

Review of Hazards Associated with Molten Salt Reactor Fuel Processing Operations



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Reactor and Nuclear Systems Division

**REVIEW OF HAZARDS ASSOCIATED WITH MOLTEN SALT REACTOR
FUEL PROCESSING OPERATIONS**

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June 2019

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ACRONYMS AND ABBREVIATIONS

ADAMS	Agencywide Documents Access and Management System
ANSI	American National Standards Institute
ARE	Aircraft Reactor Experiment
CEA	Commissariat à l'Energie Atomique
CFR	US Code of Federal Regulations
CO	carbon monoxide
DOT	US Department of Transportation
FP	fission product
GMODS	glass material oxidation and dissolution system
HF	hydrogen fluoride
KI	potassium iodide
KOH	potassium hydroxide
LWR	light-water reactor
M	metals
MSBR	molten salt breeder reactor
MSR	molten salt reactor
MSRE	Molten Salt Reactor Experiment
NO _x	nitric oxide
NRC	US Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
PNNL	Pacific Northwest National Laboratory
TRL	technology readiness level
TRU	transuranic
TWA	time-weighted average

1. INTRODUCTION

This document provides a review of the hazards associated with molten salt reactor fuel processing operations. Project objectives, scope, and an overview of the report are presented in the sections below.

1.1 OBJECTIVES

This project supports the US Nuclear Regulatory Commission (NRC) non-LWR Vision and Strategy Near-Term Implementation Action Plans (Agency-wide Documents Access and Management System [ADAMS] Accession No. ML17165A069). The main objective is to assure technical and regulatory readiness by identifying and resolving gaps in the regulatory framework for non-light water reactor (non-LWR) technologies and their associated fuel cycles. One of these gaps is the availability of aids for the review of hazards associated with fluid-fueled molten salt reactor (MSR) fuel processing operations, which is the subject of this work. Such operations involve hazards that are substantially different from those associated with uranium oxide fuel fabrication and handling.

1.2 SCOPE OF WORK

This report presents the results of an effort to identify hazards associated with MSR fuel processing operations and activities. The report describes processes for storing, synthesizing, using, treating, and disposing of MSR fuel salts and the hazards associated with each process. Many of these processes will be performed at a reactor facility as part of normal operations. However, some activities, such as bulk salt preparation for the initial reactor load and refueling aliquot preparation, appear more likely to be performed at a dedicated fuel salt processing facility. Processing hazards associated with MSR fuel salt preparation are largely independent of whether they are performed at offsite facilities or at the reactor site. Therefore, this document identifies both on- and off-site hazards.

Reactor operations associated with fuel salt processing are also addressed in this report. However, hazards associated with general reactor operations are beyond the scope of this effort. Additionally, common industrial hazards such as poor ergonomics, trips/falls, noise, electricity, movement of heavy or bulky materials, etc., are outside the report scope. The report also includes qualitative assessments of the maturity of likely fuel processing operations and activities, which may require both technology maturation and scale-up for industrial use. The report also addresses the consequences of potential hazards. These expert judgments convey the confidence of the present knowledge of the processes and identify the most hazardous aspects of the processes or operations.

MSR designs are not fully mature; nor are the designs for the primary and ancillary support systems for the synthesis and treatment of molten salt fuel. The types of processes and their hazards addressed in this report are extrapolated from experience at MSRs and from fuel salt laboratory-, test-, or operating-scale (for non-fuel salts) facilities. Therefore, this report is not a process hazards analysis (PHA), which would typically be performed on a specific design for a particular application. However, this document could inform the design process and subsequent PHA or other safety studies for deployed systems.

1.3 REPORT OVERVIEW

Section 2 of this report provides an overview of the types of fuel salts that are anticipated to be used in future MSRs and the rationale for selecting a salt type. An overview of the historic facilities and processes used to prepare fuel salt for experimental and reactor use is also provided.

Section 3 describes the processes and hazards associated with the synthesis of MSR fuel salt. Fuel salt synthesis is likely to take place at a dedicated fuel salt preparation facility. Fuel salt synthesis includes

preparation of carrier salts and subsequent integration of fissile salt with the carrier salt. Section 4 describes the fuel salt processes and hazards associated with reactor site operations.

Section 5 presents summary tables of the hazards associated with MSR fuel processing operations and activities, along with qualitative assessments of the technical readiness of the processes, the potential consequences of the hazard to operations staff, and potential hazard mitigation methods. Section 6 summarizes the report.

2. BACKGROUND

This section provides a background information on the types of fuel salts likely to be employed in MSRs, including a description of the types of fuel salts used in MSRs and the general characteristics of reactors that would use those types of salts. Also, descriptions are provided of the historic facilities and operations used to prepare and process the fuel salt for experimental and reactor use.

The concept of liquid reactor fuel originated with Nobel Laureates Harold Urey and Eugene Wigner during the Manhattan Project as a means to obtain desirable reactor and fuel cycle characteristics. Shortly thereafter, R. C. Briant of Oak Ridge National Laboratory (ORNL) suggested that alkali halide salts could have thermophysical and thermochemical properties to enable high-temperature, low-pressure operation.

2.1 TYPES OF FUEL SALTS

MSR fuel salts consist of mixtures of fissile and possibly fertile materials, halides, and carrier salts. The primary purpose for carrier salts is to lower the melting point of the mixture, as the melting temperatures of the fissile and fertile halide salts are too high for practical use, and to be able to adjust the concentration of fissionable material to control criticality. MSRs will use one of three classes of fuel salt:

1. Fluorides with low concentrations of fissile and fertile materials
2. Fluorides in which the fissile and fertile materials make up a substantial portion of the salt
3. Chlorides in which fissile and fertile materials make up a substantial portion of the salt

Liquid fuel salt provides the opportunity to alter the salt composition as part of reactor operations. This can occur as a result of adding or removing fuel, fission products (FPs), chemistry adjustment materials, contaminants, or corrosion products. The fact that fuel salt serves as both fuel and coolant in MSRs establishes the performance objectives for fuel salt properties.

The specific composition of the reactor salt is selected by the designers to meet the plant's performance objectives. These objectives could include the amount of power to be produced and the role of the reactor in the fuel cycle as envisioned by its designers and operators.

During the historic Molten Salt Breeder Reactor (MSBR) Program, primary goals were corrosion control and breeding additional fissile resources from a thermal-spectrum $^{232}\text{Th}/^{233}\text{U}$ fuel cycle. A key step in this cycle was separation of ^{233}Pa to decay in a low-flux region following neutron capture by ^{232}Th . Therefore, the selected fuel salt was optimized for coupling with separations processing. Both the Molten Salt Reactor Experiment (MSRE) and the planned MSBR accomplished this by using less than one mole percent uranium in the fuel salt. The MSBR planned to include 12 mole percent fertile ThF_4 to enable breeding. Overall, the MSRE fuel salt thermophysical properties were approximately those of the solvent salt. Modern designs that intend to employ the thermal spectrum $^{232}\text{Th}/^{233}\text{U}$ fuel cycle are anticipated to use a similar fuel salt. More details of the logic underlying the fuel salt selection process are provided in Chapter 12, "Chemical Aspects of Molten-Fluoride-Salt Reactor Fuels," in *Fluid Fuel Reactors* (developed for the Atomic Energy Commission).¹

Table 1. Fuel salt optimization characteristics and rationale

Property	Rationale and relevance
High boiling point	Low-pressure operation; primary safety feature High-temperature; more efficiency
Reasonably low melting point (<~550 °C)	Readily available, well-known structural alloys; pure actinide halides have too high melting points for practical use
Dissolve or incorporate useful amounts of fissile and fertile materials if desired	Sustains criticality; principally a concern for fast-spectrum fluoride salt reactors due to limited actinide trifluoride solubility
High radiolytic stability	Required for in-core operation; desirable for long-term, post-use storage
Chemical compatibility with moderator and structural materials	Construction and long-term operation using readily available, well-known materials
Chemically unreactive with the atmosphere and coolant fluids	Safety characteristic to prevent accident cascade following salt leakage
Large volumetric heat capacity	Efficient heat transfer; safety characteristic promoting effective natural circulation cooling
Low viscosity	Efficient heat transfer; safety characteristic promoting effective natural circulation cooling
High thermal conductivity	Efficient heat transfer; safety characteristic promoting effective natural circulation cooling, as salts generally have low to moderate thermal conductivity
Large thermal expansion coefficient	Safety characteristic promoting effective natural circulation cooling and assisting with criticality control
Low parasitic neutron capture	Maintains criticality and efficient fissile resource utilization
Low long-lived solvent activation	Avoids additional radiotoxicity from non-fuel portion of salt; ^{36}Cl production is a potential concern for chloride salts, S causes corrosion
Strong retention of FPs	Safety characteristic to minimize potential source term; noble gas FPs readily escape fuel salt, and noble metal FPs can plate out onto structures or precipitate from the fuel salt

Thermal spectrum reactors that are intended to maximize their conversion ratio and thereby minimize their fissile resource requirements use fluoride fuel salts with the highest possible uranium content while maintaining a low melting point and chemical compatibility with available structural materials.

Maximizing the uranium content minimizes the fuel salt volume within the core, minimizing parasitic neutron capture. The moderator is chosen to be graphite that has a lower parasitic neutron capture than fuel salt, so maximizing the ratio of graphite-to-fuel salt in the core improves fuel utilization. Another consideration for fuel salt selection is the availability of separated isotopes. LiF-UF₄ has advantageous properties as a fuel salt, maintaining a melting point below 550°C for a UF₄ concentration of up to 32 mole percent, but it is only viable if highly separated ^7Li is available at a reasonable cost. Note that at higher concentrations of UF₄ and other uranium-bearing salts, only a small fraction would be ^{235}U .

Fast-spectrum reactors require a substantially higher concentration of fissile materials in their fuel salts to maintain criticality. While either fluoride- or chloride-based salts can be used, only chloride-based salts enable a sufficiently hard spectrum to enable re-fueling with natural uranium without resulting in actinide separation.² These breed-and-burn fast-spectrum MSRs will maximize the amount of uranium in their fuel salt while preserving an acceptably low melt temperature. The phase diagram of NaCl-UCl₃—a

representative chloride fuel salt—shows a melting temperature of less than 550°C for UCl₃ compositions of up to 35 mole percent. The neutronic efficiency of chloride salt reactors will also be impacted by the availability of isotopically selected chlorine. A high ³⁷Cl-to-³⁵Cl ratio will have decreased ³⁵Cl(*n,p*)³⁵S reactions as well as decreased parasitic neutron absorption and ³⁶Cl production.

2.2 HISTORIC FUEL SALT PREPARATION FACILITIES

While the feedstock chemicals for MSR fuel salts have been produced in large quantities, only two relatively small test MSRs have ever been operated: the Aircraft Reactor Experiment (ARE) in 1954, and the MSRE from 1965–69. Consequently, no large-scale fuel salt production facilities have ever been built. A description of the processes and equipment used to produce the MSRE’s fluoride salts is provided by Shaffer.³ Similar information is available for the aircraft nuclear propulsion fluoride fuel preparation facility.⁴ The information presented below describes the ARE and MSRE fuel salt production facilities. Anticipated fuel salt fabrication processes are described in Sections 3 and 4, along with the hazards associated with these processes.

An important limitation of this report derives from the fact that large-scale MSRs have not been previously operated. Some systems and activities can be extrapolated from prior small-scale MSRs, and some can be inferred from larger scale halide salt use. However, there are no direct antecedents for key reactor-specific hazards such as inadvertent criticality during the initial transfer of fuel into the reactor vessel. For example, both the MSRE and ARE cores were initially loaded with flush salt to remove the native oxide layer. ARE staff members then assessed the oxide contamination and decided to keep the flush salt, while MSRE staff members drained the flush salt, cleaned it, and then refilled the fuel circuit. Fissile material concentrate was then gradually added to both circuits to achieve criticality. It does not appear practical to gradually add the much larger quantities of fissile concentrate needed for larger reactors. Commercial-scale reactors may not even perform a flush and fill sequence after emplacement. One potential approach is for smaller integral reactor vessels to (1) be loaded with a slightly subcritical fuel salt mixture at a fuel preparation facility, (2) be transported to the reactor site, and then (3) additional fissile material may be added after installation to achieve criticality. However, the initial fueling process and its attendant hazards remain undetermined.

The fuel and coolant salts for the ARE and MSRE were produced in the uranium processing facilities at the Y-12 National Security Complex in Oak Ridge, Tennessee. Fissile materials were taken from existing US Atomic Energy Commission stockpiles, and non-nuclear chemicals were obtained from commercial sources. The ⁷Li used in MSRE was taken from the tailings of the Y-12 lithium isotope separation facilities and enriched further before use.

Fluoride and chloride fuel salts are chemically similar to salts used in other industries, and their preparation methods are similar. The most distinctive element of fuel salt preparation derives from the fact that the fuel salt becomes much more corrosive if it contains moisture, sulfur or free oxygen ions. Consequently, the MSR salt synthesis emphasizes the removal of moisture, sulfur and oxygen from commercial grade salts and precursor chemicals. Non-nuclear MSR feedstock chemicals were purchased from commercial suppliers and were re-dried and processed to remove oxides and sulfides before being incorporated into fuel salt.

The basic fuel salt purification process consisted of weighing and mixing the precursor materials and then bubbling a mixture of hydrogen and hydrogen fluoride through the salt until water evolution decreased to the desired level. Hydrogen bubbling was continued to remove residual hydrogen-fluoride and to reduce the structural metal fluorides corroded into the melt by the hydrogen fluoride. This resulted in suspended structural metal particles which were removed by filtering. The melt was then sparged with helium to remove residual hydrogen.

The equipment configurations for ARE and MSRE fuel salt fabrication were similar. Both took place in the same building. Prior to the preparation of the MSRE salt mixtures, this facility had produced roughly 60,000 kg of fluoride mixtures of high chemical purity. A flow diagram of the fluoride salt production facilities for the ARE is shown in Figure 1.

