistry will ensure fuel properties remain acceptable across the anticipated fuel lifetime. Methods for adjusting the chemistry of the molten salt include additions of fresh fuel and metallic or oxide buffers and sparging with gases.

3.4.4. Summary

Fuel qualification will require a demonstration that fuel salt will maintain acceptable properties under normal and accident conditions. Reactor developers will need to establish operational salt composition ranges or windows that maintain acceptable fuel salt properties. These compositional windows must include variances caused by the in-growth of fission and corrosion products and contamination due to the ingress of oxygen and moisture. The allowable levels of contaminants will depend on the effect of these species on the molten salt properties. Therefore, the effects of contaminants such as fission and corrosion products on fuel salt properties must be quantified. Quantifying the effect of contaminants will rely on verifiable methods of measuring the composition and properties of fuel salts. The properties, redox state, and composition of fuel salts must be measured both off-line to determine fuel specifications and on-line to monitor salt condition. Issues discussed and specific research needs identified during this session are divided into two future research directions. First, a newly defined direction to ***Develop and demonstrate salt chemistry monitoring technologies*** and a future research direction, previously defined in Chapter 3.2, ***Understand the impact of impurities on molten salt properties.***

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3.5. Technologies for Recovering Actinides

3.5.1. Introduction

A significant portion of the actinide inventory in a molten salt fuel will remain unreacted as neutron-absorbing fission products accumulate in the fuel, reducing its reactivity (Grimes 1970; Holcomb et al. 2011). Some developers will pursue a once-through fuel cycle, while others will pursue closed fuel cycles. In closed fuel cycles, actinides are recovered for reuse. In once-through fuel cycles, end-of-life salt must be treated to immobilize actinides and fission products in a stable waste form, to ensure repository performance requirements are met. Additionally, any stable isotopes in the fuel, either ^{7}Li or ^{37}Cl, are a valuable resource that could be recovered for reuse in synthesizing new fuel. Recovering actinides from used molten salt fuel can be accomplished via electrochemical, chemical, or volatility-based methods. These methods were originally developed for recycling metal or oxide fuels and will need to be adapted for processing molten salt fuels.

3.5.2. Current State of Actinide Recovery Technology

As Krista Hawthorne points out in her abstract in Appendix C.8, recovering actinides from used fuels is typically required prior to the removal of fission products. Otherwise, actinide materials will be retained in the fission product materials, increasing waste disposal costs and removing usable fuel materials from the reactor. Technologies developed for recovering actinides from LWR fuel and metal fuels can be adapted for recovering actinides from molten salt fuels. Processes for removing actinides include electrochemical, chemical, and volatility-based methods.

Electrochemical methods use electrical current to deposit a metal or metal alloy by reducing the dissolved ionic species to metal at a cathode (Laidler et al. 1997). Electrochemical methods have been developed and demonstrated for chloride salts and have not been demonstrated for fluoride salts.

Electrorefining is the deposition of a metal or metal alloy at a cathode as metals are oxidized into the salt at an anode (Laidler et al. 1997). It is the primary separation employed during the pyroprocessing of used oxide or metallic fuels. The metal species that is oxidized into salt during the recovery of actinides must be chosen such that it does not introduce a major impurity to the salt (Johnson 1988). For example, if the salt is $NaCl\text{-}UCl_3$, sodium can be used as the metal species to be oxidized at the anode, and a NaCl salt and U metal product would be produced. Using a metal not already present in the salt, such as potassium, would add significant KCl to the salt, radically changing the properties of the salt.

Electrolysis is an electrochemical method for recovering actinide or lanthanide species from salts as metals, collecting them at either a solid or liquid metal electrode while chlorine gas is evolved at the opposite electrode (Inman and White 1978). The process has been demonstrated for recovering very small amounts of actinides from electrorefiner salt before then drawing down lanthanides to produce a pure electrorefiner salt for reuse. The process is very flexible and can be optimized to produce an actinide product with minimal lanthanide contamination, or it can be optimized to recover the maximum amount of actinides, accepting a small lanthanide contamination. Despite this flexibility, the process does not allow for the separation of individual actinides from each other. Of all the actinides, the $U^{3+/0}$ reaction occurs at the least negative potential, which means transuranic elements cannot be deposited without co-depositing uranium.

There are two approaches for recovering actinides from the salt using chemical methods: reductive extraction and precipitation as an oxide or oxyhalide species followed by filtration of the precipitate (Grimes 1970). Reductive extraction chemically reduces the actinide chloride to an insoluble metal by reaction with a metal reductant. This metal reductant is converted to a metal chloride, as in Equation 1.

$$AcCl_x + M \rightarrow Ac + MCl_x \tag{1}$$

The resulting metal chloride becomes incorporated into the salt and must be carefully chosen to not adversely impact the properties of the remaining salt. Alternatively, this metal chloride can be removed in subsequent operations, such as drawdown of lanthanides. The metallic actinide product can be collected into a liquid metal or at a solid electrode.

Chemical recovery of actinides by conversion to oxides or oxyhalides is accomplished by adding an oxide-containing compound less stable than the UO_2 or UOCl/UOF, for example, Li_2O. The solid actinide product generated in situ must be filtered from the liquid salt phase. An added complication is that oxyhalide and oxide actinide species can have some solubility in molten salts, reducing the recovery of actinides.

Differences in the volatility of actinide chlorides or fluorides may be used to separate actinides from the base salt and fission product salts. Differences in volatility increase at higher oxidation states, e.g., UCl_4 is more volatile than UCl_3. Molten salt fuel is halogenated to raise the oxidation states of the fuel components to increase the differences in volatility between species. The temperature can then be increased stepwise to recover the more volatile actinide species without evolving the fission product or base salt species (Steindler et al. 1959). Recovered actinides then need to be reduced to oxidation states required for MSR fuels.

Some of the methods used to recover actinides from chloride salts release ^{37}Cl. This chlorine is a valuable resource that should be recovered. Chlorine scrubbers are currently implemented in electrolysis systems to capture the chlorine as $FeCl_2$.

Rehalogenation of recovered actinides would be required to implement a closed fuel cycle for MSR fuel salts. Halogenation of actinide metals was discussed extensively in Chapter 3.1 and can be done using strong halogenating agents, such as HF or HCl, or through an exchange reaction in a molten salt flux with a halide source, such as $FeCl_2$ or $ZnCl_2$. $FeCl_2$ is created during ^{37}Cl capture during electrolysis. This valuable stable isotope could be subsequently reused for synthesizing molten salt fuel.

3.5.3. Challenges and Opportunities

The development of actinide recovery processes has historically been focused on oxide and metal fuels, but many of the processes can be adapted to molten salt fuels. It would be advantageous to recover and reuse all the transuranic species in MSR salts. Recovery of actinides from used molten salts will allow the reuse of the fuel elements and the separate drawdown of fission products, which will minimize the amount of salt waste.

Electrolysis methods were developed to recover residual amounts of actinides from chloride salts after co-deposition during pyroprocessing and to separately remove lanthanide species to purify the salt for return to the electrorefiner. **Electrolysis of high actinide concentration salts for co-recovery of actinides should be demonstrated in both fluorides and chlorides.** Electrolysis for the co-recovery of actinides from high actinide concentration salts can be accomplished at solid or liquid metal electrodes. The use of liquid metals may provide enhanced separation between actinides and lanthanides. The activity of actinides and lanthanides in liquid metal electrodes determines the separability between actinides and lanthanides. **Measuring the activity of actinides in a variety of liquid metal electrodes will enable the optimization of electrolysis for the recovery of actinides.**

Chemical methods of recovering actinides include reductive extraction and conversion to insoluble oxide or oxyhalide species. Chemical methods dependent on the precipitation of actinide species rely on filtration to recover the actinide product. **Robust filters for removing particulates from the aggressive molten salt environment should be developed.**

Volatility-based methods have thus far been used to separate uranium from a simple mixture of uranium oxide and trace metals, such as tin, strontium, cerium, and neodymium (Fitzgerald et al. 2023). It is unclear if adequate separation of actinides can be achieved in a simulated irradiated mixture containing many more fission products, activation products, and contaminant species. **Separation of actinides using their relative volatility from a complex salt containing fission product salts should be demonstrated at the lab scale.** Once actinide salts have been collected, they will need to be reduced to oxidation states appropriate for use in an MSR prior to reuse.

In some of the processes being considered for the recovery of actinides from chloride salts, a metal product is recovered and the chlorine is released. ^{37}Cl is proposed for use in chloride-based MSRs to prevent the formation of ^{36}Cl. The production of ^{37}Cl is itself still experimental in nature, and, therefore, ^{37}Cl is a valuable material with a limited supply available. Recovery and reuse of the ^{37}Cl from chloride-based MSR fuels will reduce fuel synthesis costs and minimize waste. **Chlorine capture technologies should allow for the reuse of chlorine in the rehalogenation of the actinides**.

If actinides are collected as metals, they can be disposed of as a stable waste form or used to fabricate new fuel. If reuse as molten salt fuel is the end goal, they will need to be rehalogenated. Rehalogenation methods include the use of strong halogenation agents or exchange reactions in a flux salt and are covered in Chapter 3.1. Recovery of actinides as salts from used molten salts makes it possible to directly reuse the actinide halides as fuel and minimize salt waste.

3.5.4. Summary

Recovering actinides from used molten salt fuel will allow the treatment of end-of-life salt to consolidate actinides and fission products into stable waste forms and assist in the recovery of stable isotopes in the fuel, such as ^{7}Li and ^{37}Cl, for reuse in synthesizing new fuel. Methods developed under NE-43 for recycling metal or oxide fuels can be leveraged for processing molten salt fuels. Recovering actinides from used molten salt fuel can be accomplished via electrochemical, chemical, or volatility-based methods. No preferred method has yet been identified. Methods must be adapted to handle higher actinide concentration salts and more complex salts and prevent contamination of the salt, which would alter its properties. A future research direction is therefore defined to ***Adapt and optimize actinide separation technologies to chloride and fluoride salts***.

3.5.5. References

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3.6. Used Fuel Salt Purification for Recycle

3.6.1. Introduction

Fission products, corrosion products, and contaminants will accumulate in molten salt during use in a reactor. Chapter 3.2 discussed the technologies for removing oxygen and water from molten salts at length. In this session, the focus was on the removal of fission product species from molten salts. These elements can change the thermal behavior of the salt or act as neutron poisons, making the reactor less efficient. In some reactor concepts, these elements are periodically removed from the fuel in-line or at-line to prolong the lifetime of the fuel. Alternatively, these elements can be removed off-line prior to disposal or recycling of the salt. Recycling purified base salt back to the reactor would significantly decrease the volume of waste to be disposed. Fission products and contaminants from corrosion, oxygen, or water can alter the properties of the salt and must be removed to maintain salt properties. Valuable ^{7}Li or ^{37}Cl should be retained and reused to reduce cost. Fission product removal processes that leave actinides in the salt would minimize the number of steps for salt recycling and extend the service life of the fuel salt.

3.6.2. Current State of Purification Technology

Techniques for removing lanthanides after the removal of actinide species have been developed to support pyroprocessing. These include electrochemical, physical, and chemical methods. These methods were developed for removing contaminants from the electrorefiner (LiCl-KCl) or electroreducer (LiCl) salts. They will need to be adapted to the processing and recycling of molten salt fuels, including fluoride salts.

Electrolysis for recovering lanthanide salts as metals was developed to support pyroprocessing, where lanthanides are collected at either a solid or liquid metal electrode while chlorine gas is evolved at the other electrode. Electrolysis was applied to drawdown lanthanides from electrorefiner salt (LiCl-KCl), and the evolved chlorine gas was collected in a scrubber; usually, it was captured on iron as $FeCl_2$. Electrolysis does not efficiently remove elements with deposition potentials that are more negative than those of the base salt constituents, such as Cs^{+}, Sr^{2+}, and Ba^{2+} (Lichtenstein and Hawthorne 2022). The deposition potentials of lanthanide and actinide elements can be shifted by depositing the species into liquid metals (Lichtenstein et al. 2018). Figure 1 from Timothy Lichtenstein's presentation at the workshop illustrates this shift for the deposition of select fuel components from LiCl/KCl eutectic salt into liquid metals versus inert cathodes.

Melt or fractional crystallization is a physical separation method for removing impurities from salts. Contaminated LiCl salts have been purified by crystallizing a pure LiCl solid phase that excludes fission product and contaminant species; the contaminants remain in the melt phase (Cho et al. 2011; Rodríguez-Laguna et al. 2024). MSRs plan to use binary or ternary base salt mixtures with chemistries that are more complex than LiCl. Thermodynamically favorable complex solid phases are expected to form in many complex salt mixtures that include fission product elements (Rose and Thomas 2023). Melt or fractional crystallization has not been successfully demonstrated in complex multi-component salts or fluoride salts.