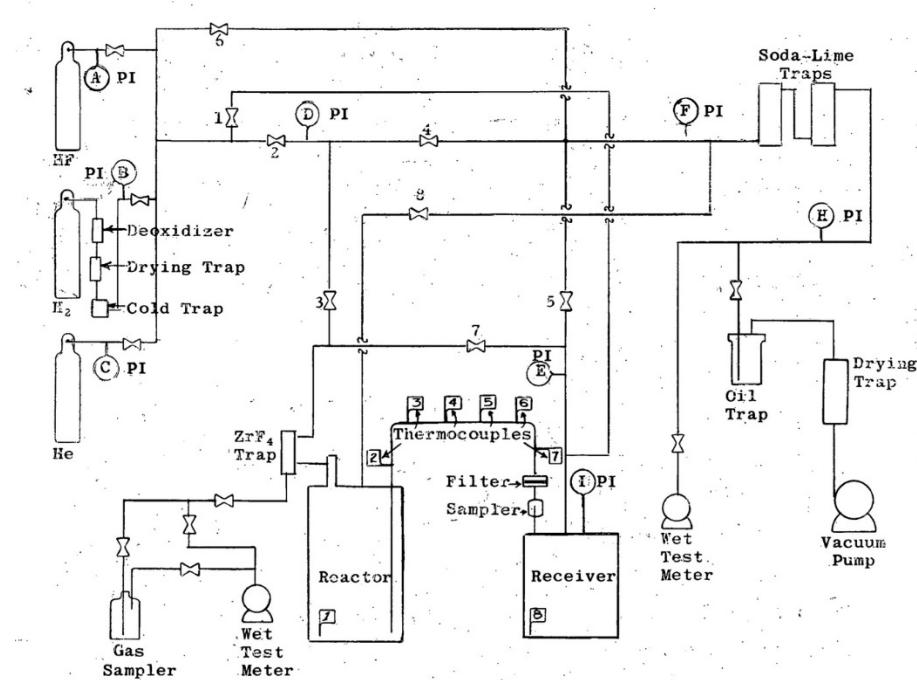


Figure 1. Flow diagram of ARE fluoride salt production facilities (Figure 1 from ORNL-CF-54-6-126).

The MSRE era fluoride salt production facility layout is shown in Figure 2. The fuel salt fabrication was separately enclosed, operated at a negative pressure, and separately ventilated due to beryllium toxicity. The MSRE fuel processing consisted of an arrangement of three cubicles. Cubicle 1 contained equipment for the weighing and mixing the loose fluoride salts. Cubicles 2 and 3 each contained a furnace where the mixture was treated, along with a receiver to which the purified melt was transferred for storage. Specific work areas within the production plant were compartmented and provided with direct exhaust air ducts and filtered makeup air. All exhaust air from the facility was passed through a bank of absolute filters before being discharged outside the building.

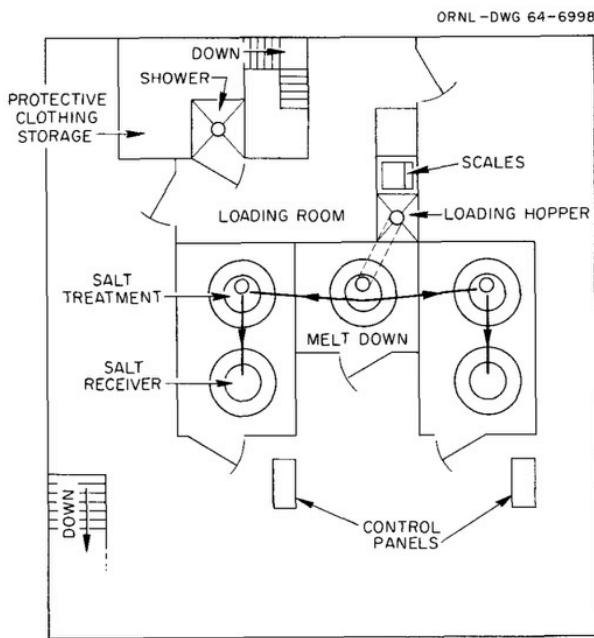


Figure 2. MSRE era fluoride salt production facility layout.

A photo of the fluoride salt production facilities for MSRE (circa 1963) is shown in Figure 3.



Figure 3. Fluoride production facility, batch-processing unit (ORNL Photo 39428).

Due to the toxicity that could cause dermal and respiratory sensitization, berylliosis, or cancer via inhalation, operators were isolated from beryllium via a plastic *fresh-air* suit (Figure 4).



Figure 4. Beryllium salt production; operator wearing a fresh-air suit (ORNL Photo 70837).

2.2.1 Fuel Loading at ARE

At the ARE, Na_2UF_6 was added to an initially barren mixture of sodium and zirconium fluorides. The procedure to add the ARE fuel involved the successive connection of numerous small concentrate containers to an intermediate transfer pot. The pot was then connected to the fuel system, which injected the concentrate into the pump tank above the liquid level. Since the ARE was not optimized for breeding, its fuel salt contained a higher concentration of uranium. The ARE final fuel mixture consisted of 53.09 mole percent NaF , 40.73 mole percent ZrF_4 , and 6.18 mole percent UF_4 , with ^{235}U enriched to 93.4 weight percent. The ARE fuel salt ^{235}U concentration was increased 8.8% over the course of operations (from 0.383 g/cc to 0.416 g/cc) as operational power was increased.⁵ A diagram of the equipment used to introduce fuel concentrate into the ARE fuel system is shown in Figure 5.

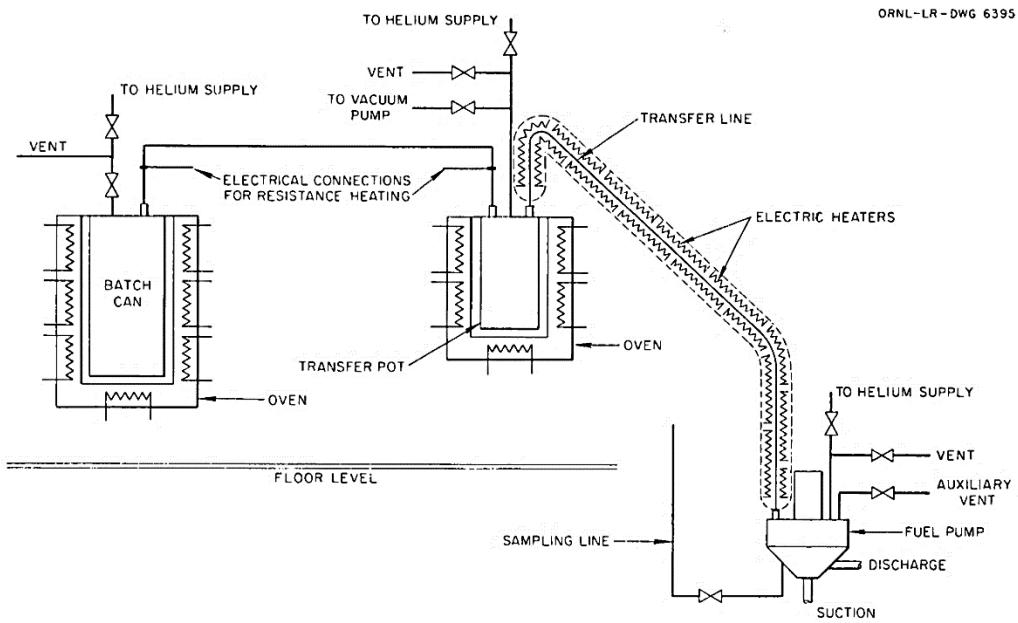


Figure 5. ARE fuel concentrate addition system layout (Figure 4.2 from ORNL-1845).

2.2.2 Fuel Loading at MSRE

The MSRE reactor fuel mixture nominally consisted of 65 ^7LiF , 29.1 BeF_2 , 5 ZrF_4 , and 0.9 UF_4 (mole percent). At MSRE, $^7\text{LiF-UF}_4$ (73-27 mole %) was separately synthesized and incrementally dissolved into barren carrier salt to start and maintain nuclear operation. Both the MSRE coolant and the flush salt were a binary mixture of 66 mole percent LiF in BeF_2 . Initial operation employed 33 weight percent enriched uranium. The operational fuel salt volume was roughly 2,067 liters. All of the lithium used was assayed to be at least 99.99% ^7Li . In 1968, the uranium was removed from the fuel salt and replaced with nearly pure ^{233}U . The last few refueling capsules in 1969 contained PuF_3 (94 weight percent ^{239}Pu). The capsules were added to the salt as a solid via the sampler-enricher mechanism, Figure 6, which lowered capsules into the pump bowl.⁶

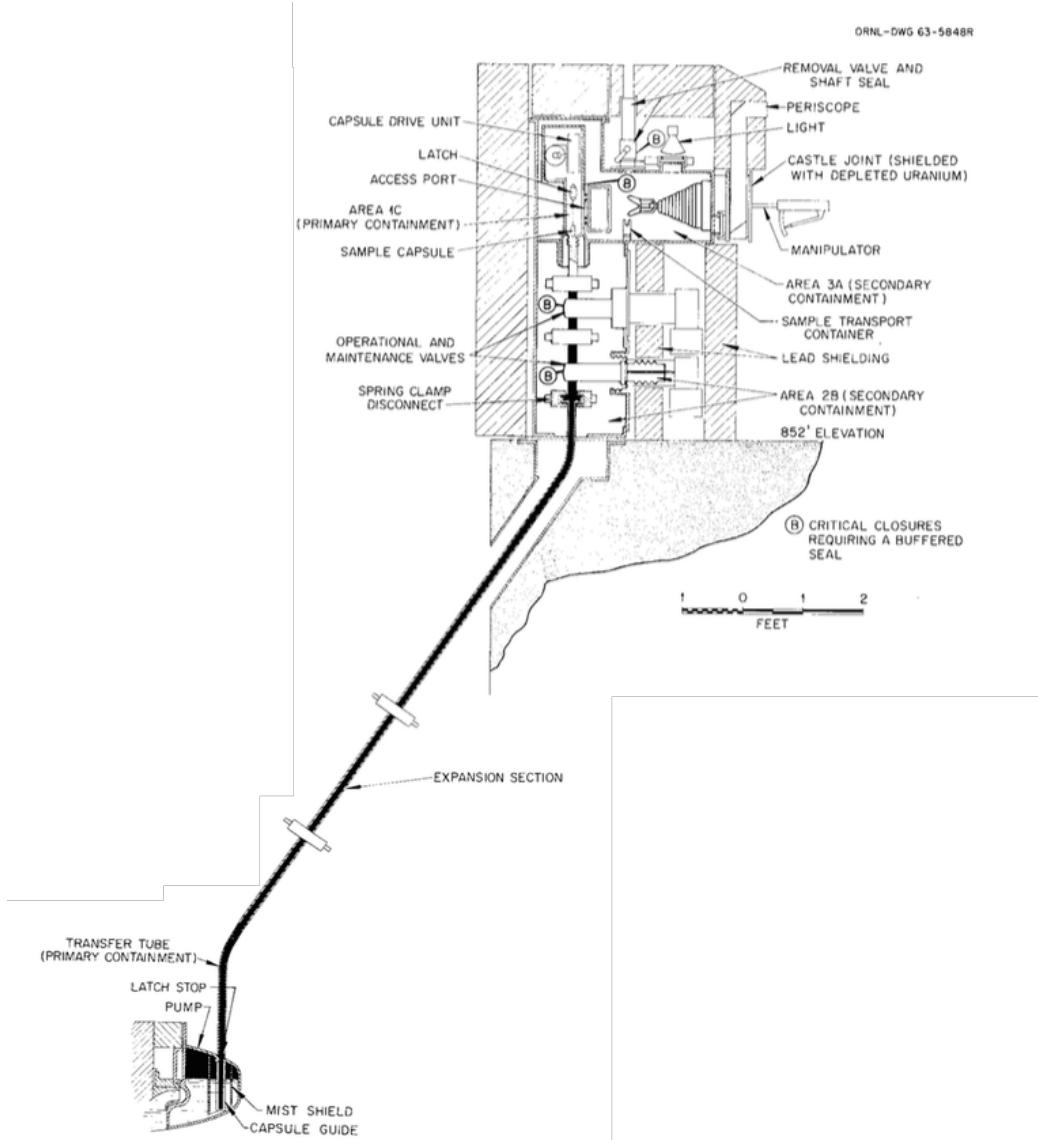


Figure 6. MSRE sampler-enricher mechanism.

The MSRE used different fuel salt capsules for different purposes. Sampling and enriching capsules are shown in Figure 7.⁷ The fuel enriching capsules were constructed from nickel tubing with an outer diameter of 1.91cm with hemispherical ends. Each filled capsule contained about 148 g of salt mixture. Special capsules with zirconium windows were used to expose powdered PuF₃, (about 30 g of plutonium per capsule) to the salt in the pump bowl.⁸

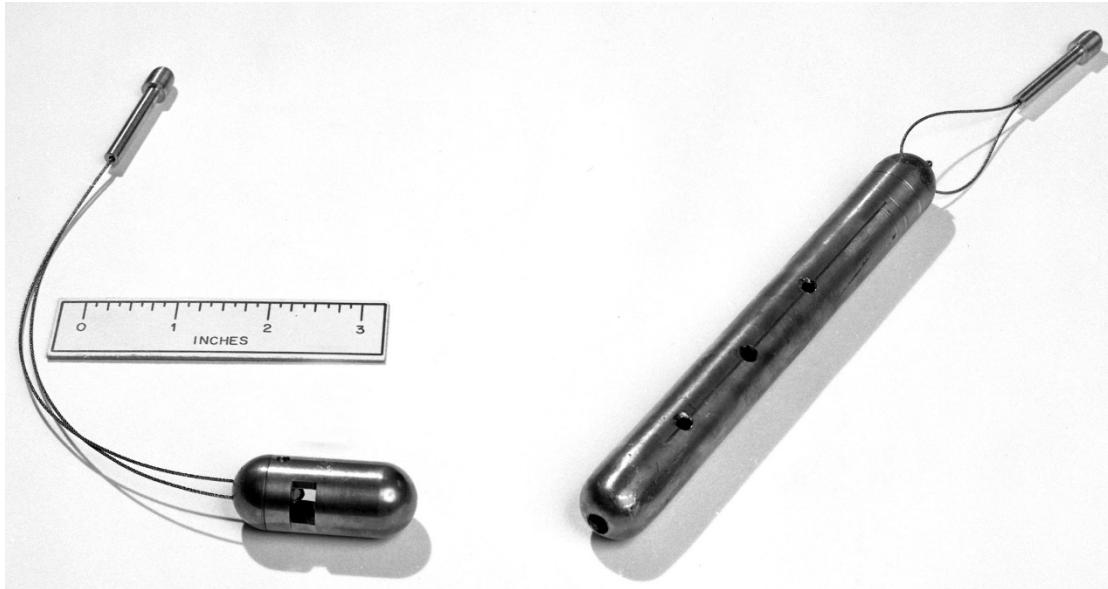


Figure 7. MSRE sampling and enriching capsules (ORNL Photo 71333).

2.2.3 Stripping Uranium from MSRE Fuel and Flush Salts

A primary purpose for development of the MSRE was to evaluate the changes in the reactor physics and chemistry that resulted from changing the fissile material type in the fuel salt. Accordingly, the original fuel salt containing a mixture of ^{238}U and ^{235}U was stripped and purified. The uranium was replaced by a smaller amount of nearly pure ^{233}U to provide equivalent reactivity. The facilities and procedures that were used to accomplish the uranium removal and fuel salt purification (oxide removal) are described in ORNL-TM-2578,⁹ which is the basis for the information in the following discussion.