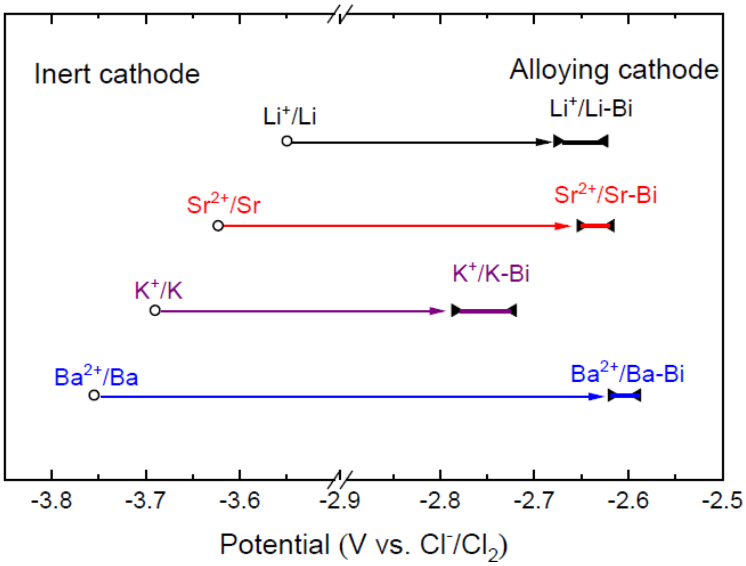

Figure 1: Deposition Potentials of Select Fission Products from LiCl/KCl Eutectic Salt on Inert and Liquid Bi Cathodes (Lichtenstein et al. 2018).

Volatility-based methods are another physical separation approach that can be used to remove trace metals in the salt. Differences in the volatilities of metal chlorides or fluorides may be used to separate trace metals from the base salts. Differences in volatility increase at higher oxidation states. Molten salt fuel can be further halogenated to raise the oxidation states of the fuel components to increase the differences in volatility between species. The temperature can then be increased stepwise to recover the more volatile actinide species without evolving the fission product or base salt species. Recovered actinides then need to be reduced to oxidation states appropriate for MSR fuels. This volatility separation is being demonstrated as part of the MCRE project to produce high-purity UCl_4. Crystals of UCl_4 have been collected from a mixture of UO_2, tin, iodine, strontium, cerium, and neodymium via the volatility method at the lab scale; the cerium, neodymium, and strontium were left in the crucible and iodine was collected in a cold zone separate from the UCl_4 product (Fitzgerald et al. 2023).

Chemical methods of removing impurities include precipitation, reductive extraction, and halogenation. Oxygen sparging to create filterable oxychloride versions of fission product species was proposed and demonstrated with $LnCl_3$. This has not been demonstrated with corrosion product metals or in fluoride salts. Removal of the insoluble species will require settling and filtering of the salt.

Reductive extraction reduces lanthanide salts to metals and collects them in liquid metals. The lanthanides exchange with the liquid metal constituents, adding these to the salt as halides. For example, $CeCl_3$ in LiCl-KCl salt can be exchanged with Li from a Bi-Li electrode to add LiCl to the salt and collect cerium in the Bi-Li alloy (Han et al. 2019). This does result in a shift of the base salt composition as the metal being exchanged for the lanthanide enters the salt as a halide. The composition of the purified salt would need to be adjusted prior to reuse.

Oxygen and water impurities can be removed by using strong halogenating agents, which were discussed in detail in Chapter 3.2.

3.6.3. Challenges and Opportunities

A variety of separation methods have been developed for used fuel management. Electrochemical methods developed in support of pyroprocessing can be leveraged for the processing and recycling of molten salt fuels. Electrolysis has been demonstrated in LiCl-KCl at the engineering scale but cannot recover elements with deposition potentials that are more negative than those of the base salt constituents, such as Cs, Sr, and Ba. **Developers need to determine if Cs, Sr, and Ba must be removed for fuel salt to be reused.** If some fission product elements can remain in the salt indefinitely without negatively impacting reactor performance, this will reduce the number of operations needed to recycle salt fuels. The proper choice of cathode material will need to be determined as well. **The activity of lanthanides in a variety of liquid metals should be measured to enable the optimization of electrolysis for fission product removal.**

While the separation of a pure LiCl phase from a contaminated LiCl salt using a crystallization technique has been demonstrated, the formation of complex phases containing impurities is favored in complex salts. Therefore, the crystallization of complex used molten fuel salt mixtures is unlikely to result in a pure base salt crystal phase, reducing the achievable separation efficiency of crystallization methods. **The achievable separation efficiency of crystallization methods for purifying molten salt fuels will need to be measured.** If a high separation efficiency can be achieved, pure salts could be recycled, reducing the need for fresh fuel salt.

Minimizing the number of steps associated with recycling molten salt fuel will reduce costs. Methods of removing impurities, such as fission and corrosion products and oxygen and water, while leaving actinide halides in the salt phase would eliminate the need to recover actinides prior to removing lanthanides and the need to then re-dissolve the actinides in the salt. **Methods that remove fission products without removing actinide species have not yet been identified.**

Oxygen sparging has been shown to produce insoluble or sparingly soluble lanthanide oxyhalide and oxide species, which can then be filtered to remove lanthanide contamination from the salt. It is unclear if sparging with oxygen creates oxyhalide actinide or base salt species as well. If the base salt or actinides also precipitate, then separation of lanthanides via this method would not be feasible. Additionally, the presence of insoluble oxide or oxyhalide species after filtering may alter salt properties. This method has not been demonstrated in fluoride salts. Many aspects of this method of removing lanthanide contamination are untested, and, therefore, its feasibility has not been demonstrated.

3.6.4. Summary

Contaminants will build up in molten salt reactor fuel during use, from fission of the actinides, corrosion of structural materials, and ingress of oxygen and water. Chapter 3.2 discussed at length the technologies for removing oxygen and water from molten salts. In this session, the focus was on the removal of fission product species from molten salts. These fission product contaminants will decrease the efficiency of the reactor over time until it becomes necessary to either replace the fuel or process the fuel to remove the contaminants. Several fuel cycle options are being considered by developers, including a once-through fuel cycle, limited processing of salt to remove contaminants, and a fully closed fuel cycle. In all cases, used molten salt fuel must be treated to either increase its lifetime or consolidate contaminants into stable waste forms. The methods for purifying molten salt fuels include electrochemical, physical, and chemical processes. Methods have been developed for applications to pyroprocessing salts. Methods should be extended to many more molten salt compositions, including fluorides, to determine feasibility, separation efficiency, and optimal operating conditions. There is intense interest in identifying a method of removing fission products that leaves the actinide salts in solution. A future research direction is, therefore, defined to ***Develop technologies to remove fission products from chloride and fluoride salts*.**

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3.7. Recovery and Transmutation of Long-Lived Isotopes

3.7.1. Introduction

Technologies for recovering long-lived isotopes, such as ^{99}Tc, ^{129}I, and ^{135}Cs, from used molten salt fuels and the design requirements for transmutation targets were discussed during this session. Used nuclear fuel and the highly radioactive waste materials produced after used nuclear fuel reprocessing are regulated as high-level waste. The used nuclear fuel components driving this designation include long-lived fission and activation radioisotopes with half-lives exceeding many thousands of years. The use of liquid fuels affords an opportunity to perform in-reactor and even on-line processing of nuclear fuel, as pointed out by Edmondson in his abstract (Appendix C.13). This could lead to efficient fuel utilization by removing only problematic materials, such as neutron poisons, for disposal. Some MSRs plan to utilize used fuel from light water reactors as source material with little to no separatory work required to burn the fissile material contained in the LWR fuel. A molten salt reactor or an accelerator-based source of charged particles or photons can be used to transmute these problematic long-lived radioisotopes into shorter-lived radioisotopes. Transmutation results in an overall lower long-term radioactive waste burden for the United States nuclear energy industry to address.

3.7.2. Current State of Long-Lived Fission Product Transmutation Technology

The recovery and isolation of long-lived isotopes to reduce radioactive waste burdens have been demonstrated in other countries. The unique liquid form of MSR fuels enables long-lived isotopes to be recovered more efficiently than can be achieved by processing solid fuels. Only preliminary, or conceptual, studies have been done to develop processing technologies for recovery of long-lived isotopes from MSR fuels. Specific fission products being targeted in these initial conceptual studies include ^{99}Tc, ^{129}I, ^{126}Sn, ^{93}Zr, ^{135}Cs, and ^{79}Se (Appendix C.12). Likewise, the transmutation of long-lived isotopes has received attention over the years, but significant advancements in evaluating the effectiveness of transmutation options are hindered by relatively large uncertainties in key nuclear data. The Nuclear Fuel Cycle Evaluation and Screening Study (Wigeland et al. 2014) concluded that the continuous recycling of actinides (uranium and transuranic elements) in nuclear reactors is the most promising nuclear fuel cycle in the United States. A transmutation project was initiated to transmute long-lived fission products (LLFPs) using incident non-neutron particles such as energetic photons and protons, as described by Kim in his abstract (Appendix C.12). This project is considering both accelerator transmutation with non-neutron particles and burning, or in-reactor transmutation via neutron irradiation, of LLFPs in reactor systems.

3.7.3. Challenges and Opportunities

It will be important to balance multiple factors in determining a waste management strategy for handling long-lived radioisotopes in used MSR fuel. Recovering LLFPs from liquid MSR fuels does not require dissolution of the fuel, but the fuel is easily contaminated and corrosive. No processes have yet been developed to extract LLFPs from molten salt, but it is anticipated to be easier than from oxide fuels because MSR fuels do not require dissolution. If LLFPs can be extracted from MSR salt, not only does that reduce salt waste volume, but may enable the production of targets for non-neutron particle transmutation. Alternatively, LLFPs could be added to molten salts to “burn” or be transmuted by neutron irradiation in an MSR.

The transmutation of LLFPs in MSRs and with accelerator-based sources of charged particles and photons both have key gaps of knowledge that need to be addressed. First, there is a lack of nuclear data used to predict the performance of all transmutation pathways. Specifically, **nuclear data for the transmutation of long-lived isotopes via neutron, photon, and charged particle irradiation need to be measured.** In order to assess the effectiveness of transmutation strategies, modeling and simulation tools need to be developed, validated, and benchmarked. Importantly, the economics of partitioning and transmutation need to be carefully considered, as it is not clear yet if either option is worthwhile economically.

The range of MSR technologies being developed includes a variety of fuel chemistries and envisioned fuel cycles. None of the fuel cycles under consideration by MSR developers have yet considered the removal and isolation of LLFPs. Nor have processes been developed for recovering LLFPs from molten salts. **Processing technologies for recovering long-lived isotopes from MSR fuel salts need to be developed.** The recovery of long-lived isotopes from MSR fuel could improve the economics of MSRs by reducing high-level waste volumes and removing neutron poisons to increase fuel reactivity.

3.7.4. Summary

LLFPs drive the long timescales over which UNF remains radioactive. The accessibility of liquid fuel in MSRs provides alternative approaches to address this challenge. Processing technologies for recovering long-lived isotopes from MSR fuels should be developed. Additionally, uncertainties in nuclear data should be reduced to enable accurate assessments of the feasibility of transmuting isotopes by neutron irradiation in MSRs and by non-neutron particles in accelerator systems.

So far, it has been confirmed that LLFPs could be transmuted to short-lived nuclides using high-intensity and energetic photons and protons. But uncertainties in the high-energy cross-sections of photons and protons, the likely expensive cost of separating LLFPs from UNF, and the availability of high-intensity beams of photons and protons are risks for this approach. There is very limited ongoing research in this field. Investment would be required to advance this field for use in MSRs. No future research direction is recommended in this topic at this time, as research into this area is not needed to enable the deployment of MSRs or develop an effective MSR fuel cycle strategy.

3.7.5. References

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3.8. Noble Metal and Insoluble Fission Product Recovery

3.8.1. Introduction

Insoluble species will form in a molten salt reactor salt during operation. These species will consist of metallic fission products such as Ag, Pd, Rh, Tc, Mo, Nb, Zr, and Ru, oxide and oxyhalide species formed by the ingress of oxygen or water, and halide species that have exceeded their solubility in the melt phase. Some elements such as antimony, tellurium, and iodine do not form stable fluoride or chloride species under these conditions and therefore are insoluble. It is not known if they will agglomerate, plate out on reactor materials, or remain suspended in the salt. It is important that the insoluble species not deposit in such a way as to restrict flow or negatively impact fluid dynamics in the reactor core or heat exchangers. The presence of heterogeneous phases in molten salts, such as suspended insoluble fission products, has been shown to increase the heat capacity of the fuel salt, thereby altering the conditions in the reactor system (Maltsev et al. 2020). Therefore, treatment options for removing or collecting these noble metals at advantageous locations were discussed during the session.

3.8.2. Current State of Insoluble Fission Product Recovery Technology

Insoluble fission products, including noble metals, may agglomerate, plate out, or remain suspended. Figure 2 highlights phenomena applicable to insoluble species in the salt that may occur in an MSR. Some elements are only insoluble under certain salt conditions; for example, zirconium and niobium have redox-sensitive chemistries, and so their solubility depends on the U^{3+}/U^{4+} ratio, which will vary with burnup and salt conditioning operations (McMurray et al. 2021). Some metals may plate out onto reactor materials, be captured in or on the graphite matrix in a thermal reactor, or collect at noble gas bubbles and appear in the off-gas systems as particulates or aerosols. During the Molten Salt Reactor Experiment (MSRE) conducted at Oak Ridge National Laboratory, these insoluble fission products were found deposited on graphite and metal reactor surfaces, in the salt, and in the off-gas system (Compere et al. 1975), but the behavior of the insoluble species was not specifically studied. Some recent research suggests that noble metals may agglomerate due to radiolysis (Dais et al. 2020). Some noble metals may form intermetallic species with other fission products, for example, PdTe (Ignatiev et al. 2013). Tellurium plays a role in stress corrosion cracking of reactor alloys. However, the formation of PdTe would prevent the tellurium from being available for this mode of degradation, reducing the deterioration of metals in the reactor (Keiser et al. 1976).