The MSRE fuel salt processing facility was located in a small hot-cell within the MSRE building. The plant's first use was to remove the oxide from the flush salt (115 ppm) that was initially circulated in the MSRE fuel circuit to strip the native oxide layer from the structural alloy surfaces.

The uranium recovery process consisted of fluorine sparging to volatilize the uranium, followed by decontamination of the gas stream with a $\sim 400^\circ\text{C}$ NaF bed, where chromium fluoride and most fission products were removed, and absorption of the UF_6 on 93°C NaF beds. The excess fluorine was removed using an aqueous scrubber. The corrosion product fluorides were reduced to the metals, which were filtered from the salt before the salt was returned to the reactor system. The flush salt contained 6.5 kg of uranium, and the fuel salt contained about 216 kg of uranium. Reduction and filtration produced carrier salt containing fewer impurities than the original salt. The recovered uranium was decontaminated from FPs by gross gamma and gross beta decontamination factors of 8.6×10^8 and 1.2×10^9 , respectively. Identifiable uranium losses were less than 0.1%. Since the first-phase MSRE fuel salt contained 66 wt % ^{238}U assay, a significant amount of ^{239}Pu was produced. At the time of processing, the plutonium concentration in the fuel salt was calculated to be 112 ppm (560 g). After fluorination, reduction, and return of the salt batch to the reactor drain tank, five salt samples that were withdrawn showed an average concentration of 110 ppm, demonstrating that the plutonium was not removed by the uranium stripping operation.

The flowsheet for the stripping process is shown in Figure 8.

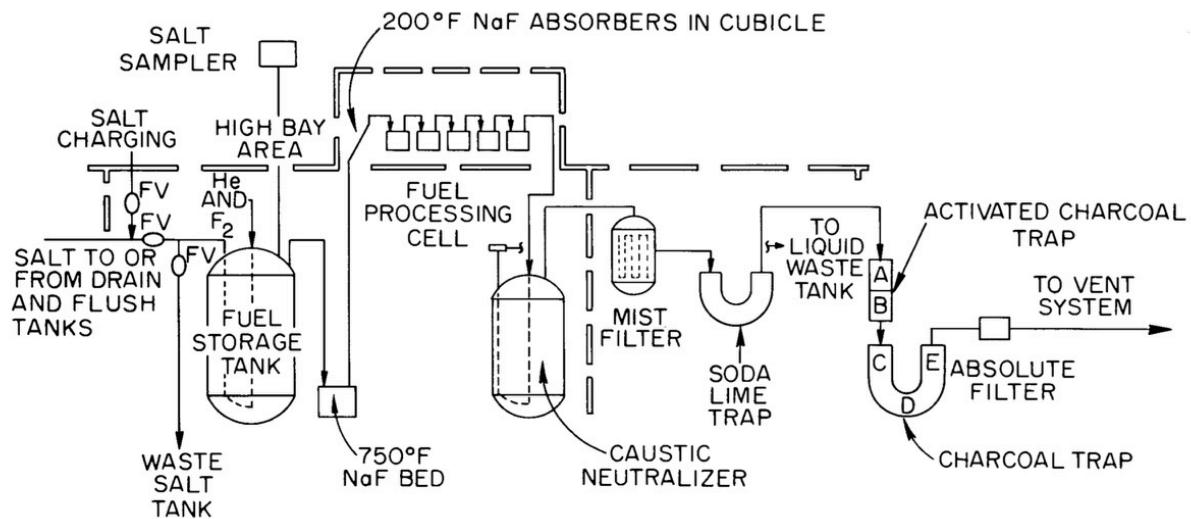


Figure 8. MSRE Uranium Stripping fuel processing system flowsheet.

Most of the processing equipment is located in the fuel processing cell shown in Figure 9. The processing cell ($3.96\text{ m} \times 3.96\text{ m} \times 5.18\text{ m}$ deep) contains the fuel storage tank (fluorinator), the 400°C NaF trap, the caustic scrubber, two remotely operated air valves, three salt freeze valves, and the blower for the absorber cubicle.

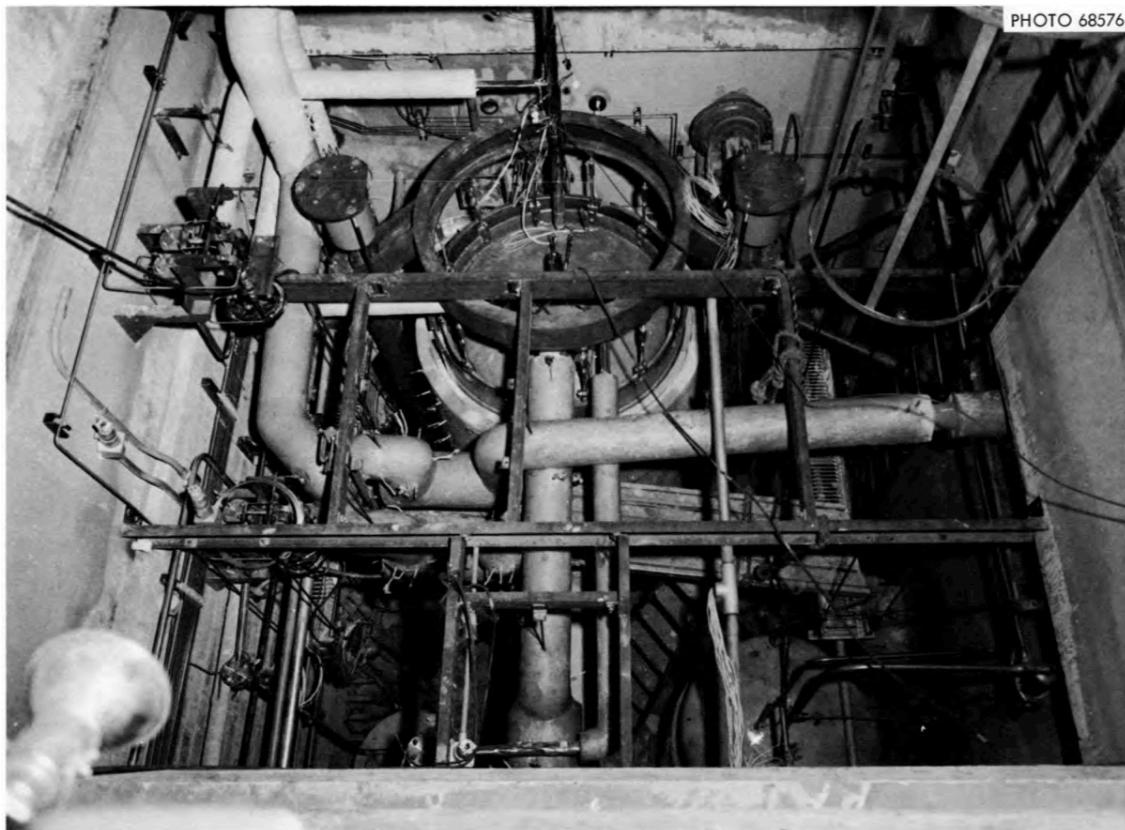


Figure 9. MSRE fuel processing hot cell.

3. NON-REACTOR SITE FUEL SALT PROCESSES AND HAZARDS

This section describes the non-reactor fuel salt production processes and operations necessary to prepare the components of fuel salts, including the non-radioactive carrier salts and salts of fissile and fertile materials. Transportation of fuel salt to the reactor is also discussed.

3.1 SALT COMPONENT SYNTHESIS

3.1.1 Non-actinides

The carrier salts are common industrial salts, such as NaCl, NaF, MgCl₂, ZrF₄, ZrCl₂, and LiF. Beryllium metal, widely used in electric devices, is prepared from BeF₂. Also, lithium would need to be isotopically separated to be usable in fuel salt, as the neutron absorption cross section of ⁶Li is too high for use in core. MSRE flush and coolant salts had a ⁷Li abundance ranging from 99.991 to 99.994%. The materials are anticipated to be commercially procured by the fuel salt synthesizer.

The lithium hydroxide-mercury amalgam column exchange-based (Colex) separation process was used in the United States in the 1950–60s on a large scale to separate ⁶Li from ⁷Li for the thermonuclear weapons program. The MSR program made use of the ⁷Li resulting from the process that was not useful for weapons. This ⁷Li was further separated again using the Colex process. As industrial-scale mercury usage presents large environmental contamination and health risks, alternative lithium isotope separation processes based on electromigration are being evaluated to support MSR and fusion technologies. Other methods involve selective capture of lithium isotopes with a crown ether, either presented as an immobile phase on a resin, or carried in an immiscible organic phase that is contacted by the aqueous lithium hydroxide phase.

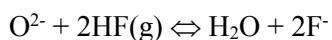
While natural isotopic abundance chlorine could be used in fuel salt, using ³⁷Cl salts would improve the reactor neutron economy and decrease the production of ³⁶Cl (long half-life beta emitter) and ³⁵S that causes corrosion. Isotopically separated chlorine is not available in large quantities commercially, as no large-scale use for specific chlorine isotopes has been established. However, several technologies that would be scalable to large size have been demonstrated in laboratory settings. Gas- phase isotopic separation for chlorine was first demonstrated at the laboratory scale in 1939 by thermal diffusion of HCl with several attempts into the 1950s to increase the quantity produced by this method.^{10,11} Liquid-phase thermal diffusion is also a well understood process for chlorine isotope separation.¹² In this process, the isotope separation was undertaken using CCl₄ as a stable chlorine-bearing compound. The process was carried out in a metal vessel under a pressure of 5 bar to ensure that the CCl₄ remained liquid. Chloroform and other impurities must be considered in the separation process. Room-temperature anion exchange chromatography has also been demonstrated for chlorine isotope separation.¹³ Elution of chlorine from the column is done by passing AgNO₃ through the bed. Recently, significant chlorine isotope separation has been shown during NaCl crystallization under magnetic fields of 20–80 mT.¹⁴ All of the proposed techniques employ readily available materials at temperatures less than 100°C, so they could be performed with commonly available tools and materials.

The primary purpose for salt purity requirements is to minimize salt corrosivity. The fission process produces comparatively large amounts of impurities in the fuel salt, somewhat contradicting the reactor physics rationale for high purity feedstock materials. Halide salts are hygroscopic and must be handled under an inert atmosphere during synthesis, mixing, and handling. Samples of the MSRE fuel mixture and (less frequently) the coolant mixture were analyzed routinely during all periods when salts were circulated in the reactor. On each occasion of its use, the flush salt also was analyzed. The concentrations of the salt constituents, oxide contaminants, and FP species were monitored on a continuing basis.¹⁵ Blankenship et al., describe the methods of salt testing before and during operation.¹⁶

Salt samples were taken to assess purity just before the reactor was loaded. Results for the average of 39 samples are given in Table 2 below, with the greatest variability in the trace elements. Before criticality, the MSRE fuel and coolant salt systems were heated to 650°C and purged with HF/H₂ in helium to remove moisture. The flush salt was also evaluated spectrochemically for Al, B, Bi, Ca, Cu, Mg, Mn, Na, Pb, Si, Sn, and Zr, and the KBrF₄ method was used to measure the oxygen concentration.

Table 2. Table of analyses of LiF-BeF₂ for MSRE coolant and flush salts (Thoma ORNL-4658).

Oxides are likely the most problematic contaminant. Oxide analysis in chloride salts is accomplished by titration. The analysis is more difficult in fluoride salts. The standard method is to use the reagent KBrF₄, but MSRE staff found that the salt absorbed water in between sampling and analysis, making the method inaccurate.¹⁷ An inert gas-fusion method was also considered.¹⁸ However, the staff at MSRE chose the reaction of



as the means by which to measure oxygen content in the salt, as this was considered to be the method least affected by externalities, although not the most sensitive. In this method, the salt is heated to 700°C, and the water evolved or the hydrogen fluoride (HF) consumed can then be measured. The water can be measured offline by Karl-Fischer titration or online with a moisture analyzer. HF can be measured after being captured in a downstream trap. Little development of oxide measurements in fluoride salts has been done since MSRE operation.

3.1.2 Actinides

3.1.2.1 Uranium from enrichment plant

All commercial uranium enrichment plants use UF₆ as the feed material, so that is the likely starting compound for producing molten salt fuel containing enriched uranium. There are no unique hazards introduced into the enrichment plants related to using their product to produce molten salt fuel.

3.1.2.2 UF₄ Production

Producing low enrichment UF₄ salt for an MSR involves many of the same processes currently used when producing UO₂ fuel for LWRs: uranium is mined, purified, converted to UF₆, transported to an enrichment facility, enriched in ²³⁵U, and then transported to a fuel fabrication facility. When producing UO₂ for an LWR, the UF₆ is converted to UO₂ by one of several available processes, and then it is used to produce fuel pellets. All these processes are performed commercially on a large scale, and the hazards are well known. Many potential processes exist for producing UF₄ for an MSR, which are described later in this report, but the most common process currently used involves reacting UO₂ with HF in a kiln. This is the first step for producing UF₆ from natural uranium oxides prior to enrichment, so the chemical hazards would be the same. The criticality concerns for producing and handling enriched UF₄ would be the same as for producing UO₂ from enriched UF₆ at a fuel fabrication facility.

The primary chemical hazard for producing UF₄ is the HF gas, which is toxic and corrosive. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for HF is 2.5 mg/m³ (as F), over 8 hours. Fluorine gas, which is used to produce UF₆ from UF₄, is more toxic, with a recommended PEL of 0.2 mg/m³, so the current UF₆ production facilities are more chemically hazardous than facilities that would only produce UF₄. UF₄ is much more chemically stable than UF₆, and it has an insignificant vapor pressure, a very slight solubility in water, and reacts very slowly with moisture in the air. UF₆ has a moderate vapor pressure (109 mm Hg @ 20°C) and reacts vigorously with water, so the product from a UF₄ production facility is less dangerous than a UF₆ product.

Several alternate processes for converting enriched UF₆ to UF₄ without first converting the UF₆ to UO₂ have been tested on a small scale. These processes would be much more efficient in terms of HF usage and would produce less fluoride waste; however, only the carbon tetrachloride reduction and hydrogen reduction methods have been used on a commercial scale.¹⁹ These processes could also be used to produce UF₄ from depleted UF₆, which is the planned fuel for a few MSR designs.

Carbon Tetrachloride Process: The reduction of UF₆ with CCl₄ has been described by Nairn et al. 1958,²⁰ Collins et al. 1960,²¹ and Galkin et al. 1961.²² The reaction takes place in the condensed phase, with heating to 120–150°C to start the reaction. The reaction stoichiometry has a molar ratio CCl₄:UF₆ of 2:1 and may be written as



Gaseous effluents include chlorine (Cl₂), freons (CCl_xF_(4-x)), and excess carbon tetrachloride (CCl₄). The reaction is exothermic, and if the reactants are confined in a batch reactor, the pressure increases to ~200 psi (~ 14 bar) with the production of gaseous products and the temperature increases slightly. Batch reactors are not the only way to implement this process, but they do tend to make material accountancy easier.

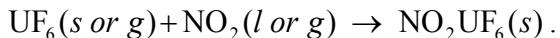
CCl₄ is a suspected human carcinogen which may cause liver and kidney damage and central nervous system depression. The OSHA PEL is 10 ppm time-weighted average (TWA), and 200 ppm is immediately dangerous to life and health (IDLH). The off-gas is corrosive due to the Cl₂ formed, which is also toxic (PEL TWA for 8 hours is 0.5 ppm).

NO_x Process: The Goodyear Atomic Corporation investigated reactions between UF₆ and nitrogen oxides (NO_x) to prepare reduced uranium compounds in the late 1950s and early 1960s.^{23,24,25} A simple two-step dry process can be used to make UF₄. The initial reaction between UF₆ and NO_x forms a binary adduct consisting of a stable powdery solid. This intermediate is subsequently reduced to UF₄ by reaction with hydrogen (H₂) or carbon monoxide (CO). Examples of the reactions with NO_x are shown below.

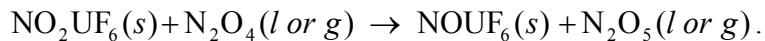
The reaction of contacting solid or gaseous UF_6 with nitric oxide (NO), produces nitrosylum hexafluorouranate. In excess NO , the reaction takes place rapidly at temperatures between 25 and 60°C.²¹ The heat of the reaction is low. The product is a whitish-green solid with low vapor pressure (<0.001 bar at 25°C).



Another intermediate, nitrylum hexafluorouranate, also is made by reacting solid or gaseous UF_6 with liquid or gaseous nitrogen dioxide (NO_2). The reaction is rapid, even at less than 0°C, and occurs instantaneously between 25–60°C, with a low heat of reaction:



The nitrylum hexafluorouranate product is a yellowish-white solid with very low vapor pressure at 25°C. Under excess NO_2 or dinitrogen tetroxide (N_2O_4) the NO_2UF_6 converts to NOUF₆.



The dinitrogen pentaoxide (N_2O_5) byproduct will convert to $\text{NO}_2/\text{N}_2\text{O}_4$ and O_2 .

In the case of either mechanism, reaction of the NOUF₆ adduct with hydrogen gas produces UF₄ at 250°C to 350°C:



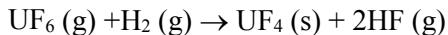
NO and NO₂ are both toxic, with PEL TWAs for 8 hours of 25 ppm and 0.2 ppm, respectively. The HF in the off gas is corrosive and toxic.

HBr, HCl or HI Process: UF₆ will react with the hydrogen halides to produce UF₄ and/or UF₅ at moderate temperatures (<100°C for HBr and HI, and ~300°C for HCl).^{26, 27} Using HBr, the reaction is



The off gas would be toxic and corrosive. Br₂ has a PEL TWA for 8 hours of 0.1 ppm.

Hydrogen Process: UF₆ will react with the hydrogen gas to form UF₄ and HF, but only at very high temperatures (1,200–1,700°C).²⁸ The reaction is exothermic, but only after the UF₄ is condensed from the vapor, which occurs at about 1,300°C. This process involves a very simple reaction with only one byproduct (HF), but the required temperature is much higher than for the alternate processes, and it must be tightly controlled. The HF in the off gas would be toxic and corrosive.



Currently it is not clear which of these processes would be chosen for large-scale production of UF₄ from UF₆, although the hydrogen reduction was used in the past. Both the NOx and HBr processes operate at mild conditions and should be relatively easy to run. Both nitrogen and oxygen concentrations must be kept very low in the molten salt fuel, which would be a concern if the NOx process were used.

Different synthetic pathways to halogenated salts have the potential to have different contaminants of concern. For instance, the reduction of UF_6 to UF_4 through reaction with CCl_4 may leave residual chlorine or chlorinated byproducts in addition to carbon. Halogenation of an oxide may leave residual oxide, as observed in MSRE fuel. Reduction of UF_6 with NO or NO_2 could leave residual nitrates. None of these results are desirable in salt systems, although additional purification steps are always possible to mitigate these issues. In the case of excess halogen, heating and sparging with inert gas is a method to remove residual acid gases. Oxides can be removed from fluorides by bubbling with HF/H_2 . A number of methods have been identified to remove oxides from uranium chlorides. In all these cases, the reactive gases are hazardous, and processing facilities must provide the correct inert atmosphere and chemical containment required for safety and efficacy.

3.1.2.3 UCl_3 Production via High Temperature Techniques

Chloride-based reactors have been designed to operate with uranium (UCl_3) or transuranic (PuCl_3 , AmCl_3 , and CmCl_3) fuels that are dissolved in a mixture of alkali or alkaline-earth chlorides, including NaCl , MgCl_2 , and CaCl_2 . The production of UCl_3 comes from the precursor UCl_4 , often from reduction in hydrogen. It will also be produced if UCl_4 contacts heated metals. UCl_4 can be made by chlorinating uranium oxides or uranium fluorides, namely UF_6 and UF_4 .²⁹ Chlorinating agents include CCl_4 , hexachloropropene, Cl_2 , phosgene, or mixtures of CO with Cl_2 .³⁰ Most of the information on uranium chloride chemistry presented here comes from a review written by Larsen (1946)²⁹ as much of the publicly available knowledge dates from the era leading up to and through World War II.

Traditional methods of UCl_4 manufacturing involve a gas phase reaction or, it is accomplished by reaction in the liquid phase. These production routes require feedstock UO_2 or a supply of UF_6 , the latter of which is currently at a surplus in the United States. The activity of the oxides to halogenation depends on the purity, oxidation state, and particle size of the powder. Freshly reduced oxides can be pyrophoric. Gas-phase halogenation at high temperatures gives a dense, crystalline product. Liquid phase reactions go further to completion, as they are often autocatalytic.

Preparation of UCl_4 from metallic uranium is possible through combustion in chlorine at 250–300°C or through reaction with HCl , phosgene, or methyl chloride. The metal is converted to the hydride before combustion to improve yield. An example of a reaction with a uranium hydride is the heating UH_3 in contact with NH_4Cl for 30 hours at 300°C to make $(\text{NH}_4)_2\text{UCl}_6$, which in turn will decompose to UCl_4 at 350°C.³¹ However, processes involving hydrides are thought to be too complicated to be feasible on a large scale, as they require the use of pyrophoric uranium metal.

Gas-phase reactions comprise two categories, gas-solid or gas-liquid, the latter of which produces a molten salt directly. Gas-phase processes tend to leave a residual oxide because of poor contact between the halogenating reagent and the solid phase. Reagents include the agents listed earlier, along with short chain organics such as CHCl_3 , as well as those with chlorine atoms bonded to a carbon atom alpha-to-a-double-bonded carbon atom, such as hexachloropropene. In addition to chlorine, inorganic reagents such as sulfur chlorides (e.g., S_2Cl_2 , SOCl_2) have also been investigated, as has been CCl_4 that was generated from passing Cl_2 over a hot carbon bed. The vapors of the chlorinating agents are highly toxic. A sweep gas, such as CO_2 , may be added to the chlorinating agent.

The best-known gas-phase process for producing UCl_4 is through the carbochlorination,²⁶ or reaction of CCl_4 , with uranium oxide.²⁶ This process has been used on an industrial scale. It is carried out at 350–450°C, and both continuous and batch processes have been developed. Reaction temperatures and selected reducing agents are optimized to produce more UCl_4 than UCl_5 . The pure and finely powdered uranium oxide reagent is made from the steam hydrolysis of UF_6 , a process that generates a large amount of HF , which is a reaction product that is both toxic and corrosive. The reaction with CCl_4 can produce

phosgene as a product (as well as CO and Cl₂), and an accident with carbochlorination caused a casualty at the Y-12 National Security Complex in Oak Ridge, Tennessee.³² Chlorine byproduct is soluble in unreacted CCl₄, making this residual mixture both toxic and corrosive.

Liquid-phase reactions include those at atmospheric pressure, those using a reflux column, and those in vessels sealed to operate at temperatures above the normal boiling point, with pressures of 3–20 bar. The reflux method uses a reagent such as hexachloropropene at 100°C, from which the reaction product can be precipitated and filtered. Heating the mixture to 165°C increases the yield of UCl₄ over UCl₅. Sulfur chlorides can also be used at atmospheric pressure and 138°C (the boiling point of S₂Cl₂), but they tend to leave a sulfur residue in the UCl₄. UO₃ refluxed with SOCl₂ at 78.8°C makes the adduct UCl₅·SOCl₂ that decomposes at 300°C to make 98% UCl₄. The reflux method has also been investigated with organic chlorinating agents other than hexachloropropene, but the latter was the only one that showed success as the boiling points are generally too low for the chlorination reaction to proceed. A pressurized vessel has been used with CCl₄ at temperatures from 140–160°C in two steps: (1) making UCl₅ from UO₃, and (2) decomposing the UCl₅ to UCl₄. However, the process is very sensitive to impurities, and it makes pressurized phosgene, which is a chemical hazard. Compounds similar to CCl₄, such as CBrCl₃ and CBr₂Cl₂, will also produce UCl₄ directly in a bomb reactor at 130°C.

Metathesis reactions (or halogen/oxide exchange) can also take place in a fusion medium, a refluxing column, or in a bomb reactor. These processes have been investigated with mixed results, and yields tend to be poor for most metal chlorides. However, molten BeCl₂ (at 500°C) was shown to completely convert UO₂ to UCl₄ in 4 hours. The conversion of the fluoride is more efficient than the oxide. For instance, AlCl₃ at 225°C will convert UF₄ to UCl₄ more efficiently than UO₂ to UCl₄ (only 30% after heating at 200°C for 12 hours). The UF₄ reaction with BCl₃ and AlCl₃ at 600–700°C will give UCl₄.

UCl₄ is very hygroscopic and will deliquesce to a liquid and fume at room temperature. When heated in air, UCl₄ will produce HCl(g) and U₃O₈(s). UCl₄ will react with fluorine to produce UF₆, and it will react with HF to produce UF₄. UCl₄ will react with metal oxides to form UO₂ and uranium oxychlorides.

Purification of UCl₄ or UCl₃ uses reagents similar to those used for the conversion reactions discussed above.

3.1.2.4 Low Temperature Uranium Chloride Salt Production Through Organic Precursors

Aqueous preparation of UCl₄ is possible by forming an oxychloride or hydrated chloride intermediate and then decomposing the intermediate into UCl₄ and UO₂. The separation is by volatility, preferentially removing the UCl₄ as a vapor species. UCl₄ is not soluble in many organic solvents, and it decomposes when mixed with alcohols, ketones, esters, and carboxylic acids. Removal of the oxygenated organics listed above by heating will also volatilize HCl and leave a uranium oxychloride residue. Organics can be used to salt out uranium-bearing salts from aqueous solution. Enough chlorinated solvent is added to an aqueous uranium-containing solution to form an azeotrope; then the mixture is heated, first driving off the water, and then the solvent. If heated to 650°C, UCl₄ can be sublimed from the UOCl₂ salt residue left behind by the organic solvent, leaving behind UO₂. This process has not been optimized.

Direct reaction of CCl₄ with UF₆ is also possible. It is a two-step process to make UCl₄ that first involves adding UF₆ to a chlorinated solvent such as CCl₄ to make UF₄ in solution. The step to produce UCl₄ is more difficult, but it likely goes through a mixed fluoro-chloro-uranium intermediate that decomposes, generating UF₄ and UCl₄. Use of BCl₃ or AlCl₃ as chlorinating agents assists the process. The product has low oxygen content, as there is no introduction of oxide or oxyhalide as starting materials, but it may contain some chlorine that must be distilled from the product.

Use of organic complexes or stabilizing reagents have been explored on the laboratory scale, starting with acetyl acetonate, ammonium benzoate, and various acetate complexes. Tetrahydrofuran has been investigated as a complexing agent, but its synthesis requires 10°C and the addition of HgI_2 to prevent unwanted byproducts.³³ Similar syntheses have been done by reacting UH_4 or uranium turnings in diethyl ether to give products at high yield, including UI_3 , $\text{UI}_4(\text{O}(\text{C}_2\text{H}_5)_2)_2$, and $\text{UI}_4(\text{O}(\text{C}_4\text{H}_9)_2)$.³⁴ Uranium (III) and (IV) iodide complexes with dioxane have been prepared by reaction at room temperature over seven days with 95% yield.³⁵ Low heat (50°C) shortened the reaction time to less than a day. The resulting $\text{UI}_4(1,4\text{-dioxane})$ and $\text{UI}_3(1,4\text{-dioxane})$ complexes can be converted by several uranium halides, including uranium (III) and uranium (IV) compounds. The dioxane complexes have already provided the building blocks for other uranium (III) compounds, as discussed in a recent report of the synthesis of pyridine complexes of U(III) compounds under mild conditions such as $[\text{UCl}_3(\text{py})_4]$ from the 1,4-dioxane suspension of $[\text{UCl}_4]$ and magnesium turnings at 100°C.³⁶ These new synthetic methods have not been tested on a large scale, but if testing is successful, this should provide a safer approach than the standard approaches to uranium chloride chemistry that require high temperatures and hazardous reagents.

3.1.2.5 Thorium Fluoride

The fluorination of thoria can be carried out in the same manner as for urania, with exposure to fluorine or HF. An alternative route that takes place at room temperature involves the mechanical contact between ThO_2 and NH_4HF_2 to initiate the reaction between them. Products were observed after two hours, forming a fluorinated $[\text{NH}_4]_2\text{ThF}_8 \cdot 2\text{H}_2\text{O}$.³⁷ The process was sensitive to the presence of water, producing the oxyfluorides. Improvements to yield were achieved with heating the reagents to 250°C for 12 hours in a closed container, followed by heating the salt to 400°C for three hours to remove NH_3 and H_2O . Purity was assessed by differential scanning calorimetry, showing a single peak at 1,110°C.³⁸

Safe handling of thorium fluorides and the materials used to prepare them will be similar to the measures used for preparation of uranium fluoride compounds.

3.1.2.6 Transuramics from used LWR fuel

There are a number of processes available to convert spent fuel, which is mostly UO_2 , into UF_4 .³⁹ First the spent fuel must be removed from the cladding and converted into a powder so that subsequent reactions will occur at a reasonable rate. The traditional method for reprocessing spent fuel uses a large shear to cut the fuel assemblies or the individual fuel pins (after removing the hardware) into small pieces and then leaching with nitric acid to dissolve the spent fuel. The uranium and plutonium can then be separated from the FPs, precipitated, and converted to oxides. The oxides can then be hydrofluorinated to produce fluoride salts for an MSR. An alternative to dissolving the spent fuel is voloxidation, a process in which the spent fuel pieces are heated with air, oxygen, or NO_x to convert the UO_2 to U_3O_8 or UO_3 . The conversion renders the higher oxides into powders that can be separated from the cladding pieces by sieving. The Zircaloy cladding can also be removed chemically by high-temperature chlorination (350–400°C) using HCl or Cl_2 and vaporizing the zirconium from Zircaloy as ZrCl_4 . The fuel could then be voloxidized to convert the pellets into powder, followed by hydrofluorination to produce UF_4 . Both the spent fuel and Zircaloy cladding can be converted into fluoride salts for use in an MSR. The details of the three processes for converting the spent fuel directly into fluoride salts are shown below. For all these processes, most of the actinides and FPs from the spent fuel would also be fluorinated and remain in the MSR fuel salt. Volatile FPs would end up in the off gas.