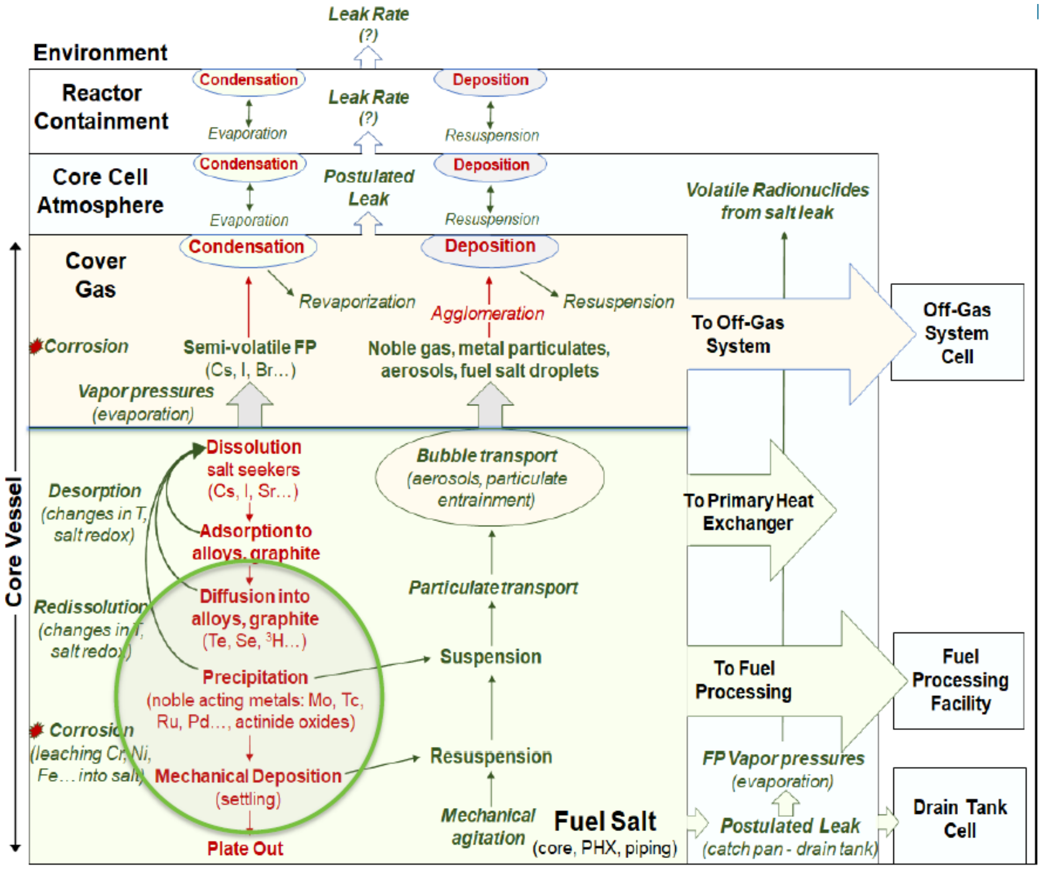

Figure 2: A Schematic of Processes That May Occur in Molten Salt Reactors with Processes Related to Insoluble Species Highlighted (Thomas and Jerden 2020).

Filtration of insoluble fission products can prevent buildup of these species in disadvantageous locations either in-reactor or during salt processing. As pointed out by Joanna McFarlane in her extended abstract in Appendix C.15, processes for the removal of insoluble fission products from molten salts have not been developed. Some modeling and simulation of the capture of noble metal particles on fission gas bubbles have been published (Lee and Jesee 2023;, Shabhazi et al. 2022; Frederix 2022), but no validation data for these simulations exist.

Some isotopes produced in MSR fuel salt may be valuable for medical imaging and diagnostics (e.g., ^{99}Mo, ^{131}I, ^{133}Xe). Recovery of these isotopes may include capture from the gas phase, solid-phase extractions, and electrodeposition or promoted deposition on removable media, as appropriate to each isotope.

3.8.3. Challenges and Opportunities

Understanding the fate of insoluble species in molten salt fuels is a major technical gap for MSRs. Specifically, it is not understood how the insoluble fission products behave when formed atom by atom from fission, if these insoluble metals agglomerate, deposit, remain suspended, or collect in gas bubbles formed by gaseous fission products. **Irradiation testing of molten salt fuel is needed to determine the behavior of insoluble fission product species.** These tests will need to be planned carefully to ensure data is gathered on the agglomeration, alloying, or adsorption behaviors of the species onto different reactor-relevant materials in flowing salt.

Which elements are insoluble at what concentrations and what effect they have on fuel properties and reactor operation will determine which elements need to be removed and which can be allowed to build up. Knowing this will allow developers to evaluate the cost-benefit analysis of removing these insoluble species. Filters may be an option for the removal of insoluble species. **Filters made of salt-compatible materials such as ceramic foams or intermetallic structures should be designed** for both in-reactor and off-line salt processing applications. Filtering insoluble species will reduce fouling of reactor piping and a reduction in piping diameter due to plate out.

Selective media should be identified that can collect targeted high-value isotopes such as those relevant to medical applications. Recovery of medically relevant isotopes from MSR fuels will support a domestic supply of these important materials.

3.8.4. Summary

Insoluble fission products form atom by atom during fission in MSR fuel salt. It is unclear if these insoluble species will agglomerate, plate out on reactor materials, collect as particulates or aerosols in off-gas systems, or remain suspended in the melt phase. The presence of heterogeneous phases in molten salts, such as suspended insoluble fission products, has been shown to increase the heat capacity of the fuel salt, thereby altering the conditions in the reactor system. Irradiation testing will be needed to understand the formation and fate of these insoluble species in molten salt fuels. A future research direction is, therefore, defined as ***Understand the behavior of insoluble fission products in molten salt fuels.***

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3.9. Safeguards Approaches for Liquid Fuels and Fuel Cycle Facilities

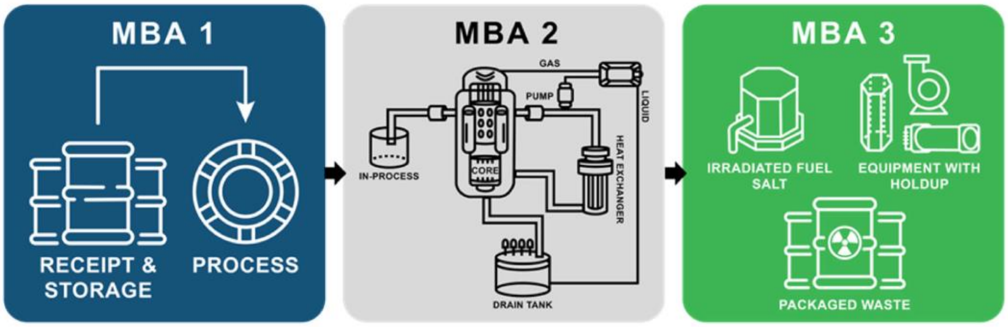
3.9.1. Introduction

Liquid fuels present unique challenges for safeguarding the radionuclide inventory of a nuclear reactor. The same accessibility that is an advantage for on-line salt processing is a challenge for safeguarding the radionuclide inventory of the fuel. Approaches to safeguarding the production, storage, and shipment of fresh MSR fuel salt, as well as recycle and treatment of used MSR fuel salt, were discussed during this session, including the complication presented by onsite and/or on-line fuel purification that is planned by many MSR developers. Domestic safeguards include physical protection and material control and accountancy (MC&A). Safeguards are regulated in the United States by the US Nuclear Regulatory Commission (NRC) and are concerned primarily with terrorist theft. Novel safeguards likely will be required for the domestic operation of reactors with fuel in non-discrete (i.e., item) forms. Internationally, safeguards are regulated by the International Atomic Energy Agency (IAEA) Department of Safeguards, whose focus is preventing nuclear proliferation by a State. Safeguards are required by the IAEA for international deployment and are implemented to support independent verification of fertile/fissile materials. The cost of implementation is reduced if they are included at the design phase of reactor development rather than being implemented after deployment.

3.9.2. Summary of Current Status

Current activities in safeguards development are focused in three areas: science and concepts, MC&A technology development, and stakeholder support and engagement. The science and concepts being explored include the development of reactor physics codes for reactors with continuously circulating fuels, conceptual MC&A approaches for MSRs, technical assessments of radiation signatures of nuclear materials in liquid fuel, radiation detection feasibility studies on materials containing ^{233}U, and the evaluation of laboratories available to support these efforts. Reactor physics models such as SCALE and its reactor physics sequence, TRITON, are being extended to enable the simulation of the depletion of molten salt reactor fuel when fission products are actively removed and makeup fuel salt is added on-line (Appendix C.16). Understanding the evolution of the fissile and fertile inventory in the salt during use is essential to safeguarding that material.

An all-encompassing MC&A approach has not been determined for molten salt reactors. One proposed MC&A approach, presented by Richard Reed during the Safeguards session of the workshop, includes the division of the reactor system into three material balance areas: salt production, where periodic inventories are performed; reactor operations, where the system is monitored to detect diversion; and spent fuel, where periodic inventories are performed as pictured in Figure 3.



Periodic inventories performed, IDs and SEIDs calculated (follows Part 74 requirements)

Monitoring performed in specific locations to detect diversion

Periodic inventories performed, IDs and SEIDs calculated (follows Part 74 requirements)

Figure 3: Proposed MC&A Approach for an MSR (Hogue et al. 2024)

There is ongoing MC&A technology development including the development of a feed monitoring system and innovative monitoring techniques for nuclear materials using isotopic ratios. Radiation detector development feasibility studies include detector evaluations, measurement campaigns, and distinguishing fissile uranium in mixed samples. Specifically, the Office of Defense Nuclear Nonproliferation Research and Development (NA-22) is sponsoring work to evaluate non-destructive analysis (NDA) techniques using neutron irradiation to distinguish fissile uranium in samples of mixed oxide species (Appendix C.16). There is ongoing work on non-invasive sensors for salt composition, redox state, and salt level at Argonne National Laboratory (Hoyt and Moore 2021), for example, the use of voltammetry for concentration monitoring, and at Pacific Northwest National Laboratory (PNNL), using Raman or UV-vis spectroscopy (Lines et al. 2020).

Discussions among reactor developers, regulatory agencies, safeguards experts, and the research and development community are ongoing to aid in the development of MC&A and safeguards solutions. Establishing which parameters must be known, such as the type of material, its quantity, its physical and chemical form, and its radioactivity or concentrations, is an important first step in developing an MC&A approach. Many reactor design decisions will have a direct impact on the choice of safeguarding technologies and their implementation, including feed rates, accessibility to the salt, chemical processing operations, and the chemical makeup of the fuel salt (Hogue 2023).

3.9.3. Challenges and Opportunities

Molten salt fuels present unique challenges for safeguarding the radionuclide inventory of a nuclear reactor. The fuel is a circulating liquid rather than discrete solid items. Fuel elements cannot be tagged and tracked; therefore, alternative approaches to safeguarding the radionuclide inventory based on material balance areas will be needed. Several developers plan to make on-line fuel additions or remove fission products on-line or at-line to maintain the efficiency or redox state of the fuel, which will further complicate the safeguards challenge. Some developers plan to co-locate a fresh fuel production facility or a used fuel purification facility at the reactor, which will also need safeguards. A cohesive strategy for materials control and accountancy based on material balance areas must be developed to support the deployment of MSRs and their fuel cycle facilities.

It is expected that many of the technologies currently used for safeguarding LWR reactors will not be applicable to molten salt reactors (Dion and Hogue 2022). Technologies for providing safeguards and MC&A information for these liquid fuels must be developed. **Reactor physics models capable of simulating the depletion of molten salt fuel during use in a reactor with on-line or at-line removal of fission products and additions of makeup fuel salt must be developed and validated.** Ongoing work in this area should be continued and extended to validation of the codes. **NDA detection technologies for fissile material in molten salts should be developed** to provide flexible methods of safeguarding MSRs and their fuel cycle facilities. Discussions among reactor developers, regulatory bodies, experts in safeguards development and application, and the research and development community will be needed to define material balance area (MBA) boundaries, the types of sensors, and the installation locations for those sensors.

3.9.4. Summary

One goal of safeguards includes quantifying, declaring, and verifying fissile and fertile materials throughout the process streams in nuclear facilities. Early consideration of incorporating safeguards is valuable to both inspectors and operators. By designing a nuclear facility with safeguards in mind, international deployment costs are reduced by avoiding redesigns and design changes to accomplish international safeguards obligations. Safeguards by design preferably includes interactions with the regulator during the design phase for all salt processing streams/facilities from salt production, reactor operation, and spent fuel. The equipment and methods used to implement nuclear safeguards are determined by reactor and fuel cycle design choices such as salt composition, chemical processing operations, and accessibility to the salt. No future research directions were defined by the discussions in this session as the research needs identified fall outside the scope of the workshop but are summarized here in this session report.