Chop-Voloxidize-Hydrofluorinate Process

Figure 10 shows the proposed flow sheet for the UO₂ to UF₆ conversion process. The steps in this process are well developed and have been deployed in full-scale facilities in other countries.³⁹ The Zircaloy cladding hulls from the spent fuel must be disposed of as high-level waste or be extensively cleaned for low-level waste disposal. The voloxidation step may use NO and NO₂, which are both toxic, with PEL TWA for 8 hours of 25 ppm and 0.2 ppm, respectively. Flammable hydrogen gas will be used in the chemical reduction step, and corrosive HF will be used in the hydrofluorination step. These two processes could be combined in one reactor.

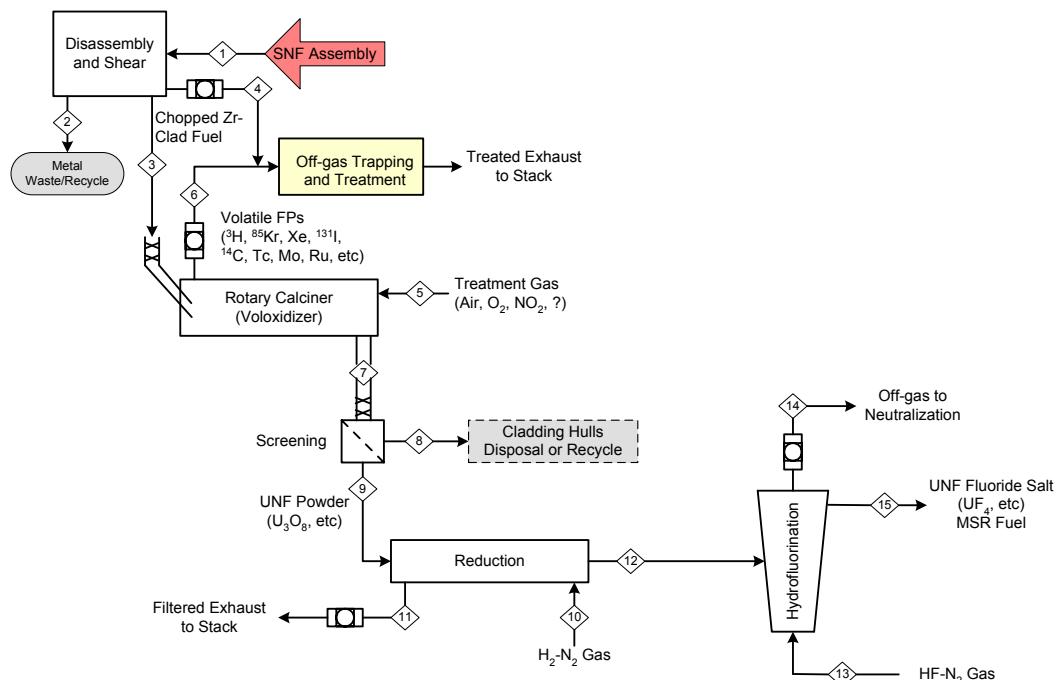


Figure 10. Schematic of the proposed chop-voloxidize-hydrofluorinate process flow sheet.³⁹

A variation on this process, which is being evaluated by several MSR vendors, is to use a fluoride flame reactor to convert the uranium oxides produced by the voloxidizer into uranium fluorides.^{40,41} This process normally produces a UF₆ stream that can be recovered separately from the nonvolatile actinide and FP fluorides. This process uses F₂ gas, which is very corrosive and toxic, with a recommended PEL of 0.2 mg/m³.

Another potential variation is to use NF₃ as the fluorinating agent rather than HF. NF₃ is much less corrosive and toxic than F₂, but it is a strong fluorinating agent at higher temperatures. Thermodynamic calculations performed at Pacific Northwest National Laboratory (PNNL) show that the reaction between NF₃ and UO₂ to produce UF₆ is favorable.⁴² This process is being evaluated for removing various oxides from MSR fuel but could possibly be used to produce the initial salt from spent fuel.

Chemical Decladding-Voloxidize-Hydrofluorinate Process

Starting with irradiated UO₂, the Zircaloy cladding can be removed using chemical methods. It will react with anhydrous chlorine (Cl₂), anhydrous hydrogen chloride (HCl) at 350–400°C, or thionyl chloride at near room temperature to produce volatile ZrCl₄.³⁹ The fuel remains intact and ready for the voloxidation and hydrofluorination. The decladding process is the main difference between the flow sheet shown in

Figure 11 and the one shown previously in Figure 10. During the chemical decladding, tritium trapped in the cladding will be released into the off-gas system as ^3HCl (or TCI). Chlorine, HCl/TCI, and thionyl chloride are all toxic and corrosive, with PEL TWA limits of 1 ppm, 5 ppm and 2 ppm, respectively. Thionyl chloride decomposes above 140°C, producing sulfur dioxide and hydrogen chloride, which are toxic and corrosive. It also reacts violently with water. The chemical hazards for the remaining steps would be the same as those used for the previous process.

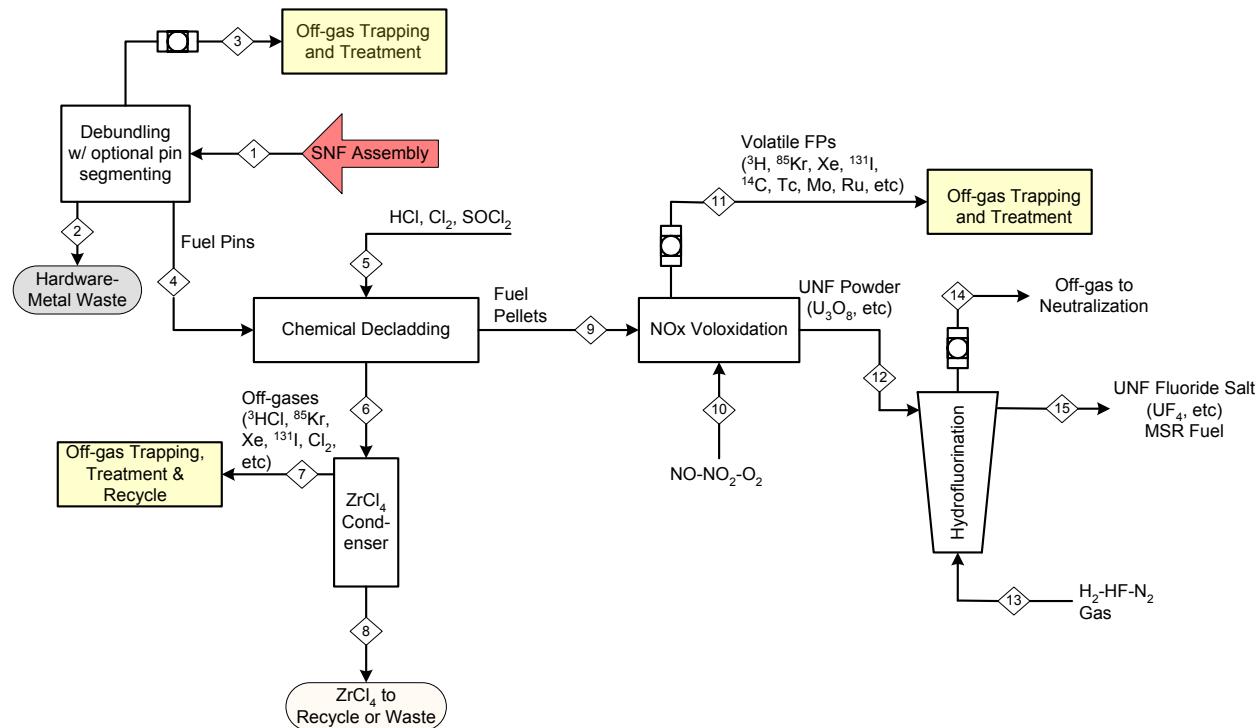


Figure 11. Schematic of the proposed chemical decladding-voloxidize-hydrofluorinate process flow sheet.³⁹

Dissolution of Fuel and Cladding in Molten Salt Process

Spent UO₂ fuel can be converted to fluoride salts by hydrofluorination in a molten salt.⁴³ The zirconium-uranium-based fuel elements are dissolved in a molten fluoride salt at 600–700°C, in which the oxides are converted to fluorides using anhydrous HF. To recover uranium from the spent fuel, the salt can be treated with F₂ to remove uranium as volatile UF₆ in a fluorination process. Two fluoride molten salts were used in these experiments: NaF–ZrF₄ and LiF–NaF. At 600°C, the NaF–ZrF₄ remained molten for compositions ranging from 40–60 to 60–40 mol%, and it could accommodate significant amounts of uranium. The 57–43 mol% LiF–NaF has a liquidus temperature of 675°C and can dissolve zirconium up to a concentration of 55 mol%. Other salts may serve the same purpose, but this requires more testing.

A flow sheet was developed by Taylor et al. (2019), shown in Figure 12. This process flow diagram shows the removal of stainless-steel hardware and conversion of fuel pins to fluoride salts.³⁹ Several variations of the process are possible, such as the development of a fuel pin cutting step to make lengths that are more easily handled. Some of these variations are listed below the figure and are taken from the same Taylor (2019) report.

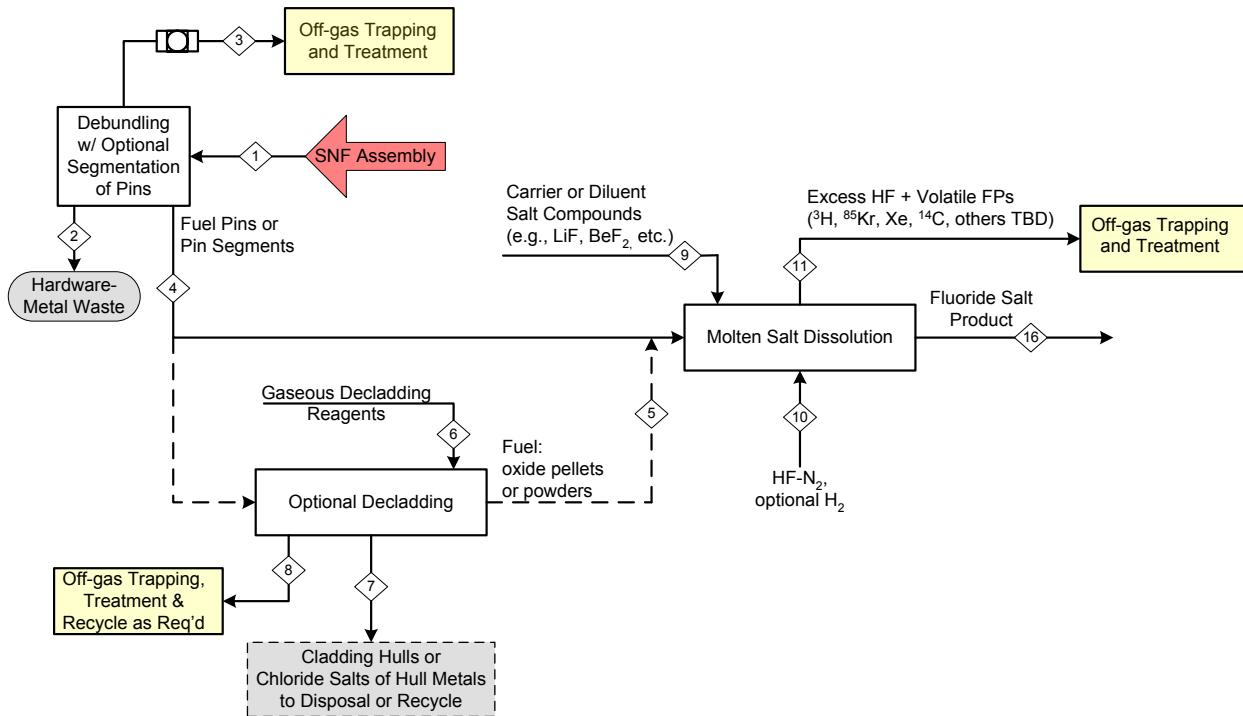


Figure 12. Concept for converting used fuel to fluoride salts by molten salt dissolution.³⁹

1. The co-conversion of fuel and cladding is essentially the process shown in Figure 12. The first step removes the stainless-steel hardware after which the fuel pins can be segmented to reduce the scale of the molten salt bath used in processing. The Zircaloy-clad fuel is then converted to fluorides in a molten salt bath. Fluoride salts are added to make the proper ratio of carrier salt and used LWR fuel in the hydrofluorination flux, although it may be possible to use only the fluorides of the clad fuel ($\text{UF}_4\text{-ZrF}_4$). Zircaloy generates a significant amount of hydrogen (and tritium) in the off-gas stream. Flammable hydrogen poses a risk that will require stringent engineering controls. The fluoride salt product will contain a higher concentration of ZrF_4 than for the fuel salt used in MSRE. This process uses toxic and corrosive HF bubbled into a hot salt bath.
2. As discussed earlier, a chemical decladding step can be used to remove the zirconium, the primary constituent of the cladding before converting the fuel. The advantage of this process is that the declad UO_2 fuel pellets can be converted to UF_4 with HF without the concern of producing hydrogen. Because Zircaloy is not present, carrier salt must be added to provide a fluxing agent. Fission product oxides will be converted to fluorides. Tritium and volatile fission products released to the off-gas must be trapped for disposal. The hazards of this process would be the same as those associated with the chemical decladding process described above, along with the hazards for the HF and hot salt bath described in item 1.
3. Decladding can also be done by voloxidation, following segmentation of fuel pins to improve the efficiency. The fuel is oxidized, and in air will convert UO_2 to U_3O_8 , and in NO_x , convert the UO_2 to UO_3 . The higher oxides form powders that can be separated from the larger cladding pieces by sieving. Neither U_3O_8 nor UO_3 is converted to UF_4 with HF; rather an oxyfluoride is produced. To achieve the production of UF_4 from U_3O_8 or UO_3 , hydrofluorination using both HF and H_2 is required.³ Tritium and other volatile fission products will have already been removed by the voloxidation process, so their release is not an issue in the subsequent hydrofluorination. Generated

water vapor will not be contaminated with tritium. Because the voloxidized fuel is in powder form, the combination dissolution and hydrofluorination step will be rapid.

3.2 SYNTHESIS OF MSR FUEL SALT

The fuel salt for an MSR will be a combination of the fissile salt, usually UF_4 or UCl_3 , with non-radioactive diluent or carrier salts, such as LiF , ZrF_4 , NaF , and BeF_2 or NaCl , CaCl_2 and MgCl_2 . It is likely that the company producing the fuel salt will produce the fissile salt, purchase the non-radioactive salts from commercial sources, and then combine them to produce the fuel salt mixture. For the MSRE, all the fuel salt components were mixed at the reactor site, but this is considered unlikely for a power reactor. The fuel salt will likely be produced by an off-site company, as is done for the fuel assemblies used in an LWR, and then loaded in the reactor. Depending on the MSR design, the fuel salt may contain other components, such as fertile salts (U or Th) for breeder MSRs. Reuse of spent LWR fuel may mean that actinides and fission products are present in the fuel. These components would have little effect on the chemistry and chemical hazards of the fuel salt, but they will impose major radiation hazards. The salt production company providing the fuel salt will likely also be asked to supply small packages of salt containing much higher concentrations of the fissile material (refueling aliquots). These will be added to burner type MSRs during operation as needed to maintain reactivity.

3.3 PACKAGING AND TRANSPORT OF ENRICHED UF_6 AND UF_4

American National Standards Institute (ANSI) N14.1-2001 provides criteria for packaging uranium hexafluoride (UF_6) for transport. It includes specific information on design and fabrication requirements for the procurement of new UF_6 packaging. This standard also defines the requirements for in-service inspections, cleanliness, and maintenance for packaging in service. The standard requires that UF_6 enriched to greater than 1.0 wt% shall be packaged in accordance with the US Department of Regulations (DOT) regulations of Title 49 US Code of Federal Regulations (CFR) Parts 173 [5] and 178 [6] or in other NRC or DOE certified package designs. These packages consist of an inner UF_6 cylinder (excluding Type 48G and 48H, which are limited to 1.0 wt% assay or less) plus an outer protective package.

Packaging and shipment of enriched UF_6 to be used for producing UF_4 for molten salt reactors is no different than packaging and shipment of UF_6 to be used for producing UO_2 reactor fuel, so there are no new hazards. UF_4 is hygroscopic and forms $\text{UF}_4 \cdot 0.75\text{H}_2\text{O}$, albeit slowly.

UF_4 has similar transportation hazards to those for UO_2 , except that UF_4 can have a very slow reaction with water to produce uranyl fluoride (UO_2F_2) and HF. Criticality concerns would be the same, and the packaging requirements should be the same or very similar. The packaging for UF_4 may need to be rated for an underlying hazard of corrosivity, which is not the case for UO_2 . UF_4 and fuel salt mixtures that will be used in an MSR must be kept free of moisture and oxygen contamination, which greatly increases the corrosivity of the mixture. The packaging must be designed to exclude moisture, and the fuel salt must be loaded under inert conditions. The packaging must also be designed to prevent criticality during transportation and storage.

4. REACTOR SITE FUEL PROCESSES AND HAZARDS

This section describes processes and operations to maintain the fuel salt within its required specifications. Chemical aspects of reactor operation are described, as well as nuclear operations and the operations of various support systems and functions necessary for the reactor to operate efficiently and safely within its design and regulatory specifications.

4.1 LIQUID-SALT OPERATIONS

An MSR operates as a chemical reactor as well as a nuclear reactor. During burnup, the FPs will accumulate in the fuel salt and will circulate throughout the core. Many of the salts' physical behaviors will depend on temperature gradients and chemical environment, the latter being governed by the chemical potentials of fuel salt components. Fission will gradually produce a more oxidizing environment. If a fluoride-based salt is being used, then activation and decay will produce oxygen and nitrogen. These processes, particularly fission, will change the redox state of the salt, in some cases changing the chemical form of FPs and the ratio of uranium redox species. The composition of the salt will affect the corrosion rates of reactor materials, the volatility of some chemical species, and the precipitation and plating of others on the internal surfaces of the reactor.

MSRs operate at high temperatures, well above the melting point of the salt (< 550°C). Normal operating conditions are typically 650°C or higher. Off-normal events may have temperatures exceeding 800°C. Salts have relatively low viscosities, and some salts wet metal surfaces, tending to creep up vessel walls and making them difficult to contain. Reactor materials need to be able to maintain structural integrity at high temperatures. Molten salt mechanical joints frequently leak, primarily due to creep of the bolts providing the sealing force. Diffusion of tritium and helium through metals is increased at high temperatures. On the other hand, elevated temperatures mean that chemical processes occur quickly and are not limited by chemical kinetics but can be described using chemical thermodynamics. At operating temperature, recombination within the salt dominates radiolytic damage production. Finally, high temperatures mean that physical property data used to describe salt thermal property data and transport are difficult to collect and have substantial uncertainty.

MSRs operate at pressures just above ambient, as the vapor pressures of the salts are very low under normal operation. A breech in the reactor vessel means that the salt will ooze through a crack and solidify rather than experiencing a pressurized mechanical break-up into a spray of aerosolized particles and gases such as in an LWR severe accident. Molten salts are hygroscopic and are readily contaminated by air exposure, but they do not have any energetic chemical reactions with air or water. Consequently, it is useful to employ an inert containment environment to minimize the potential for contamination during any maintenance activities in which the salt boundary is broken. The containment floor will almost certainly be made of stainless steel to prevent hot salt from directly interacting with concrete in the event of a severe accident.

Moving fissile material through a heat transfer loop results in additional safety issues. Any inhomogeneities in the concentration of the fissile material will lead to variations in reactivity. As some fuels melt incongruently and some fuel salts operate near fissile material solubility limits, over cooling accidents may result in solidifying fissile materials at the coldest part of the heat transfer loop. The actinide trifluorides have limited solubility and at low temperatures, their joint solubility is much less than their individual solubilities.^{44,45,46} Off-line fuel handling or recovery of actinides will pose similar concerns about inadvertent criticality. Also, salt vapors, mists, and aerosols released at the fuel's surface will plate out on the walls of the cover-gas system.

Undissolved (noble) FPs will plate out onto surfaces. The largest surface is the heat exchanger. These highly radioactive materials will likely constitute the largest potential dose to personnel during maintenance/replacement activities and may result in long-term fouling of the heat exchange surfaces.

4.2 FUEL LOADING

The process for loading fuel into the salt reactor is distinctly different from that of solid fuel reactors. For example, solid fuel reactors cannot be overfilled. On the other hand, solid fuel reactors must have

sufficient excess reactivity available to maintain criticality until their next refueling interval. MSRs will only have the reactivity necessary for current operation and will be nearly continuously refueled (or defueled in the case of breeders), making inadvertent criticality less likely. Fuel salt will arrive at the reactor site in a solid form in standardized containers. The salt will be melted prior to being introduced into the fuel salt circuit. The multiple containers of fuel salt will likely be combined into a salt maintenance/storage vessel within containment near the reactor vessel. From there, the fuel salt will be hydraulically transferred into the fuel salt circuit.

An alternative method for initial fueling of an MSR (apart from the concentrate salt addition method discussed in Section 2.2) would be to externally heat the core materials and the fuel salt to above operating temperature, after which the fuel salt would be introduced into the core. This process would avoid criticality during fueling because of the strong negative reactivity temperature feedback.

Refueling systems for future MSRs have not yet undergone final design, or if designed, then not publicly disclosed. Consequently, descriptions of specific mechanisms or hazards is not yet possible. However, the general requirements for introducing to and/or removing fuel salt from an MSR limit the potential methods and mechanisms for refueling. Refueling will likely be performed by adding and/or removing premeasured aliquots of fuel salt into the fuel salt circuit at the time intervals required to compensate for burning/breeding. (Metering liquid fuel salt is much more complicated than changing the interval at which premeasured quantities of fuel salt are added.) Uniform individual fuel salt portions will likely be prepared at the fuel salt facility and melted or dissolved into the fuel salt circuit as needed to maintain criticality. For example, if the plant is operating at 100% power, then a fuel aliquot may be added every shift, but if the plant is operating at reduced power, then fuel addition would occur less frequently. Planned reductant addition methods to compensate for fuel salt oxidation due to fission have not yet been selected. The refueling salt may be in a reducing state, or a separate reductant (likely Be or Mg) will be added to the fuel salt circuit. A recent review lists several means to achieve redox control: gas sparging, adding a reductant, and using redox buffers.⁴⁷ The plant will likely receive a significant quantity (months) of fuel portions so as to minimize the frequency of fuel shipping and the requirement to break containment to introduce additional material. Remote systems would be employed to select an individual aliquot and transfer it into the fuel salt circuit.

At the MSRE, the same system was used for sampling and for enrichment through the gas-locked system, as discussed in the section on online sampling and shown in the schematic below.⁴⁸ The enriching capsule was capable of adding 90 g of ^{235}U to the reactor. Because the primary and secondary containment barriers had to be breached to add the fuel, the system was set up so that two barriers were always present between the core and the atmosphere, as well as between the sample and the atmosphere. Pressurization was used to determine if the penetrations in the barriers were closed at the required times to maintain an inert gas buffer. The enriching capsule was made of nickel tubing and was drilled with holes to allow the salt to escape. Operational details are given by Gallaher and in the summary report compiled by Guymon.⁴⁹ The device was functional, but modifications were made in response to problems encountered during operation. One modification allowed for the use of magnetic alloys for the keys and capsules. This allowed the keys and capsules to be retrieved or manipulated if they came out of alignment. Repair of the drive unit required shut down and draining of the reactor. However, the enrichment-sampler was deemed a success and was operational at the end of the MSRE project.

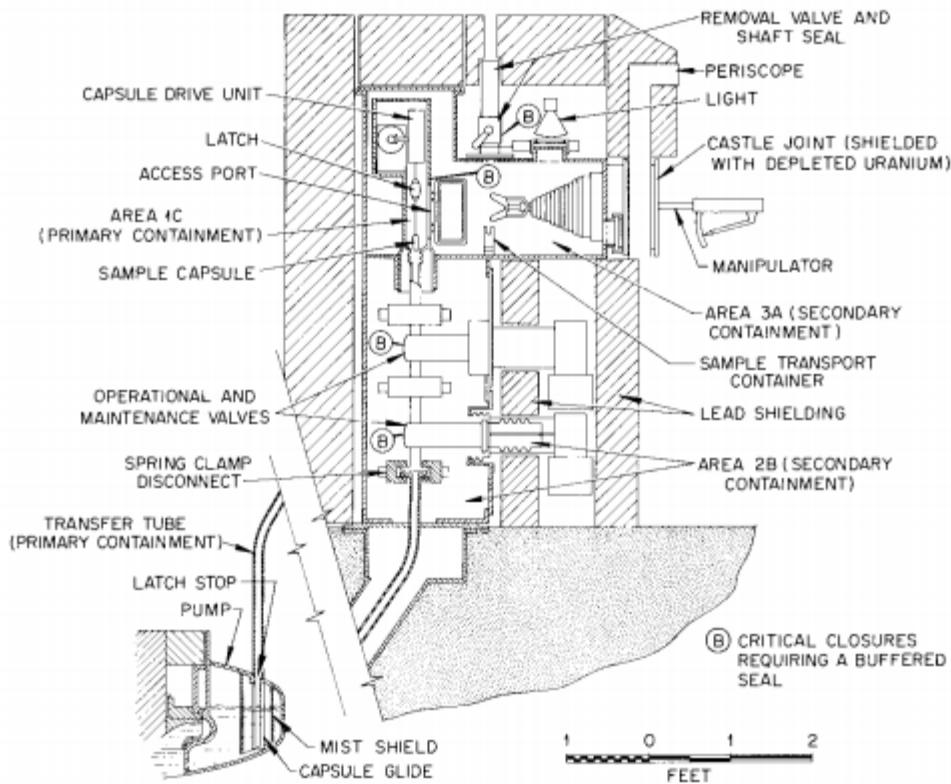


Figure 13. MSRE sampler-enricher.⁴⁶

4.3 FUEL SAMPLING

MSR operators will periodically need to sample the fuel salt. MSRE surveillance sampling methods were reviewed in the ORNL progress report compiled by Briggs.⁵⁰ These samples included specimens immersed in the salt: graphite, Hastelloy-N tensile bars, and wires for monitoring the flux. Salt samples were also extracted from the reactor for analysis in nearby facilities. A sampler-enricher was developed for adding material and taking salt from MSRE.⁴⁸ The sampling vessel was inserted into the pump surge tank, and molten salt was collected in a scoop. The vessel was introduced into the core through an antechamber that was evacuated or purged to prevent air from contacting the salt during introduction of the vessel. A carousel was used so that multiple samples could be taken during a cycle.

4.4 OFF-GAS SYSTEM

Fission gases and aerosols will be released from the fuel salt into the cover gas. The location of the free surface within the fuel salt loop will depend on the reactor design. While the MSRE included its free surface within the pump bowl, a free surface could instead be provided in a dedicated component located at the high point of the fuel salt loop. As the released materials are highly radioactive, the fuel salt cover gas system is part of first layer of radionuclide containment.

The radionuclides transported with the cover gas will release substantial thermal energy, resulting in a need to provide decay heat removal for the cover gas system. Roughly 40% of FPs transition through a gaseous element in their decay chains. The amount of thermal loading in the cover gas system will depend

strongly on the degree to which the short-lived fission gases evolve from the salt. If the short-lived FPs are retained in the fuel salt, then their decay heat will contribute to the fuel salt's thermal load. However, if the short-lived FPs transport with the cover gas, then the cover gas system will have a much higher thermal load. Whether fission gases should be aggressively stripped from the fuel salt is a design choice, so no general conclusions can yet be reached about the cover gas thermal performance requirements.

A general summary of the technologies for an MSR off-gas system was recently developed by Riley and colleagues,⁵¹ much of it based on MSRE operational experience.⁵² The paper specifies the species that are expected to be found in the headspace of an MSR, including salt aerosols, noble gases, reactive gases, tritium, volatile and semi-volatile halides, and activation products. These species will be swept through a set of traps for decay and storage using a helium sparging gas. Various methods for trapping and immobilizing the gaseous species were described as follows:

1. Molten hydroxide scrubber for particulates, aerosols, reactive gases, and halides
2. Immobilized zeolite for capture of tritium (and hydrogen), which can be recombined to form HTO (and H₂O).
3. Silver-functionalized packed beds to capture residual iodine and other halides
4. Cryogenic capture and release of non-radioactive gases such as N₂ and O₂ generated by radiolysis
5. Capture and separation of noble gas FPs through cryogenic distillation, activated carbon, metal-organic frameworks

Some of these systems were tested at MSRE, and others were tested at the laboratory scale. Implementation of an off-gas system has been considered for reactor operations and for associated fuel processing. Some examples are given in the discussion below.