3.9.5. References

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4. Conclusions and Recommendations

Discussions during the workshop sessions identified many specific research needs, which are collected in Table 1. The summation of these research needs into groups yielded seven future research directions (FRDs). Research is recommended in these FRDs to enable the deployment of molten salt reactors by ensuring access to the technologies needed for synthesizing, purifying, and delivering molten salt fuels, as well as the disposition or recycling of molten salt fuels. The FRDs are:

FRD 1: Develop and Demonstrate Efficient and Scalable Synthesis Processes

FRD 2: Understand the Impact of Impurities on Molten Salts

FRD 3: Optimize and Demonstrate Separation Technologies for Removing Impurities from Molten Salts

FRD 4: Develop Salt Chemistry Monitoring and Control Technologies

FRD 5: Adapt and Optimize Actinide Separation Technologies to Chloride and Fluoride Salts

FRD 6: Develop Technologies to Remove Fission Products from Chloride and Fluoride Salts

FRD 7: Understand the Behavior of Insoluble Fission Products in Molten Salts

These FRDs encompass the research necessary to successfully deploy MSRs and support fuel cycle facilities. Specific research needs to support FRD 1 (Develop and demonstrate efficient and scalable synthesis processes) were identified during Session 1: conversion of fuel sources to salt and Session 3: scale-up of fuel synthesis, packaging, and delivery. These specific research needs are summarized in Table 1 and are discussed at length in Chapters 3.1 and 3.3, respectively. Closing the technological gaps in synthesizing molten salt fuels at scale would enable a robust supply chain of molten salt fuel in advance of the deployment of MSRs.

Specific research needs to support FRD 2 (Understand the impact of impurities on molten salt) were identified during Session 2: fresh fuel salt purification technology and Session 4: fresh fuel salt characterization and qualification. These specific research needs are summarized in Table 1 and are discussed at length in Chapters 3.2 and 3.4, respectively. Understanding the impact of contaminants on fuel performance will allow developers to set the fuel specifications and fuel synthesis processes to be optimized to meet these requirements without undue cost.

Specific research needs to support FRD 3 (Optimize and demonstrate separation technologies for removing impurities from molten salts) were identified during Session 2: fresh fuel salt purification technology. Specific research needs are summarized in Table 1 and are discussed at length in Chapter 3.2. Purification technologies will enable the production of high-purity salts for use in measuring salt properties and synthesizing fuel salts.

Specific research needs to support FRD 4 (Develop salt chemistry monitoring and control technologies) were identified during Session 4: fresh fuel salt characterization and qualification. These specific research needs are summarized in Table 1 and are discussed at length in Chapter 3.4. Technologies for the control and monitoring of salt chemistry will ensure that fuel properties remain adequate throughout the anticipated fuel lifetime.

Specific research needs to support FRD 5 (Adapt and optimize actinide separation technologies to chloride and fluoride salts) were identified during Session 5: technologies for recovering actinides. These specific research needs are summarized in Table 1 and are discussed at length in Chapter 3.5. Recovery of actinides from used molten salts will allow the reuse of the fuel elements, enable the drawdown of fission products, and minimize salt waste.

Specific research needs to support FRD 6 (Develop technologies to remove fission products from chloride and fluoride salts) were identified during Session 6: used fuel salt purification for recycle. These specific research needs are summarized in Table 1 and are discussed at length in Chapter 3.6. Removal of fission products would enable salt recycle, minimizing salt waste and, therefore, cost.

Specific research needs to support FRD 7 (Understand the behavior of insoluble fission products in molten salts) were identified during Session 8: noble metal and insoluble fission product recovery. These specific research needs are summarized in Table 1 and are discussed at length in Chapter 3.8. Understanding the behavior of insoluble species in MSR fuels will inform fuel qualification, reactor design, and licensing activities.

These FRDs encompass the research necessary to successfully deploy MSRs and support fuel cycle facilities. Some of the FRDs address fuel salt issues relevant during reactor operation, such as FRDs 2 and 7, and some address fuel cycle issues, such as FRDs 1, 3, 5, and 6. FRD 4 addresses safeguards challenges that will be relevant both in reactor and fuel cycle facilities. Investigations addressing fuel behavior relevant to reactor operation are currently being conducted under the Advanced Reactor Technology Program's MSR campaign. Based on presentations and discussions held during this workshop, it is recommended that research addressing molten salt fuel cycle chemistry and technologies that is described as parts of FRDs 1, 3, 5, and 6 be initiated and that the impactful research addressing the issues described in FRDs 2 and 7, which is underway, be continued to enable deployment of MSRs.

Appendix A: Participant List

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Kim Pamplin*	Abilene Christian University
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Krista Hawthorne*	Argonne National Laboratory
Nathan Hoyt*	Argonne National Laboratory
Bethany Kersten	Argonne National Laboratory
TK Kim*	Argonne National Laboratory
Timothy Lichtenstein*	Argonne National Laboratory
Colin Moore	Argonne National Laboratory
Daniel O’Hanlon	Argonne National Laboratory
Amber Polke*	Argonne National Laboratory
Melissa Rose	Argonne National Laboratory
Sarah Stariha	Argonne National Laboratory
Sara Thomas	Argonne National Laboratory
Devin Rappleye	Brigham Young University
Cemal Cakez	Curio Solutions Inc.
Alex Wheeler	Curio Solutions Inc.
James Willit	Department of Energy
Rodolfo Vaghetto	Electric Power Research Institute
Ed Pheil*	Exodys Energy
Kirk Sorensen	Flibe Energy Inc.
Steven Herrmann	Idaho National Laboratory
David Holcomb*	Idaho National Laboratory
Robert Hoover*	Idaho National Laboratory
Ken Marsden	Idaho National Laboratory
William Phillips*	Idaho National Laboratory
Kevin Tolman*	Idaho National Laboratory
Ken Baer	Metatomic Energy
Tom Osmundsen	Metatomic Energy
Wendy Reed	Nuclear Regulatory Commission
Tony Birri	Oak Ridge National Laboratory
Sheng Dai*	Oak Ridge National Laboratory
Dianne Ezell	Oak Ridge National Laboratory
Joanna McFarlane*	Oak Ridge National Laboratory
Kristian Myhre	Oak Ridge National Laboratory
Richard Reed*	Oak Ridge National Laboratory
Patricia Paviet	Pacific Northwest National Laboratory
Perry Motsegood*	TerraPower
Daniel Carleton	Terrestrial Energy Inc.
Dane Wilson	ThorCon Power
Michael Edmondson*	United Kingdom National Nuclear Laboratory
Michael Simpson*	University of Utah
Jinsuo Zhang	Virginia Tech University
Amanda Leong	Virginia Tech University

*Speaker

Appendix B: Workshop Agenda

Molten Salt Reactor Fuel Cycle Chemistry Workshop Agenda

Supported by US Department of Energy
Office of Materials and Chemical Technologies (NE-43)
(Times are all in central time)

Tuesday September 19, 2023

8:30 – 9:00 am	Gather
8:45 – 8:55 am	Welcome – Melissa Rose (Argonne)
8:55 – 9:00 am	James Willit (DOE)
9:00-11:30 am	Session 1: Conversion of fuel sources to salt
9:00 – 9:20 am	Sheng Dai (ORNL)
9:20 – 9:40 am	Ed Pheil (Exodys Energy)
9:40 – 11:30 am	Open Discussion
11:30 – 12:30 pm	Working Lunch
	A Historical Perspective on Molten Salt – James Willit
12:30-2:30 pm	Session 2: Fresh fuel salt purification technology
12:30 -12:50 pm	Perry Motsegood (TerraPower)
12:50 – 1:10 pm	Amber Polke (ANL)
1:10 – 2:30 pm	Open Discussion
2:30 – 2:45 pm	Break
2:45-4:45 pm	Session 3: Scale-up of fuel synthesis, packaging, and delivery
2:45 – 3:05 pm	Michael Simpson (University of Utah)
3:05 – 3:25 pm	Bill Phillips (INL)
3:25 – 4:45 pm	Open Discussion
4:45 pm	Poster Set-Up
5:00 pm	Poster Session (Upstairs)
5:30 – 7:00 pm	Hors D ’Oeuvres Are Served

Wednesday September 20, 2023

8:30 – 9:00 am	Re-gather	
8:45 – 9:00 am	Welcome – Melissa Rose (Argonne)	
9:00 – 11:30 am	Session 4: Fuel salt characterization and qualification	
9:00 – 9:20 am	David Holcomb (INL)	
9:20 – 9:40 am	Nathan Hoyt (Argonne)	
9:40 – 11:30 am	Open Discussion	
11:30 – 12:30 pm	Working Lunch – Overview of Fuel Cycle Capabilities at Argonne National Laboratory – M. Williamson	
12:30 – 2:30 pm	Session 5: Technologies for recovering actinides	
12:30 – 12:50 pm	Krista Hawthorne (Argonne)	
12:50 – 1:10 pm	Robert Hoover (INL)	
1:10 – 2:30 pm	Open Discussion	
2:30 – 2:45 pm	Break	
2:45 – 4:45 pm	Session 6A: Used fuel salt purification for recycle	Session 6B: Safeguards for liquid fuels and fuel cycle facilities (Upstairs)
2:45 – 3:05 pm	Tim Lichtenstein (ANL)	Richard Reed (ORNL)
3:05 – 3:25 pm	Kevin Tolman (INL)	
3:25 – 5:00 pm	Open Discussion	Open Discussion
5:30 – 7:00 pm	Networking Dinner (BBQ Buffet)	

Thursday September 21, 2023

8:30 – 9:00 am	Re-gather	
8:45 – 9:00 am	Welcome – Melissa Rose (Argonne)	
9:00 – 11:30 am	Session 7A: Recovery and transmutation of long-lived isotopes	Session 7B: Noble metal and insoluble fission product recovery (Upstairs)
9:00 – 9:20 am	TK Kim (Argonne)	Joanna McFarlane (ORNL)
9:20 – 9:40 am	Mike Edmondson (UKNNL)	Kim Pamplin (NEXTlab)
9:40 – 11:30 am	Open Discussion	Open Discussion
11:30 – 12:00 pm	Closing Remarks Melissa Rose (Argonne) James Willit (DOE)	
12:00 – 1:00 pm	Working Lunch for Organizing Committee	
1:00 –3:00 pm	Wrap Up for Organizing Committee	

Appendix C: Extended Abstracts Submitted by Speakers

C.1 Advancements in Molten-Salt Chemistry for Nuclear Energy Applications

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In recent years, there has been a remarkable resurgence of interest in the development of nuclear reactors that utilize molten salts as coolants for heat exchangers and as liquid carriers for nuclear fuels. Molten salt coolant and liquid-fuel systems offer the advantage of operating at high temperatures without undergoing chemical decomposition, while maintaining significantly lower vapor pressures compared to traditional water/steam systems. However, to fully harness the potential of these systems, it is imperative to gain a comprehensive understanding of the chemistry of actinides and their radioactive progeny within molten salts. This presentation will delve into two key topics that are pivotal to the successful advancement of molten salt-based nuclear reactor technology:

(1) Technologies for Synthesis and Purification of Nuclear Applications:

Efficient and robust methodologies have been established to synthesis and purification of halide salts including uranium halide and oxide compounds at various oxidation states. A direct synthesis route for high-purity, anhydrous binary salt mixtures has been developed through mechanochemistry. This atom efficient, solvent-free process is easily scalable, with the potential to produce salt mixtures that meet the purity standards required for nuclear applications.[1]

(2) Development of Dissolution and Separation Chemistry for Actinides and Fission Products in Molten Salts:

To comprehend and regulate the solubilities of actinides and fission products in molten salts, we employ the Flood-Forland-Grjotheim (FFG) Thermodynamic Cycle Analysis as a robust framework.[2, 3] The solubility trends will be critically examined, paving the way for more precise control over the dissolution process. We will explore a novel approach utilizing gas sparging to achieve separation selectivity based on the unique melt structures of molten salts.[4] This technique promises to significantly enhance the management of fission products in molten salts.

Throughout the presentation, we will highlight our prior and current research activities, shedding light on the significant progress made in the aforementioned areas. A quantitative, fundamental understanding of the mechanisms governing solvent tunability, factors limiting control over solvent properties, forces driving chemical speciation, and methods of controlling redox reactions will be thoroughly discussed. These insights are crucial in establishing safer and more sustainable nuclear energy solutions for the future. In summary, this presentation aims to contribute to the advancement of molten salt-based nuclear reactor technology by offering a deeper understanding of the chemistry involved, which in turn will lead to innovative applications with potential benefits for the energy sector.

Acknowledgment: The work was supported by the U.S. Department of Energy, Office of Nuclear Energy. This abstract has been authored by UT-Battelle, LLC, under Contract no. DE-AC05-00OR22725 with the U.S. Department of Energy.

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C.2 UF_4 Purification for Use in MSRs

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Commercially available UF_4 is typically contaminated with dissolved oxygen anywhere from 10 to 50 weight percent. Molten Salt Reactors (MSRs) operating with UF_4 require purification of the dissolved oxygen to ensure proper thermophysical properties of the salt for process monitoring and control, reduction of particulate formation, and homogeneity of the salt. This work was performed to develop a method to purify commercially purchased UF_4 from UO_2 impurities in a large (>100 g) lab-scale batch process.

Traditional methods to fluorinate UO_2 to UF_4 include the direct fluorination with anhydrous gaseous or aqueous HF. The direct fluorination with anhydrous HF gas requires excess amounts of the extremely corrosive and dangerous gaseous HF at high temperatures (>450 °C) [1,2]. The direct fluorination with aqueous HF is a volatile reaction and has been known to result in oxyfluoride products [3,4]. Both direct fluorination methods would be dangerous to scale-up due to the large starting amounts of HF. For this work, a dry process fluorination with NH_4HF_2 was investigated as an alternative method to UO_2 fluorination to UF_4. This method has previously been used to fluorinate small-scale batches (1-5 g) of UO_2 [5,6]. This work scaled up this fluorination process to be able to purify 200 g of UF_4 per batch contaminated with ~10 wt% UO_2.

In the dry process fluorination, NH_4F_2 is introduced to UF_4 at room temperature in a pressure vessel under inert atmosphere attached to an HF scrubber. As the system is heated up to 125 °C, fluorination then dehydration occurs in the following reactions:

$$UO_2 + 4\,NH_4\,HF_2 \rightarrow (NH_4)_4UF_8 \cdot 2H_2O \qquad (1)$$
$$(NH_4)_4UF_8 \cdot 2H_2O \rightarrow (NH_4)_4UF_8 + 2H_2O \qquad (2)$$

The system is then heated to 450 °C to decompose the ammonium uranium fluoride complex, off-gassing NH_4F, and leaving UF_4 in the following reactions:

$$(NH_4)_4UF_8 \rightarrow (NH_4)_3UF_7 + NH_4F \qquad (3)$$
$$(NH_4)_3UF_7 \rightarrow (NH_4)_2UF_6 + NH_4F \qquad (4)$$
$$(NH_4)_2UF_6 \rightarrow NH_4UF_5 + NH_4F \qquad (5)$$
$$NH_4UF_5 \rightarrow UF_4 + NH_4F \qquad (6)$$

During initial experimentation, it was determined that 8 hours at 125 °C and 24 hours at 450 °C were optimal for fluorination of 200g UF_4 contaminated with ~10 wt% UO_2, and the removal of all residual H_2O and NH_4F. The process was monitored with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to ensure all bi-products were removed. The final purified UF_4 was analyzed with X-ray diffraction (XRD), inert gas fusion oxygen analyzer, inductively coupled plasma mass spectrometry (ICP-MS) and DSC/TGA. Results indicated that on average the UF_4 was purified to less than 1.5 wt % UO_2. There were no additional contaminants introduced during purification. There were no bi-products (NH_4F, H_2O) found in the final product. Finally, no oxyfluorides were produced with this process. Overall, the dry process fluorination using NH_4HF_2 has been demonstrated to successfully purify UF_4 of dissolved oxygen contaminants at the 200g scale.

The dry process fluorination using NH_4HF_2 has the potential to be scaled up to an industrial scale however, many factors must be taken into consideration. Because this process produces gaseous HF, careful consideration must be made when choosing materials for the reaction vessel materials and off-gas system. Regular maintenance of the system is also required due to the highly corrosive nature of the HF. Sealing the system up will also generate an amount of gaseous NH_3 that would need to be trapped/scrubbed. Additional considerations also need to be made for safeguards, as materials control and accountancy will need to be tracked when material changes form.

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C.3 Advancements in Chloride-Based Volatility for Waste Reduction and/or Reuse of Metallic, Oxide, and Salt-Based Reactor Fuels

Hilary Fitzgerald, Katie McBride, Aaron Unger, Howard Hendrix, Dev Chatterjee, Pradeep Perera, and Perry Motsegood

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Chloride salts possess interesting levels of volatility at temperatures that can be achieved with existing structural materials. Considerable work went into the study and use of chloride-based volatility (CBV) from the 1940s through 1960s.[1-4] Some work even demonstrated irradiated oxide fuels could convert into chlorides and then be used to perform useful separations via differential volatility.[5-10]

Chloride-based volatility could enable removal of bulk uranium and possibly serve as a treatment option for large quantities of used nuclear fuel (chlorides, oxides or metallic), either be recycled, or can be disposed of at a lower cost compared to the isotopes that need to be stored in a deep geologic repository. This offers the potential to reduce the waste entering the repository by a factor of ten or even twenty while reducing the total cost of disposal. Recovery of better than 99% of uranium in the form of UCl_4 has been demonstrated.[9]

TerraPower utilizes fast reactors because the fast neutron spectrum does not require fuel reprocessing to maintain a viable fuel. Impurities bred into the fuel during operation do not become neutron poisons, allowing for higher burnup than thermal spectrum fuels. As a result, the once-through fuel cycle is the baseline for the Natrium™ reactor and the Molten Chloride Fast Reactor (MCFR). Development of the backend of the fuel cycle is required for the MCFR to ensure a means of disposal since used fuel is a key part of the development of the MCFR.

Even with this previous work, use of CBV was not approached through the filter of waste reduction. This presentation will discuss progress on a potential method for recovery of uranium from used fuel using nonaqueous chemistry without electrometallurgical methods. Recovery of plutonium is expected to occur as part of co-waste stream laden with noble metals, rare-earth fission products, and minor actinides, which is beneficial for non-proliferation goals. This work is agnostic of fuel type and will demonstrate the ability to treat oxide fuel and chloride salt-based fuel from Light Water Reactors (LWRs) and Molten Salt Reactors (MSRs), respectively. Although not in this proposed scope of work, the same chemistry could also apply to metallic fuel. Capitalizing on the inherent volatile properties of chloride salts could result in less process waste generation than current methods. Figure 1 illustrates a schematic of the TerraPower approach toward CBV and waste preparation of used fuel.

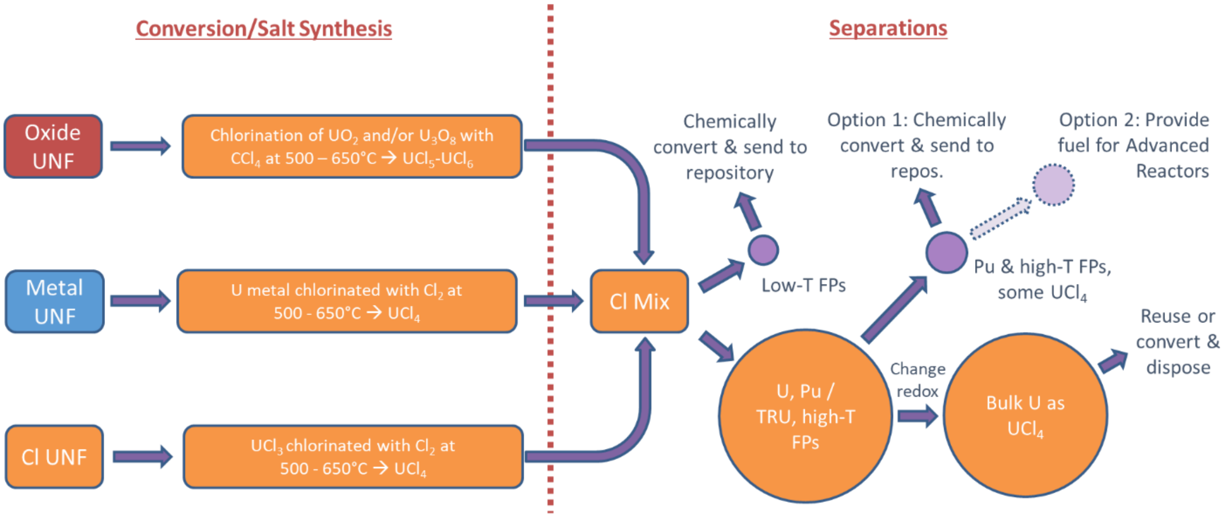

Figure 1. Chloride Based Volatization Method Schematic

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C.4 Options for Industrial Production of Fuel Salt for Molten Salt Reactors

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Liquid fuel based molten salt reactors broadly fall either into the category of fluoride-based or chloride-based. Fluoride salts are preferred for thermal spectrum cores, while chloride salts are preferred for fast neutron spectrum cores. This presentation focuses on production of chloride salts with consideration of fuel mixtures involving eutectic compositions. Examples include NaCl-UCl_3, NaCl-$CaCl_2$-UCl_3, and NaCl-$MgCl_2$-UCl_3. There are several important issues to consider with respect to industrial production of such fuel mixtures, including availability of high purity base salts, source of fissile actinides, method for conversion of fissile actinides into salts, and form of salt for storage/transportation.

Base salts such as NaCl, NaCl-$CaCl_2$, and NaCl-$MgCl_2$ invariably must be treated thermally and chemically in order to achieve the necessary purity prior to introduction of the select actinide chlorides. This involves heating the salt to above its liquidus temperature, allowing as much water as possible to vaporize, and bubbling anhydrous HCl to react with residual hydroxide/oxide species. Hydroxide/oxide forms from hydrolysis of salts, typically above about 300 °C. The HCl treatment process has been shown to achieve residual hydroxide content as low as 10^{-7} moles/gram.

Fissile actinide sources are limited, especially if U enrichment levels of higher than 5% are needed for the fuel salt. Options include HALEU generated and stored at Idaho National Laboratory (INL), dismantled weapons material, and recycled spent fuel. Since these actinides are typically sourced as metals or oxides, a critical step is conversion to UCl_3 to make fuel for chloride based MSR's. Broadly, synthetic approaches can be broken into gas-solid or liquid-solid reactions. The liquid-solid approach has several important benefits, including high rate of reaction, efficient handling of by-products, and redox control to achieve high selectivity for UCl_3. Excess U metal can buffer the chlorination reaction to minimize formation of UCl_4. Several chlorination reactions have been demonstrated/reported with U or UO_2 as listed below.

$$3HCl + U = UCl_3 + 1.5H_2$$

$$1.5FeCl_2 + U = UCl_3 + 1.5Fe$$

$$FeCl_3 + U = UCl_3 + Fe$$

$$1.5CdCl_2 + U = UCl_3 + 1.5Cd$$

$$1.5ZnCl_2 + U = UCl_3 + 1.5Zn$$

$$1.5SnCl_2 + U = UCl_3 + 1.5Sn$$

$$BiCl_3 + U = UCl_3 + Bi$$

$$0.75ZrCl_4 + 0.25Zr + UO_2 = UCl_3 + ZrO_2$$

$$CCl_4 + UO_2 = UCl_4 + CO_2$$

By products from reaction with oxidizing metal chlorides is an important consideration. For low melting temperature metals such as Cd, Zn, Sn, and Bi, two immiscible molten liquids will form. Removal of the salt product could be achieved by pumping it out from the salt layer. Interestingly, Fe metal dendrites were found to form when U metal was immersed in salt containing $FeCl_2$. There appears to be a galvanic coupling that occurs resulting in electrodeposition of Fe on the basket. This is a beneficial phenomenon that allows for most of the iron to simply be pulled out of the salt. Reaction of HCl with U metal is also appealing, because it's byproduct (H_2) simply off-gases from the salt. While gaseous HCl can be difficult to handle, it can also be delivered via thermal decomposition of solid NH_4Cl. Successful synthesis of UCl_3 in LiCl-KCl is reported from bubbling the gaseous decomposition products of NH_4Cl into the salt with U metal immersed.

In the case where UCl_3 is a major component of the salt that is key to the formation of a eutectic point, a novel approach to chlorinating U metal is proposed. It involves starting with a eutectic such as NaCl-$ZnCl_2$ and immersing metallic U. As the U metal reacts with $ZnCl_2$, the concentration of $ZnCl_2$ decreases, while the concentration of UCl_3 increases. Potentially, the liquidus temperature can be kept low as the salt transforms from NaCl-$ZnCl_2$ to NaCl-UCl_3. This is completely hypothetical and experimental evidence/data is needed.

Chlorination of actinide oxides has less reported options to date —including reaction with $ZrCl_4$ and CCl_4. The key is to form oxide compounds that are more stable than UO_2. Evidence is needed that near complete chlorination of UO_2 can be achieved, considering the high affinity of U for O.

In the case of salt mixtures produced by reaction in the molten state, consideration must be given for how the product salt will be recovered. When molten salt is cooled in a crucible, it forms a rock hard solid that literally must be crushed to be recovered. At the lab scale in glove boxes, molten salt can be poured and quenched into thin solid sheets that can be easily broken and milled to a powder if desired. It is questionable whether this process can be scaled-up and used with fuel salt containing enriched uranium. Formation of the salt product is important, because long term contact of the salt with air will result in substantial uptake of water and formation of UO_2. Data is available that indicates this process is much faster for powder than for cast ingots.

C.5 Molten Salt Reactor Fuel Production and Packaging Requirements

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For Molten Salt Reactors (MSRs) utilizing molten salt as both the fuel and as the primary coolant, chemical processes must be developed that are capable of producing the salt constituents at the purity levels required. This talk will discuss the requirements that are general to MSR fuel synthesis and purification, as well as handling and packaging requirements to ensure that the purity of the fuel salt is maintained prior to transportation and loading into the reactor system. While the emphasis of this talk will be on uranium bearing salt-fueled reactors, similar considerations should be taken into account with thorium-fueled and waste burning designs that have higher transuranic element concentrations in the fresh fuel. Many of the purification and handling requirements in this presentation are also relevant to the purification and handling of molten salt coolants for salt-cooled reactors as well.