In MSRE, a flow of helium through the fuel pump bowl was used to flush FPs to activated charcoal beds.⁵³ Helium was also used to move salt from one tank to another, and the gas was also passed through the charcoal beds. The helium was treated by passing it through a hot titanium sponge with specifications set at <1 ppm O₂ and <6 ppm H₂O. However, the pressure in the cover gas system was difficult to control because of the deposition of solids and tar in the off-gas throttling valve and filter.⁵⁴ The solids were derived from the coolant salt and from Hastelloy-N mixed with oil that had seeped into the system down the shafts of the fuel pump and coolant pump (including ⁸⁹Sr, ¹⁴⁰Ba, ¹⁴⁰La, ¹⁰³Ru, ¹³²Te, and ¹³⁷Cs as measured by gamma spectrometry). Spectrochemistry showed lithium, beryllium, and zirconium. A filter deliberately placed to remove solids in the off-gas mainly trapped solid daughters of noble gas FPs. However, other FPs also form solids during operation and can be swept from the salt. These include tellurium, molybdenum, ruthenium, niobium, and antimony. Niobium can build up after reactor shutdown, as it is the daughter of ⁹⁵Zr. ²³⁹Pu is not volatile and remained in the salt.

The stripping efficiency of the helium flow from the pump bowl and graphite was tested by the injection of ⁸⁵Kr. The void fraction in the salt was 0.6%.⁵⁵ The authors recommended chemical surveillance of the reactor during operation for (1) oxide contaminants in the fuel salt, (2) corrosion, (3) oils and hydrocarbons, and (4) isotopic composition of uranium and plutonium through grab samples.⁵⁶ Areas that need to be sampled are the gas phase above the fuel salt, the salt itself (to ascertain its oxide content and its redox potential), and the outflow of online processing streams (to check for species such as bismuth).

The off-gas system for a molten salt breeder reactor design was described by Kasten.⁵⁷ In the MSBR, both the fissile and fertile streams were to be recycled, with Pa removal by liquid bismuth from the fertile loop. Uranium was to be cycled online over 30 days as volatile UF₆. A slip stream of the UF₆ would pass through a scrubber to remove volatile FPs and then would be recycled to the reactor. The volatilization of the UF₆ and the diluent LiF/BeF₂ at 500°C would leave behind a slag of rare earths. Reduction of the UF₆ to UF₄ with hydrogen reduces and precipitates metals (Cr, Fe, and Ni) that would be filtered and sent to

waste. The off-gas system would serve both the reactor and the processing plant and would include a NaF-MgF₂ sorber operating at 100–400°C, as well as a cold trap operating at 70°C. The reactor was designed so that the residence time of entrained fission gases was less than one minute. The gases would be removed by sparging the salt with an inert gas. Key safety features included continuous cooling of the processing equipment and concerns about criticality. Xenon and krypton would be stripped from the fuel salt by sparging with an inert gas such as helium. The processing of UF₆ by volatility included the use of hydrogen and fluorine, gases that must be kept separate. In the off-gas flowsheet, fission product gases would be allowed to decay and then would be passed through water-cooled charcoal beds that retain ¹³⁵Xe for 48 hours. ⁸⁵Kr would be captured on a molecular sieve and cooled by liquid nitrogen, and then it could be transferred into a tank for storage, regenerating the sieves. The purge gas would be filtered, compressed to 40 psia, and returned to the reactor, or alternatively, vented. Design details were lacking in two important respects. One area where design details are lacking is in the effective capture of tritium, which needs more study, as has been reiterated in a review of the MSRE experience.⁴⁸ The second area of concern is that aerosol capture must be achieved using cold traps or filtering, and these separations must also be able to remove contamination from organics coming from the lubrication of pump machinery.

Fluorine volatility was used to recover uranium in MSRE.⁵⁸ In the MSRE fuel processing facility, the fuel (<30°C above the liquidus) was collected in a storage tank and exposed to fluorine in helium. The off-gas included UF₆, excess fluorine, helium, MoF₆ (FP and resulting from corrosion), CrF₄ and CrF₅ from corrosion of the tank, IF₇, and the fluorides of tellurium, niobium, ruthenium, and antimony. The gas then passed through a NaF trap kept at 400°C that retained most of the FPs, including NbF₅. The gas that now included UF₆, fluorine, helium, MoF₆, IF₇, TeF₆ and traces of the other FPs then was passed through a series of NaF absorbers heated from 90–120°C to retain the UF₆ but not the other gases. In MSRE, the off-gas without uranium was sent through a molten hydroxide (2M KOH/KI) scrubber to capture the fluorine and residual FP fluorides. The caustic scrubber captured the iodine, but this method was not as effective at eliminating tellurium from the gas flow. A final series of filters and traps polished the gas before venting it through the stack, including alumina to remove volatile tellurium hexafluoride. A flame arrester was included because of the generation of oxygen (25% of the fluorine) in the molten salt scrubber.

In future designs, the unreacted fluorine can be recycled through a surge chamber by a positive displacement pump. Kasten proposed a NaOH-KOH scrubber⁵⁹ operating as a continuous countercurrent packed bed. A slip stream of the hydroxide could be sent to waste, enabling online replenishment. The scrubber's off-gas could be contacted with steam to hydrolyze FPs such as tellurium, the oxides and hydroxides could then be filtered. The processing off-gas and the reactor off-gas could undergo similar final treatment steps if they co-located in the same facility. Handling of hydroxide mixtures has been considered, along with their use as media for thermal energy storage.^{60,61}

Proper handling of the off-gas system will be important to reactor operation and site safety. Configuration of the off-gas system to confine fission gases and trap particulates means that it will be operating continuously and also that on-line maintenance will be required. Maintenance will have to be performed with remote handling because of the quantity of radioactive elements. In some cases, such as if a hydroxide scrubber is used, there will be a chemical hazard, but this is being used in other industries, and similar safety protocols can be used. Replaceable components of the off-gas system such as filter beds or hydroxide salt will need to be contained on site in the same manner as for used fuel before preparation for permanent disposal. ⁸⁵Kr may be separated and sold as a byproduct of operation.⁶² The greatest technical challenge for reactor developers will be in assessing off-gas performance during reactor operation. Gamma spectroscopy is used for current reactor designs, but the background in an MSR off-gas may reduce the effectiveness of gamma analysis. Online sampling methods for FP compounds such as the use of optical spectroscopy are being considered. Laser-induced breakdown spectroscopy and laser-induced

fluorescence analyses have been shown to be effective in determining metals loading in industrial environments such as flue gas emissions.⁶³

4.5 INSOLUBLE FISSION PRODUCT FILTERING

Some of the FPs produced in the MSR will be insoluble in the molten salt, so they will require filtration for removal. The filter is likely to be made from porous metal such as Hastelloy and will likely be placed in a recirculating side stream from the reactor core. The filter will require periodic changing, which will involve pulling the filter out of the salt, allowing any remaining salt inside the filter to drain, installing a new filter, and then packaging the old filter for disposal. The dose rate on the old filter will be very high due to the insoluble FPs and any residual fuel salt remaining on the filter. All these operations must be performed without allowing significant amounts of moist air to contact the molten salt. Prior to changing the filter, the recirculating salt flow should be turned off, and it may be possible to drain the salt from the recirculation loop. The historic MSR program provides basic information on the design and performance of large molten salt mechanical filters.⁶⁴ Design of the filter, the filter holder, and the filter removal equipment for commercial-scale MSRs to allow for remote removal and replacement remains a significant challenge.

4.6 SOLUBLE FISSION PRODUCT SEPARATION

4.6.1 Chlorides

Burn-up produces a myriad of elements in molten salts, but electrorefining provides a method to selectively separate metals. This method has mostly been studied in the context of pyroprocessing in chloride salts.⁶⁵ In pyroprocessing, the actinides are removed at the cathode, leaving FPs such as rare earths in the melt. The volatile FPs (e.g., Cs, I, and the noble gases) are removed during the head-end processing. To increase the solubility of metallic FPs by converting them into chlorides, an oxidizing agent such as UCl₃ can be added to a chloride melt if it is not already present, with the uranium being plated out as the metal.⁶⁶ Besides the hazards already noted when using chloride and fluoride salts—such as elevated temperatures and corrosivity—electrorefining processes are likely to have fewer chemical hazards than salt preparation, such as those processes discussed in Section 3. This is because the salts are already in the halide form. However, the radiolytic hazards will be considerable due to working with spent fuel. Therefore, operations must be performed remotely, and the collected materials must be stored appropriately for recycling (in the case of the carrier salts) or waste disposal (FPs).

4.6.2 Fluorides

There has not been much electrorefining work performed on fluoride salts in the context of nuclear fuel remediation; however, the aluminum industry has been achieving separations in fluoride salts since the 1880s.⁶⁷ For a fluoride salt in which many of the metals (M) are in the form of MF₃, contact with a reducing agent—a soluble metal solvent such as aluminum or an aluminum-copper alloy—allows precipitation of the metal on the cathode. A liquid metal such as bismuth has also been used as an electrode in fluoride salt separations⁶⁸ or as an immiscible extractant phase in a centrifugal contactor.⁶⁹ Aluminum has also been considered for use in separating lanthanides from actinides.⁷⁰ In the case of used nuclear fuel, once the actinide has been removed, the other metals such as the rare earths can be separated from the salt. This has been demonstrated using the hydrofluorination of oxide fuel by the French Commissariat à l’Energie Atomique (CEA).⁷¹ More recently, an electrochemical cell was used to separate samarium and gadolinium in LiF-BeF₂ by plating the metals onto insoluble electrodes: molybdenum and nickel, respectively.⁷² Glassy carbon served to contain the melt and also acted as a counter electrode. Platinum was used as the pseudo-reference electrode. However, this method of separation requires research before it can be used for an MSR. For instance, the Czech study found that gadolinium formed

an alloy with nickel that may also have contained some beryllium. The small electrochemical window of the LiF-BeF₂ melt meant that the samarium reduction was limited to one electron: Sm³⁺ to Sm²⁺. However, the relative simplicity of working with molten material under argon and generating solidified products leaves reductive extraction as one of the safer separation methods that can be carried out to remove FPs from the salt.

4.6.3 Vacuum Distillation

Tests were conducted at ORNL to assess the relative volatility of FPs in LiF-BeF₂⁷³, the removal of LiF-BeF₂-ZrF₄ from MSRE salt⁷⁴, and recovery of unburned fuel ²³³UF₄, LiF-BeF₂, and LiF-ThF₄ in the MSBR.⁷⁵ Results from these experiments were used to inform the design of the waste handling system of the MSBR.⁷⁶ Vacuum distillation achieves better separation at lower temperatures.

The apparatus had four components, all made of Hastelloy-N: (1) a feed tank, (2) an annular still, (3) a condenser, and (4) a holding vessel. The apparatus was certified to handle external pressures of 1 atm at temperatures ranging from 600°C (for the feed tank) to close to 1,000°C (the still). The apparatus was mounted above a catchment vessel in case of leaks. An Inconel filter was used upstream to remove metal particles from the salt before it entered the apparatus. A filter was also placed in the line to the vacuum pump. Valves and piping that did not contact the salt were made of stainless steel. Instrumentation included conductivity probes to measure salt levels, pressure taps, ionization chamber radiation monitors on the filters and liquid nitrogen trap, and Geiger counters on the pumps. Discrete sampling during the process involved filling a vessel with 10 g of condensed salt. The vessels were manipulated in the vertical direction by a sampling tool and in the horizontal plane with a turntable. The sampling chamber was alternatively purged with argon or evacuated to minimize contamination of the distillation process with air.

An experiment with irradiated MSRE salt followed commissioning tests with pure salt and simulants. The isotopes that were followed included ⁹⁵Zr, ¹⁴⁴Ce, ¹⁴⁷Pm, ¹⁵⁵Eu, ⁹¹Y, ⁹⁰Sr, and ¹³⁷Cs. The relative volatilities of the rare earths were higher than expected at 0.01 to 0.001. However, the concentrations in the distilled salt were reduced to about 3% of the initial values, and 95% of the ⁷Li was recovered.

Chemical hazards from vacuum distillation are likely lower than in other methods. However, pressure and vacuum envelopes must be manipulated and maintained to achieve the desired separations. Processing of slag from the distillation, filters, and other equipment must be performed remotely, as these will be highly radioactive. Online sampling to assess performance would also be desirable, as the tests with MSRE salt showed that experimentally determined volatilities were different from calculated values, as they were higher for lanthanides and lower for ¹³⁷Cs than expected.

A variation on vacuum distillation includes a prior reaction to the distillation step. This was tested on a chloride mixture, LiCl-KCl-rare earth chlorides.⁷⁷ The salt was reacted with a mixture of lithium and potassium phosphates that immobilized the rare earth chlorides as phosphates in the mixture, facilitating the separation of the carrier LiCl-KCl salt.

4.6.4 Oxidative Precipitation

Removal of rare earths from LiCl-KCl salt can be achieved by using oxidative precipitation. This has been demonstrated at bench scale by sparging with oxygen at 750°C for several hours. Rare earths are precipitated as the oxides or oxychlorides.⁷⁸ Introduction of pure oxygen into the chemical reactor will require precautions to minimize the possibility of combustion or explosion. However, once volatiles have been removed during the head-end process, the precipitate should be ready for waste disposal in the appropriate container.

4.6.5 Melt Crystallization

Purification through freeze-thaw cycles is a well-known method for purifying substances. Melt crystallization was demonstrated at the bench scale to remove LiCl from simulated FPs, namely CsCl and SrCl₂, which have lower melting points.⁷⁹ Using this method, LiCl frozen onto a cold finger might be separated from the bulk of FPs. Salt transfer and handling may be more complicated than in the previously discussed examples of using gaseous or liquid separations, but the possibility of having a release of material from the vessel is likely lower when using this process.

4.7 WASTE FORM PREPARATION

Wastes from an MSR will include those generated during salt preparation or purification prior to irradiation; those generated during operation such as through sampling, analysis, online processing, filter change-out, or off-gas management; those generated at the end of a fueling cycle; and those generated at the end of reactor operation. Many of the radiological hazards will be similar to those for operation of other nuclear power plants, so these will not be discussed in detail. The unique aspects of MSR wastes relate to the chemistry of the salt and the possible needs for actinide recovery and preparation of stable waste forms.

4.7.1 Actinide recovery

Salt separation processes can be used to remove the volatile FPs and recover carrier salts. Actinides can also be recovered either for reuse in a reactor or for segregated disposal. Recovery of used LWR fuel in a molten salt has been discussed earlier, Section 3.1.2.6., and the CEA has used hydrofluorination to process oxide from used nuclear fuel.⁸⁰ Additionally, pyroprocessing has been used to extract actinides from LiCl-KCl⁸¹. In a molten salt pyroprocess, actinides are collected at the cathode under an applied electrochemical potential. As fuel in the MSR is already in the salt form, a similar process could readily be applied.