In the case of chloride fuels, synthesis of uranium chloride will require significant scale-up efforts to produce the quantities of fuel salt that will be needed to fuel commercial-scale reactors. Preliminary results from scale-up efforts at Idaho National Laboratory (INL) in support of the Molten Chloride Reactor Experiment (MCRE) will be discussed. An update on the salt synthesis and irradiation conducted for the Molten Salt Research Temperature Controlled Irradiation (MRTI) project at INL will also be given.

C.6 Fuel Salt Qualification and Associated Fuel Cycle Opportunities & Issues

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NRC staff have defined fuel qualification as *a process which provides high confidence that the physical and chemical behavior of fuel is sufficiently understood so that it can be adequately modeled for both normal and accident conditions, reflecting the role of the fuel design in the overall safety of the facility. Uncertainties are defined so that calculated fission product releases include the appropriate margins to ensure conservative calculation of radiological dose consequences* [1]. The Advisory Committee on Reactor Safeguards (ACRS) has accepted the methodology described in NUREG/CR-7299 [2] as an acceptable method for fuel qualification for molten salt reactors. The fuel salt qualification process described in NUREG/CR-7299 is based upon understanding the role that the fuel salt plays in achieving the fundamental safety functions, which in-turn is based on the fuel salt thermophysical and thermochemical properties.

Fuel salt links the chemical and physical behavior of the fuel to the overall facility safety. In a salt fueled MSR, the fuel salt has two primary operational functions: (1) to contain the fissionable and fertile nuclei that constitute the nuclear fuel, and (2) to serve as the reactor coolant. The fuel salt supports achievement of each of the fundamental safety functions. Fuel salt supports containing radionuclides by chemically binding most of the radioactive material and by not causing unacceptable stresses on the plant systems, structures, and components (SSCs) that provide containment. Fuel salt supports removal of decay heat through its heat transfer properties, notably including its buoyancy driven heat transfer characteristics. Fuel salt supports reactivity control through both through its high tolerance of reactivity excursions (cannot be mechanically damaged and large temperature margin to boiling) and its negative reactivity feedback. The liquid state of the fuel also facilitates draining the fuel salt from the critical region to subcritical, passively cooled tanks as a safety response.

The first parts of an application for a commercial nuclear power plant license, including for its siting evaluation, requires evaluation of an accident in which a substantial fraction of the fission products leak from the core into the containment. As having a sloped catch pan guiding spilled fuel salt flow to cooled, subcritical drain tanks would be a typical feature of MSRs, even a complete reactor vessel failure would only drive the plant into a maintenance configuration, with its fuel salt in drain tanks, but would not significantly stress containment. Note, however, that MSRs have substantial design variability and not all designs will include all potential features.

The properties of fuel salt need to be understood well enough to be able to enable modeling the role of the fuel salt in overall plant safety under both normal and accident conditions. Fuel salt properties are determined by its composition and state (largely temperature). Fuel salt qualification is dependent on development of an adequate quality map of the fuel salt composition to properties. Fuel salt will have a range of acceptable properties that result in adequate plant safety. Developing the fuel salt acceptable property envelope is a key aspect of accident progression modeling. For example, the fuel salt would need to provide adequate buoyancy driven heat transfer following a loss of forced flow accident. Fuel salt properties such as viscosity, heat capacity, and density as a function of temperature are needed to model heat transfer.

Fuel salt qualification applies from the time the salt is brought on site until it is transferred to an independent spent fuel storage facility. Fuel salt includes the vapors and aerosols released from the bulk of the fuel salt until their radionuclides have been adequately trapped such that they have no reasonable means for release or return to the bulk of the fuel salt. Fuel salt circulates independently from its container. Fuel salt qualification only considers container materials to the extent that they become incorporated into the fuel salt (e.g., via corrosion).

MSR facilities will incorporate fuel cycle elements outside of power operation. Current regulations (NUREG-2157 [3]) require the ability to store fuel on-site indefinitely in the event that a permanent repository never becomes available. The fuel salt composition and consequently properties change due to irradiation. A principal difference between liquids and solids is the relative ease of access to the constituent materials. Unlike solid fuel, liquid salt composition can be changed during operation. Nuclear fuel only becomes waste when it can no longer perform its functions. The content of MSR fuel salt can be adjusted as part of normal operations. Consequently, fuel salt does not have a predetermined lifetime and with sufficient processing (composition adjustment) can continue to be used indefinitely.

The reactor and fuel cycle are inherently more deeply integrated in liquid fueled systems. Liquid fuel salt composition can be altered for multiple purposes. For example, material can be added to the fuel salt to adjust its redox condition to maintain low corrosivity. Other likely adjustments to the fuel salt composition are to remove parasitic neutron absorbers (chiefly fission products) and to add or remove fissile and/or fertile materials to achieve the desired reactivity.

The historic molten salt breeder reactor program was focused on achieving breeding using a thermal neutron spectrum and the thorium-uranium fuel cycle. As thermal spectrum molten salt breeder reactors (TS-MBSRs) have the potential for highly desirable characteristics for cost-effective energy production, especially not requiring the use of high assay low-enrichment uranium or uranium enrichment at all once following fuel cycle startup, they are currently receiving significant development consideration. While TS-MSBRs can achieve all the Generation IV nuclear energy goals, they remain immature, and both non-breeding and fast spectrum MSRs are also options for MSR development and deployment.

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C.7 Fuel Salt Characterization and Qualification

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Fuel qualification is an essential part of the licensing process for advanced nuclear reactors including molten salt reactors (MSRs). Qualification of MSR fuels ultimately involves (1) identification of the fuel salt production specifications and the resulting fuel attributes, and (2) demonstration that salt manufactured per the specifications will enable the reactor to achieve the reactor's safety basis [1]. Specifications for qualified fuel will likely not be prescribed by the NRC, but it will instead be the job of the applicant to prove that the salt that they have adopted and produced will satisfy the panoply of reactor-relevant regulations. These regulations are far-ranging and include items related to radionuclide release, independent storage of nuclear fuel, and general safety feature demonstrations [1]. Regulations related to corrosion and material accountancy are not typically considered during the fuel qualification stage, but may need to be for molten salt reactors whose requirements may differ greatly from traditional LWR-oriented approaches [2].

The primary safety criteria that are targeted by fuel qualification activities typically include maintaining margins for radiological releases, ensuring adequate heat removal for reactor shutdowns, and maintenance of proper reactivity control [2]. All these safety criteria involve a broad array of chemical reaction mechanisms and phenomena [3]. As such, comprehensive understanding of fuel salt chemistry is needed to make meaningful predictions. Accurate knowledge of a variety of thermochemical and thermophysical salt properties is also essential [2].

A variety of characterization techniques including in-line, on-line, and at-line analyses may be needed to ensure that qualified fuel meets specifications both during the synthesis/purification stage and throughout reactor operations. These techniques could include salt sampling followed by destructive analyses, or could instead leverage in situ approaches to provide assurance that the salt composition and chemical state have not deviated from allowable ranges. Many monitoring tools exist to support these types of fuel assessments (e.g., salt samplers, electrochemical sensors, optical sensors, etc.), but most are still at an insufficient technology readiness level to permit deployment. Substantial effort has been made by national laboratories, universities, and industry to support development of the needed tools, but much work remains to be done.

This presentation will provide an overview of the measurement needs required to ensure proper production and long-term operations of qualified fuels for MSRs and describe current technologies available to support those goals. Requirements for accuracy, longevity, and sensor placement will also be considered.

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C.8 Actinide Recovery and Reuse from Molten Salts

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Molten salt reactors (MSRs) are a class of advanced nuclear reactors that use molten salts as fuel carriers and coolants. [1] In MSRs with molten salt fuel, the actinide halides are dissolved in a halide carrier salt with the desired physical and chemical properties. During reactor operation, fission products build up in the salt which can interfere with reactor operation over time. Periodically removing fission products from operating MSR salt is desirable to maintain optimum reactor performance. [2,3] Additionally, treatment of end-of-life salt to consolidate actinides and fission products in stable waste forms may be desired to ensure repository criteria are met. However, fission product removal typically requires that actinides are recovered first, otherwise actinide materials will be contained within the fission product materials, increasing waste disposal costs and removing useable fuel materials from the reactor. This presentation will discuss (1) methods for recovering actinides from MSR salts to facilitate fission product cleanup and (2) methods for reusing recovered actinides in MSRs to decrease reactor operating costs and improve sustainability of advanced reactor deployment.

Electrochemical removal of actinide materials from MSR salts uses electric current to deposit a metal alloy by electrochemically reducing the dissolved ionic species to metal at the cathode surface. [4] The cathode can be constructed from a solid, inert metal such as stainless steel or a molten metal such as bismuth where the deposited species will form an alloy with the molten metal cathode. [5,6] The species in the salt will deposit at the cathode in order of the standard reduction potentials, which is proportional to the Gibbs free energy of the reaction. [7] Metal species that are more noble than the actinides (e.g. deposit at less negative electrode potentials) will co-deposit with the actinides at the cathode if they are present in the salt. The cathode potential can be controlled so that the actinides in the salt deposit with minimal lanthanide contamination. The $U^{3+/0}$ reduction potential is the least negative of the actinides, meaning that transuranic elements cannot be deposited without co-depositing uranium. Liquid metal alloying cathodes shift the standard reduction potentials of all the species in the salt more positive, meaning that less energy is required to deposit the actinide species than on an inert cathode. [8] However, the recovered product will require separation of the actinides from the alloying species (e.g. Bi) before recycling actinides back to the MSR salt.

For an electrorefining process, the deposition cathode is paired with a metal anode such as uranium that is oxidized into the salt. [4] The metal species used as the anode must be chosen carefully for recovering actinides from MSR salts. If the anode species has a standard reduction potential that is less negative than the actinide species, it will be transported across the electrochemical cell and co-deposit with the actinides at the cathode. [7] If the standard reduction potential of the anodes species is more negative than the standard reduction potentials of the actinide species, then it will remain in the molten salt while the actinides are recovered. For an electrolysis process, the deposition cathode is paired with a gas-evolving anode that produces Cl_2 or F_2, depending on the salt composition. [9] Electrolysis does not introduce new species into the salt, but the gases generated at the anode are typically hazardous and must be collected. The gas can either be scrubbed or can be used to rehalogenate the actinide materials for reuse. In the case of chloride-based salts, retention of specific chlorine isotopes may be desired, further increasing the need to retain and reuse the generated Cl_2.

Non-electrochemical methods will rely on either a chemical reaction to separate the actinides or a physical separation through relative volatility of each species. [2,10] Chemical separations will generate an insoluble actinide product such as a metal or an oxide that precipitates from the salt. The actinide product must then be separated from the liquid salt before it can be rehalogenated and reused in the MSR. Metal products can be directly halogenated for reuse but oxide or other species may require further processing before rehalogenation. Additionally, many chemical reagents that precipitate actinides will similarly precipitate lanthanide fission products from the salt. The selectivity for actinides over lanthanides must be carefully evaluated to ensure the desired actinide product is collected with minimal lanthanide contamination. Volatility separations relies on differences in vapor pressure of the salt species to recover the actinides from the salt mixture. [10] The actinide species in the salt may not be in the preferred oxidation state for effective volatile separation, so further oxidation of the actinides may be required. The recovered actinide species would then require subsequent reduction to the desired oxidation state before being returned to the MSR salt.

After the desired MSR salt processing is complete, the actinides that were recovered from the salt should be rehalogenated and returned to the MSR to maximize fuel usage, decrease costs associated with refueling the reactor, and improve MSR fuel cycle sustainability. The method and halogenating agent and process steps will depend on the form of the recovered actinides and additional steps may be needed to convert the actinides to a metal or oxide that can be halogenated. [11] Halogenation can be performed directly on the recovered actinides (e.g. HF fluorination of actinide oxides) or within the carrier salt (e.g. $CdCl_2$ dissolved in chloride salt to chlorinate actinide metal). In all cases, the halogenation chemistry must be carefully chosen to ensure that the correct oxidation state of the actinides is reached and that side products or contaminants are compatible with the MSR salt.

The general methods discussed in this presentation can be applied to chloride- or fluoride-based MSR salt compositions, but detailed operating parameters and reagents will depend on the specific composition and concentrations of active species in the salts during processing. These recovery methods can be implemented as an online or batch process, depending on the vendor needs. In all cases, the facility footprint, physical removal of the actinides from the process equipment, additional processing needs, and rehalogenation chemistry must be considered during implementation. Additionally, actinide recovery methods should maintain the desired product composition to ensure maximum actinide retention while minimizing unwanted impurities such as lanthanide or noble metals. Minimizing facility footprint and impurities will improve cost-effectiveness of MSR salt processing operations. Finally, material control and accountancy (MC&A) measures must be considered and incorporated into the salt processing operations.

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C.9 Technologies for Recovering Actinides from Molten Salts

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Actinides dissolved into molten salts are present in various fields within nuclear science. This can include molten salt reactors and used nuclear fuel pyroprocessing. Recovery of these actinides is desirable for both waste minimization and reuse purposes. Most actinide recovery techniques fall into two different categories, chemical or electrochemical. Both of these techniques generally involve converting the salt soluble actinide into an insoluble form.

Chemical techniques can include reduction of the salt-soluble actinide to an insoluble metal and conversion to an insoluble oxide or oxyhalide. These techniques require an additional step to physically separate the phases. Common methods include gravitational settling and/or distillation.

Reducing the salt-soluble actinide to an insoluble metal is accomplished via addition of a metal whose halide is more stable (has a more negative Gibbs free energy of formation) than the actinide halide(s) being recovered. Preferably, the metal used is one that is already a constituent of the salt. The metal reductant reduces the salt soluble actinide halide(s) to an insoluble actinide metal. Recovery of the actinide(s) may occur in a liquid metal phase. Both alkali and rare earth metals are commonly used. As an example, lithium metal can be used to reduce UCl_3 to uranium metal.

$$UCl_3(\mathit{salt}) + 3Li(\mathit{l}) \rightarrow U(\mathit{s}) + 3LiCl(\mathit{salt}) \quad (1)$$

Conversion of the salt-soluble actinide to an insoluble oxide and/or oxyhalide can be accomplished via addition of an oxide material that is less stable than the actinide oxide(s) being recovered. Again, ideally the oxide used is already a constituent of the salt. Alkali metal oxides, including lithium oxide, are commonly used for this purpose.

$$UCl_3(salt) + 3/2Li_2O(salt) \rightarrow 3LiCl(salt) + ¼U(s) + ¾UO_2(s) \quad (2)$$

$$UCl_3(salt) + Li_2O(salt) \rightarrow 2LiCl(salt) + UOCl(s) \quad (3)$$

Electrochemical techniques all involve reducing the salt-soluble actinide halide(s) to a salt-insoluble metal at a cathode. The primary differences between the techniques lie in the choice of the electrodes. The cathode could be either solid or liquid and the anode could be either a sacrificial metal or inert. Recovery of actinide(s) onto a solid cathode occurs in uranium electrorefining with the use of steel, tungsten, or aluminum as common cathode materials. Common liquid metal cathodes used for actinide recovery include cadmium and bismuth. A sacrificial metal anode can be used which is oxidized into the salt with both uranium and gadolinium having been studied. An inert anode can be used to avoid the addition of any other species into the salt. At an inert anode the halide (e.g. Cl^-) is oxidized to a gas (e.g. Cl_2) which bubbles out of the system.

The majority of the experience in recovering actinides from molten salts is based in used nuclear fuel pyroprocessing. Molten salt reactor fuel salts can differ from those used with pyroprocessing by the actinides present in the salt and their concentrations. Recovery of actinides from proposed fuel salts should be further studied. Technologies for recovering uranium are, generally, better developed than for the other actinides. Improved co-recovery of uranium/transuranics from molten salt is being studied and may require a more complex process using liquid metals. Co-recovery using a solid cathode introduces other complexities that require additional studies.

C.10 Electrochemical Purification of Molten Salts

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Efficient elimination of fission and corrosion products from molten salts used in Molten Salt Reactors (MSRs) is necessary to extend the service life of process salts while minimizing generated waste. The accumulation of active metals such as ^{90}Sr and ^{137}Cs is responsible for significant decay heat and radiotoxicity of the salts. Furthermore, the accumulation of other fission products such as lanthanides will affect the MSR salt properties if they are allowed to accumulate excessively. Periodic elimination of the fission products will extend the service life of MSR salts. Molten salt electrolysis has been under development as part of the DOE-NE research portfolio to purify molten salts used in pyrochemical reprocessing of used nuclear fuel. Electrolysis is a scalable process that has been used to produce high purity metals in industry. During electrolysis, a cathode and an anode are submerged into the molten salt electrolyte. A voltage is applied across the electrodes that oxidizes the halide ions in the salt at the anode to produce a halide gas product and reduces cations at the cathode, forming a metal product.

This talk overviews the practical considerations for adapting electrochemical purification to next generation MSR fuel cycles. The underlying thermochemical and electrochemical considerations that are needed to define appropriate process conditions are discussed. Two basic thermochemical and electrochemical properties are necessary for defining process conditions. The first is the electrochemical standard reduction potential for each fission and corrosion product being removed and the second is the activity of the targeted products in the MSR salt. Defining these values under process-relevant conditions provides a starting point for electrochemical separations as they can be used to define deposition order and the theoretical limit of separation for each individual fission and corrosion product.

A brief discussion of electrode choice for electrochemical purification is included in the overview, including the impact of electrode choice on the deposition properties of fission products and how the choice of electrode affects process control. Inert and alloying electrodes can be used to eliminate different fission products based on the unique properties of each electrode. Inert electrodes are capable of separating species from the MSR salts that are less electrochemically stable than the base MSR salt. Inert electrodes are advantageous as they can be constructed out of commercial materials such as steel, nickel, and graphite without adding additional complexity in their design as simple shapes (e.g., rods, plates, meshes) are preferential for electrochemical processes. Alloying electrodes offer a unique path towards eliminating species that are more electrochemically stable than the base MSR salt. Alloying electrodes take advantage of the thermochemical driving force for forming an alloy during electrochemical processes to separate the stable species from the salt. Alloying electrodes require additional design considerations. Commonly used alloying electrodes are low melting temperature metals (e.g., Bi, Sn, Sb, Pb) and post processing of the alloy electrode to generate waste forms is necessary.

Products obtained through electrolysis are typically highly porous and contain significant amounts of entrained salt. The exact morphology is dependent upon the process conditions and combination of co-deposited materials. The combination of metal and salt need to be considered when processing the electrolysis products as significant loss of MSR salt is detrimental to the service life of the salt. Electrolysis is ideally suited for fission product removal after the actinides have been removed from the salt. If actinides are present, they will co-deposit with the fission product deposit. Actinide contamination of the fission product deposit would result in unwanted disposal of actinide material.

Electrochemical purification is a promising technology that can be adapted to MSR fuel cycles. A fundamental understanding of process relevant conditions is first necessary to adapt electrochemical purification to MSRs. Equipment design, electrode material, and process operations will impact the product morphology and composition, which must be controlled to ensure the collected fission and corrosion products can be converted to a stable waste form for disposal.

C.11 Melt Crystallization Studies for Used Fuel Salt Purification Applications

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Molten Salt Reactor (MSR) fuel salt purification strategies are needed to minimize salt waste volumes while maximizing recovery of usable salt. Significant challenges are expected for purifying and recovering fuel salt from their fission product counterparts. Some of these challenges are due to similarities in salt structures, solubility, affinities, miscibility, diffusion limits, and similar ionic valency (e.g., LiCl-KCl, LiF-NaF). A fractional melt crystallization apparatus and strategy for the extraction of purified salt has been successfully developed and applied as a salt waste stream treatment for pyrochemical applications, and these methods should be equally applicable to purification of used MSR salt streams. However, additional work remains in order to extend this technology and prepare for treatment of MSR salts.

A melt crystallization apparatus was used to separate salt components from a liquid melt by cooling until a particular component was crystallized as a solid from the liquid. A LiCl based salt system was separated and recovered using this melt crystallization apparatus and the recovered crystallized solids were analyzed for impurities. A follow up LiCl-KCl eutectic salt system was studied for salt fractional crystallization with CsCl and NaCl and were investigated to show the proof of concept for fractional melt crystallization in chloride eutectic salts. The crystallization results of this work illustrated the usefulness of liquid to solid separation and recovery of these chloride systems (i.e., non-eutectic systems and eutectic systems). Fractional melt crystallization is a powerful technique that can be applied to both non-eutectic and eutectic fuel salt systems and beneficial towards future recycle technologies. However, further melt crystallization investigations are needed to demonstrate fuel salt purification feasibility for advanced chloride and fluoride fuel salt systems.

C.12 Projection of Nuclear Energy Demand and LLFP Transmutation

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The Systems Analysis and Integration Campaign of the DOE Nuclear Energy Office conducted a series of fuel cycle scenario studies to project the requirement of the nuclear fuel cycle capacities and facilities targeting a net-zero emissions economy in the United States by 2050 and a potential economic growth by the end of this century [1, 2]. The study concluded that a significant fraction of clean-and-firm energy (such as nuclear, bio, hydro, and renewables along with energy storage, etc.) is required for a secure and reliable supply of electricity when the capacity of renewables is significant in the grid. The study observed that more than 20% of clean-and-firm energy is required to achieve the net-zero emissions goal by 2050, and it increases further depending on the total capacity of renewables in the grid [3].

Because nuclear energy has the potential to be cost-competitive with other clean-and-firm energy sources, the nuclear energy demand for achieving the deep decarbonization goal would increase significantly. The projected demand for nuclear capacity by 2050 is 200–450 GWe, and the variation results from the capital cost of the nuclear power plant. Projections of the nuclear energy demand by other organizations (see the predictions in Ref. 3) show a similar trend with a variation due to assumptions used in the projections.

Based on the nuclear energy demand, the used nuclear fuels (UNF) were evaluated. The evaluations were performed for two hypothetical fuel cycle scenarios: once-through using the legacy light water reactors (LWRs) and advanced reactors, and continuous recycling fuel cycle of actinides in advanced reactors starting in 2051. The evaluation shows that the cumulative UNF will be ~150,000 metric tons (MT) by 2050 and 300,000–400,000 MT by 2100. Considering the capacity of the Yucca Mountain repository capacity of ~70,000 MT, the U.S. requires many geological repositors for disposing of UNFs.

To reduce the nuclear waste materials to be disposed of and maximize the utilization of uranium resources, the Nuclear Fuel Cycle Evaluation and Screening Study [4] concluded that the continuous recycling of actinides (U and Transuranic) in nuclear reactors is the most promising nuclear fuel cycle in the United States.

By assuming the U.S. nuclear fuel cycle option will evolve into a promising fuel cycle, a transmutation project was initiated to transmute long-lived fission products (LLFPs) using incident non-neutron particles such as energetic photons and protons [5]. The primary goal of this project is to substantially reduce the disposal impacts of the recovered wastes from used nuclear fuels by eliminating the need for a geologic-time-scale repository in which nuclear wastes have to be interred for several hundred thousand to million years. Six fission products (Tc-99, I-129, Sn-126, Zr-93, Cs-135, and Se-79) were selected as target LLFPs of the project. To achieve a high transmutation performance, various options are currently under evaluation, which include the target-and-blanket concept and the hybrid option of energetic protons and spallation neutrons. In the target-and-blanket concept, the LLPFs having high (γ,xn) or (p,xn) cross-sections (e.g., I and Cs) are first transmuted in the central target using the non-neutron particles from an external source, and those of low cross sections with photons or protons (e.g., Tc) are transmuted in the blanket through (n,g) reactions using the emitted neutrons from the target.

So far, it has been confirmed that the LLFPs could be transmuted to short-lived nuclides using high-intensity and energetic photons and protons with challenges, which are uncertainties in the high-energy cross sections of photons and protons, the expensive cost of the separation of LLFPs from UNF, the availability of high-intensity beams of photons and protons, etc.

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C.13 Reducing the UK Stockpile

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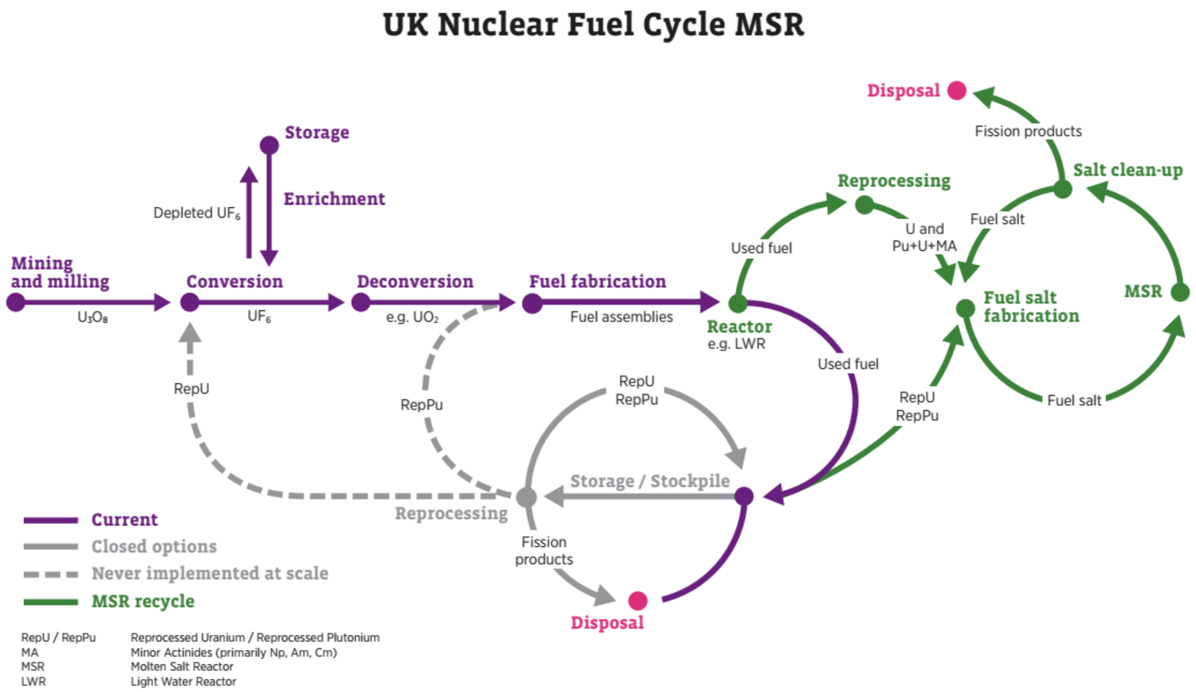
Long-lived isotopes in used nuclear fuel extend the time used fuel will be more radioactive than background levels. Technologies for recovering these long-lived isotopes from used molten salt fuels and design requirements for transmutation targets will be discussed.

The UK National Nuclear Laboratory (NNL) has a long history of working on molten salt, the majority of this work has historically been on pyrochemical processing. NNL have generated example flowsheets, built bespoke apparatus and carried out wide ranging investigations from instrumentation and electrochemistry to off-gas and waste treatment. NNL have recently completed a significant package of work re-invigorating that capability. As part of that work and more recently we have investigated integration with molten salt reactors (MSRs) and in particular their impact on the UK stockpile of nuclear material.



C.14 Fueling the Natura Resources Molten Salt Research Reactor at ACU's NEXT Lab

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Natura Resources will license their 1 MWth MSR design to Abilene Christian University (ACU) to own and operate a Molten Salt Research Reactor (MSRR) as part of ACU's Nuclear Energy eXperimental Testing Laboratory (NEXT Lab) on the ACU campus in Abilene, Texas. The initial design and licensing work for the MSRR was produced by a collaboration of the Natura Resources Research Alliance (NRRA), which includes ACU, the Georgia Institute of Technology, Texas A&M University, and the University of Texas. The construction permit application for the MSRR was docketed for review by the US Nuclear Regulatory Commission (NRC) in November 2022 with a target review completion date of May 2024. Front-end engineering design was completed in 2022 by Teledyne Brown Engineering, and Natura Resources contracted with Zachry Nuclear Engineering in July 2023 to complete the final engineering design for the MSRR, the same month that ACU completed construction of the Dillard Science and Engineering Research Center, a multi-use 28,000 sq ft $23M facility that will house the MSRR. The final engineering design is scheduled for completion in mid-2024 at which point the construction of the reactor will begin and the operating license application will be submitted to the NRC. MSRR operation is expected to begin by the end of 2025 or early 2026.

The MSRR is a 1-MWth reactor with UF4 fuel dissolved in molten $^{7}LiF-BeF_2$ (FLiBe) salt. The fissile feed will be High-Assay Low-Enriched Uranium (HA-LEU-235) possibly obtained from the current US Department of Energy (DOE) inventory. The uranium enrichment is expected to be 19.0–19.5% ^{235}U and the lithium enrichment is expected to be greater than 99.99% ^{7}Li. NEXT Lab and the NRRA are currently in discussions with various entities regarding the sources and forms of the fuel, fuel salt, and coolant salt (also FLiBe). The reactor is designed for five full-power years of operation with a 20-year total lifetime.

Potential sources of fuel from the DOE inventory will likely be in metallic uranium form. For fuel like this in the metallic uranium form, it will have to be converted into UF_4 prior to use for the MSRR. While the pathway for the conversion of UO_2 to UF_4 has been well-documented, a large- scale process for the conversion of uranium metal to UF_4 has not been demonstrated. A significant effort in the Fuel Cycle and Materials Lab at Texas A&M University will be to investigate methods of conversion of uranium metal into UF_4. Potential fluorinating agents for this conversion include ammonium bifluoride, bismuth trifluoride, and hydrogen fluoride.

A concern for some potential users of certain potential fuel sources is that some fuel contains non-uranium nuclides, which will put significant restrictions on its use and processing. This fuel may not be appropriate for some potential users without extensive purification. However, the impurities present in such fuel do not pose a problem for potential use in the MSRR.

The MSRR is designed specifically for a salt chemical composition like the Molten Salt Reactor Experiment (MSRE) coolant salt. The isotopic composition of the MSRE FLiBe is also ideal, with ^{7}Li enrichment of over 99.99%. There could be a significant advantage for the MSR community if the MSRR is commissioned with the HA-LEU-235 obtained from an impure fuel source and with a salt like the coolant salt from the MSRE, demonstrating the versatility of the MSR concept and ability to re-use fuel and salt.

Whatever the source, the FLiBe received for use in the MSRR coolant loop will be purified with the HF/H_2 process to remove oxygen and sulfur impurities, and this salt will be used to rinse the fuel-salt loop, scrubbing oxygen from salt-facing components in the reactor. The salt will then be moved back to the purification vessel for HF/H_2 treatment. This process can be repeated as necessary. When the reactor is sufficiently cleaned, the salt will be purified a final time and then moved into the coolant loop, which will have its own purification system. The coolant salt can be purified and returned to the coolant loop without ever having to re-enter the fuel-salt side of the reactor.

After the reactor is cleaned with purified salt that is transferred to the coolant loop, the fuel salt will be purified with the same HF/H_2 process and transferred to the reactor. Whether this salt is delivered to the site already containing UF_4 or whether the fuel is added on-site, the initial loading of fuel salt into the core will not contain sufficient fuel to reach criticality. Ingots of UF_4 will be added to the reactor to reach criticality.

Packaging and delivery of the UF_4 salt and FLiBe salt are issues that remain to be resolved with the suppliers, but NEXT Lab and the NRRA are considering several options that may be available. One of our loop systems has been charged with salt using the granular form. Another is receiving salt from two different suppliers, with one using several large ingots that are loaded manually into a transfer vessel. Another supplier shipped the solid salt in large casks which will be heated to melt the salt and then transferred pneumatically to the loop system. NEXT Lab will use the knowledge gained from each of these experiences to inform the discussion with the supplier about packaging and delivery of fuel and salt for the MSRR.

At all stages during the life of the reactor, the chemical composition of the fuel salt will be monitored, from initial receipt of the UF_4 and FLiBe, to purification, to loading in the reactor, to operation, to end of life. Salt samples will be collected at each stage and periodically during the life of the reactor. Salt samples will be examined with multiple analytical techniques to establish elemental and isotopic composition. Real-time on-line electrochemical measurements of the salt and other measurements of the headspace gas will help provide a complete picture of the fuel salt chemistry during the life of the reactor. This extensive chemical composition data will be incorporated into modeling, simulation, and digital twin efforts focused on the MSRR.

C.15 Recovery of Noble Metals and Insoluble Fission Products from Used Molten Salt Fuel

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Molten salts are excellent solvents, which is one reason why they are being considered as carrier fluids of fissionable materials. However, there are elements that have limited solubility in the salt or whose solubility is dependent on the redox state of the salt. These elements will be produced during fission. Noble gases have limited solubility and they escape the salt during reactor operation into the headspace. This abstract focuses on the noble metals that precipitate from the salt and the fission products that have solubilities that are redox sensitive. Important noble metals produced from fission include Pd, Rh, Ag, Ru, Mo, and Tc. Sb, Te, and I do not form stable fluorides, and I is the daughter of Te. Although all mixed valence elements have redox sensitive chemistry, Zr and Nb, a daughter of Zr, can exhibit a mixed valence state depending on the redox condition established by the U(III)/U(IV) ratio. The latter will change depending on burnup and conditioning of the salt during operation.

The solubility of the elements in the salt is expressed as their ability to form fluorides or chlorides based their Gibbs free energies of formation. Elements that form fluorides with greater stability than the U(III)/U(IV) couple will remain as fluorides in the salt. Those elements that form halides with lower stability, less negative Gibbs free energies of formation, will stay in a reduced, or elemental form [1]. Noble metal precipitates can form intermetallic alloys. Tellurium chemistry is complex, and can form tellurides with noble metals, such as PdTe [2]. There has been consideration of the secondary effect of noble metals gettering Te, to reduce the uncombined chemical potential of Te in the salt. Capture of labile Te could reduce the deleterious enhancement of stress-induced corrosion of reactor surfaces, by destabilizing species such as Cr_xTe_y [3]. Lanthanides and actinides have sparing solubility in fluorides salts but are highly soluble in chloride salts [4], leading to less concern about solubility limits in the carrier salt.

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Within the nuclear reactor primary cooling system, the noble metal particles will behave differently from the salt-soluble materials. Some data have come from published reports on the ORNL Molten Salt Reactor Experiment (MSRE) that tracked how fission products of all types were dispositioned between the salt, the off-gas, and on graphite and metal, and speculation about gas bubble surfaces [5]. In sampling after shutdown, the observed salt inventory of ^{99}Mo, ^{103}Ru, ^{106}Ru, and ^{111}Ag, was at least an order of magnitude less than calculated by accounting for decay, suggesting that loss mechanisms dominated. As tracked through ^{95}Nb, Nb(IV) should be in equilibrium with Nb(0) when U(III)/U(IV) ranges from 0.01 to 0.001. At higher oxidation conditions, the redox couple will change with Nb(III)-Nb(IV) being the primary redox couple. In MSRE, with the addition of Be, the activity of the Nb became negligible, suggesting that the Nb(0) was formed. Iodine, tracked as ^{131}I, should have remained in the salt under MSRE conditions. However, the ^{131}I numbers were highly variable, indicating that the Te precursors had volatilized –0.017 bar at 650 °C— complicating I disposition and leading to only half remaining in the salt. MSRE results suggested that the noble metals agglomerated into a distinct mobile phase in the fluoride salt as the concentrations of the various noble metal isotopes tracked together: in salt, deposited in pump bowl, etc. Within the salt, the noble metals could have agglomerated on fine particles of graphite, other noble metal precipitates, or on the surfaces of fission gas bubbles. The capture of noble metal particles on fission gases has been explored by modeling and simulation [6,7] and rates for this process have been estimated from a fission gas bubble size distribution [8]. However, validation data are lacking for any of these processes. As the fission gas bubble nucleation and growth may be an important aspect of noble metal transport, experiments are underway to evaluate fission gas solubility as well as the properties of bubble transport in molten salt reactors [9].

In chloride salts, it is the reprocessing of fuel materials that has generated data on noble metal transport. Pyroprocessing by electrorefining takes place in LiCl-KCl and has been applied to used nuclear fuel. The goal of pyroprocessing has been the separation of actinides from lanthanide fission products because of their high neutron capture cross section. The solubilities of lanthanide fission products in chloride salts are much greater than in fluoride salts [10]. However, fission products Mo, Ru, Rh, Pd, and Tc are similarly "noble" in chloride- as in fluoride- salts. Zr is also noble, as $ZrCl_4$ has a chloride oxidation potential that is between U(III) and U(IV). Nb is also quite resistant to oxidation and has been considered as a structural material. In its most studied application, pyroprocessing involves dissolution of ceramic fuel in the chloride salt, followed by application of an electric field. The cathode is a metal electrode that can be used to preferentially getter uranium from the salt, for instance, reducing it to U metal. Lanthanides are left in solution. Noble metals, which aggregate in the grain boundaries in UO_2 fuel, are insoluble in the salt and end up as slag in the electrorefining process and, thus, can be easily separated [11]. Volatile fission products (I, Xe, Kr, ^{3}T) are recovered in the off-gas. Although fission product disposition in a chloride-salt MSR has not been investigated during operation, the formation of insoluble particulates and association with high surface area secondary phases could be reasonably expected to occur.

Removal technologies for noble metal particles have not been extensively studied. In reactor, it is anticipated that these secondary phases will not be of concern until their concentrations affect the viscosity of the fluid. Indeed, introduction of heterogeneous phases is being considered to increase the heat capacity of the carrier salt [12]. It is possible, though, that because of mechanical abrasion and potential clogging of high surface area structures, such as the heat exchanger, there may be a need to remove particles from an online slip stream off the reactor primary loop.

Out of reactor, certain noble metal particles may need to be removed prior to encapsulation in a waste form. In general, the noble metals appear to be easily separated from the bulk of the salt, although separation of one noble metal from another may not be feasible or required. An exception could be long-lived ^{99}Tc, with a half-life of 210,000 years, that might be removed via volatility [13].

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C.16 Oak Ridge National Laboratory Support of Molten Salt Safeguards

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International safeguards are implemented to prevent nuclear proliferation by a State, and the International Atomic Energy Agency uses various measurement and monitoring tools to independently verify a State's declared nuclear material quantities and facility operations. The field of nuclear safeguards encompasses a wide variety of topics including domestic nuclear material control and accountancy and international obligations. These efforts require determining the amount, type, and form of nuclear material in the process or facility. Oak Ridge National Laboratory is supporting International Atomic Energy Agency and domestic safeguards for molten salt reactors and related fuel cycle technologies in the areas of science and concepts, nuclear material control and accountancy technology development, and stakeholder support and engagement. This presentation will outline recent and current efforts to support safeguards for molten salt technologies. These efforts will show the breadth of work at Oak Ridge National Laboratory and provide a brief look at the types of considerations needed for implementing safeguards for molten salt technologies. The presentation will discuss the importance of incorporating "safeguards by design" to meet international safeguards obligations. Nuclear facilities operating in non-nuclear weapons States will be under international safeguards obligations implemented by the International Atomic Energy Agency. Therefore, any advanced reactor developer planning to sell, license, or operate in one of these countries will benefit from incorporating ways to meet these obligations in the design phase to prevent costly redesigns and the need to retrofit equipment.