Other industries are interested in recovery of metals from fluoride salts. For instance, extraction of rare earth elements from a fluoride salt electrolytic slag has been considered as a way to recover these valuable materials that would otherwise be lost. Various methods include dissolution in acid, roasting with Ca(OH)₂ at temperatures up to 1000°C, heating with NaOH at temperatures up to 500°C to form hydroxides, and silicate roasting to form water-insoluble rare earth silicates. In the silicate roasting case, after a roast of 1.5 hours at 850°C, the lanthanides were converted to the silicate minerals.⁸² The soluble fluoride salt components were removed by washing. Recovery of lanthanides was stated to be over 90%. Studies involving formation of uranyl silicates have been carried out, but this was done under hydrothermal conditions.^{83,84} An advantage of separations in the molten state is that large volumes of acidic waste water are not generated as found in actinide separations based on PUREX-type processes.

Electrochemical methods were mentioned earlier in the context of FP removal from salts. The separation of uranium by FLiNaK was studied jointly by a group in the Czech Republic and Slovakia.⁸⁵ They were able to achieve some success in depositing uranium on a working nickel electrode, but only up to 25 mass%. The process was very sensitive to the presence of oxygen in the salt.

4.7.2 Radiolytic stability

Besides the issue with solubility, another important reason to remove the halide from the salt is to impart radiolytic stability to the waste form. Dehalogenation would allow the use of waste forms that have already been assessed for high-level nuclear waste. Reaction with phosphates such as phosphoric acid, ammonium phosphate, or lithium-potassium phosphate converts the metallic chlorides to phosphate

glasses, liberating ammonium chloride that can easily be removed, as it has a high volatility. This process has been demonstrated at the bench scale for chloride salts, and it is anticipated that it could work for fluoride salts based on thermodynamic stabilities.⁸⁶ Rare-earth phosphates form a stable mineral, monazite or xenotime. Trapping of salt cations in zeolites is also being explored.⁸⁷

4.7.3 Potential forms

Because of its solubility in water, the MSR salt is not a good medium for immobilization. Therefore, conversion to another form is necessary. Options include glass, ceramic, glass-ceramic,⁸⁸ glass-bonded ceramic, and ceramic-metallic forms. Waste form possibilities were reviewed by Riley.⁵¹ Residue from pyroprocessing can be incorporated into a fluoride glass-ceramic waste form. Dehalogenation produces oxides, phosphate glasses, or borosilicate glasses. Zeolites can be hot pressed into low porosity ceramics. Phosphate minerals can be mixed with a glass to form a glass-composite material. The Glass Material Oxidation and Dissolution System (GMODS) developed for radioactive waste can handle many different materials, such as, metals, ceramics, and organics.^{89,90} The material is dissolved in a mixture of glass and sacrificial molten lead oxide, oxidizing the transition metals and forming a glass waste form. Reduced metallic lead is recovered from the bottom of the furnace for recycling through the process. It is possible that this one-step process could also be applied to molten salts, but this has not yet been tested. There are many options for molten salt waste forms. These have not been demonstrated at the pilot scale, but several converge on technologies that have already been tested for pyroprocessing and other activities. The primary hazards are the high radiological fields and contamination that will necessitate processing in shielded facilities. Thus, operations and maintenance must be optimized for remote handling.

Waste structural materials will also be generated during reactor decommissioning. Graphite will be a major waste form in the case of thermal salt reactors, and it may be the limiting factor of the reactor lifetime. The graphite will be contaminated with FPs captured by recoil and fluoride from the salt itself. The graphite may also have a significant loading of tritium from activation of lithium in the core. Recovery of graphite by removing the tritium has been proposed and would greatly reduce the volume of the waste.⁹¹ Options for removal of tritium and other FPs have been evaluated by CARBOWASTE, and handling of graphite will follow procedures developed for other in-core graphite materials.⁹²

Metals from the reactor core will also comprise a waste material and will be laden with reduced FP metals that plate out on colder surfaces in the core. Measures to decontaminate and reduce the size of metal waste include removal of entrained salt from structural materials including leachable FPs such as technetium. Any decontamination activity will be performed with remote handling but can take advantage of salt water solubility, so it is within the scope of current handling of nuclear materials.⁹³

5. FUEL SALT PROCESSING HAZARD TABLES

Many of the MSR hazards discussed herein are common with other nuclear reactors, but specifics resulting from reactor design features such as molten fuel salt can change the relative importance of these concerns. Also, MSRs have distinctive attributes not found in other reactor types. This section provides a brief overview of an MSR's fuel hazards due to the liquid nature of its fuel. Fuel salt hazards are not limited to the core. They exist in all phases of operation, from initial fueling to waste storage and handling.

General reactor hazards such as change in reactivity margin due to mobile delayed neutron precursors are outside the scope of this report. In addition, categories of hazards such as exposure to radiation, the possibility of contamination, handling actinides in the form of oxides, and exposure to lead and graphite, are not explicitly listed in the hazard tables, as these are well known to nuclear regulators and reactor operators.

Table 3 presents a compilation of identified MSR fuel salt processing hazards. Table 3 is divided into a series of sub-tables, each presenting fuel salt processing hazards of a different phase of MSR operation.

- Table 3a describes off-site nuclear fuel preparation and handling.
- Table 3b describes onsite activities prior to criticality.
- Table 3c presents onsite hazards when the reactor is operating.
- Table 3d describes activities during maintenance outages.
- Table 3e presents fuel salt processing and conditioning during operation.
- Table 3f presents hazards of activities after shutdown.
- Table 3g presents hazards of waste form generation.

The hazard tables are all formatted the same: Each row refers to an activity such as a chemical process or monitoring activity. The activity is briefly described in the first column. The second column describes the salt or component being processed and the goals of the process. A reference to location in this report that provides additional details and context about the process is given in the third column. The fourth column lists important hazards associated with the activity. The state of knowledge about each activity is given in the fifth column in terms of its technical readiness level (TRL),⁹⁴ and the 6th column gives a qualitative assessment of the potential severity of the hazard to operations staff. In cases where multiple hazards are identified, the ranking is based on the most severe hazard. The final column lists ways that the hazards can be mitigated.

Many of the activities and hazards listed in Tables 3a–g are repeated several times, i.e., monitoring of the off-gas system. This redundancy is deliberate, allowing each set of operations or each row within a set of operations to be considered individually.

Table 3a. Off-site nuclear fuel preparation and handling

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Salt synthesis ▪ Colex	⁷ Li production	3.1.1	▪ Mercury: ▪ caustic (LiOH)	6: downgraded due to lack of practice for 50+ years	5	▪ Alternatives to using mercury are being assessed
▪ Salt synthesis ▪ Electromigration	⁷ Li production	3.1.1	▪ Heat	3	2	
▪ Salt synthesis ▪ Crown ether	⁷ Li production	3.1.1	▪ Organic chemicals: ▪ caustic (LiOH _{aq})	3	2	
▪ Salt synthesis ▪ Liquid diffusion	³⁷ Cl production	3.1.1	▪ CCl ₄ , chloroform ▪ Pressure: 5 bar	3	4	
▪ Salt synthesis ▪ Anion exchange chromatography	³⁷ Cl production	3.1.1	▪ HNO ₃ ▪ AgNO ₃	3	2	
▪ Salt synthesis ▪ NaCl crystallization	³⁷ Cl production	3.1.1	▪ 20–80 mT magnetic field	3	2	
▪ Salt synthesis ▪ Reduction with CCl ₄	Conversion: UF ₆ to UF ₄	3.1.2	▪ Uranium contamination ▪ CCl ₄ , Cl ₂ , COCl ₂	5	3	▪ Standard contamination control for unirradiated materials ▪ Neutralize acidic and toxic gases
▪ Salt synthesis ▪ Reduction with NO _x	Conversion: UF ₆ to UF ₄	3.1.2	▪ Uranium contamination ▪ NO _x , NOF, HF, H ₂	3	5	▪ Standard contamination control for unirradiated materials ▪ Neutralize acidic and toxic gases
▪ Salt synthesis ▪ Fluorination	Conversion: oxides to fluorides	3.1.2	▪ HF, H ₂ ▪ UO _{2+x} , ThO ₂ contamination	9	4	▪ Standard contamination control for unirradiated materials
▪ Salt synthesis ▪ Reaction with NH ₄ HF ₂	Conversion: oxides to fluorides	3.1.2	▪ ThO ₂ contamination ▪ 400°C ▪ NH ₄ F, NH ₄ HF ₂	3	2	▪ Standard contamination control for unirradiated materials

Table 3a. Off-site nuclear fuel preparation and handling (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Salt purification Hydrofluorination	Removal of oxides/hydroxides from fluoride salts	3.1.1	<ul style="list-style-type: none"> ▪ H₂/HF ▪ Be if present as the BeF₂ salt component ▪ Heat (650°C) Contamination if actinides present 	7	4	Standard contamination control for unirradiated materials
▪ Salt purification ▪ Chlorination	Removal of oxides/hydroxides from chloride salts	3.1.1	<ul style="list-style-type: none"> ▪ CCl₄, Cl₂, COCl₂, HCl ▪ Heat ▪ Contamination if actinides present 	7	5	▪ Standard contamination control for unirradiated materials
▪ Packaging and transportation	Actinides and nonfissile components	3.3	<ul style="list-style-type: none"> ▪ Contamination if actinides present ▪ Air-sensitive ▪ Be (if present as BeF₂) 	9	3	▪ Double barrier container

Table 3b. Operations conducted on site prior to reactor operation (initial criticality)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Receipt of materials at reactor site	Actinides and nonfissile components	3.3	<ul style="list-style-type: none"> ▪ Contamination ▪ Air sensitive ▪ Be (if present as BeF₂) 	9	2	<ul style="list-style-type: none"> ▪ Double barrier container
▪ Onsite storage prior to loading	Actinides and nonfissile components	3.3	<ul style="list-style-type: none"> ▪ Contamination ▪ Air sensitive ▪ Be (if present as BeF₂) 	9	1	<ul style="list-style-type: none"> ▪ Double barrier container
▪ Preparation for use ▪ Making aliquots for loading	Actinide fluoride and chloride salts	2.2.1, 2.2.2, 3.2	<ul style="list-style-type: none"> ▪ Contamination ▪ Air sensitive ▪ Criticality 	5	3	<ul style="list-style-type: none"> ▪ Inert gas flush when transferring salts ▪ Double barrier
▪ Core load prior to criticality	Nonfissile fluoride and chloride salts	2.2	<ul style="list-style-type: none"> ▪ Air sensitive ▪ Be (if present as BeF₂) 	7	2	<ul style="list-style-type: none"> ▪ Inert gas flush when transferring salts ▪ Double barrier
▪ Initial core load	Fissile components of fluoride and chloride salts	2.2.1	<ul style="list-style-type: none"> ▪ Contamination ▪ Air sensitive ▪ Criticality 	5	4	<ul style="list-style-type: none"> ▪ Inert gas flush ▪ Double barrier
▪ Online sampling of salt during loading	Fluorides, chlorides, fuel salt, coolant salt, flush salt composition, and mixing by density measurement	4.2, 4.3	<ul style="list-style-type: none"> ▪ Contamination ▪ Air sensitive ▪ Criticality ▪ Be (if present as BeF₂) 	4	5	<ul style="list-style-type: none"> ▪ Gamma, densitometer, control rod measurements ▪ Inert gas flush ▪ Double barrier containment

Table 3c. Onsite fuel processing hazards during power operations

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Online sampling of fuel salt during operation	Fluorides, chlorides to give salt composition	2.2.3, 4.3	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt & entrained aerosols) ▪ Heat ▪ Air sensitive ▪ Be (if present as BeF₂) 	4	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Inert gas flush ▪ Double barrier containment
▪ Online sampling of fuel salt when loading salt during operation	Fluorides, chlorides to give salt composition	2.2.3, 4.3	<ul style="list-style-type: none"> ▪ Flow restrictions/pressure due to plate-out/freezing ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt & entrained aerosols) ▪ Criticality ▪ Heat ▪ Air sensitive ▪ Be (if present as BeF₂) 	2	2	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid measurements (pressure, temperature, salt density) ▪ Purge gas pressure relief ▪ Secondary containment

Table 3c. Onsite fuel processing hazards during power operations (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
<ul style="list-style-type: none"> ▪ Off-gas with helium sparge of reactor headspace ▪ Possible scrubbers: NaF-MgF₂, KOH-NaOH, zeolite, silver-functionalized packed beds, cryogenic capture, activated carbon, metal-organic framework 	Fluoride, chlorides to reduce fission gas build-up in the headspace and to reduce emissions	4.4	<ul style="list-style-type: none"> ▪ Flow restrictions/pressure ▪ Very high radiation ▪ Heat 	2	4	<ul style="list-style-type: none"> ▪ Remote and rapid measurements for rad and process variables (temperature, pressure, flow etc.) ▪ Purge gas pressure relief ▪ Secondary containment
<ul style="list-style-type: none"> ▪ Online sampling of off-gas 	Fluorides, chlorides	4.4	<ul style="list-style-type: none"> ▪ Flow restrictions/pressure ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in entrained salt aerosols) ▪ Heat ▪ Halogens ▪ Be (if present as BeF₂) 	2	2	<ul style="list-style-type: none"> ▪ Remote handling and rapid measurements for rad and process variables (temperature pressure, flow, etc.) ▪ Purge gas pressure relief ▪ Secondary containment
<ul style="list-style-type: none"> ▪ Salt filtering ▪ Online removal of precipitates 	Fluoride (FP + graphite), chloride salts (FP)	4.5	<ul style="list-style-type: none"> ▪ Flow restrictions/pressure ▪ Very high radiation 	2	3	<ul style="list-style-type: none"> ▪ Rapid online measurements for process variables (temperature, pressure, salt flow, etc.)

Table 3c. Onsite fuel processing hazards during power operations (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies	
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)		
▪ Refueling ▪ Reductant addition	Chlorides: Mg, redox compensation	2.2.2	<ul style="list-style-type: none"> ▪ Mg pyrophoricity ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Flow restrictions in sparge 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, pressure flow, etc.) ▪ Pressure relief ▪ Secondary containment 	
38	▪ Refueling ▪ Reductant addition	Fluorides: Be, redox compensation	2.2.2	<ul style="list-style-type: none"> ▪ Be as Be, BeF₂ ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Flow restrictions in helium sparge 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, pressure, flow, etc.) ▪ Pressure relief ▪ Secondary containment

Table 3c. Onsite fuel processing hazards during power operations (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Refueling ▪ Fissile material addition	Chlorides, e.g., UCl ₃	2.2.2	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Flow restrictions in sparge ▪ Accountability 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, pressure, flow, etc.) ▪ Pressure relief ▪ Secondary containment
▪ Refueling ▪ Fissile material addition	Fluorides, e.g., UF ₄	2.2.2, 2.2.3	<ul style="list-style-type: none"> ▪ Be as BeF₂ ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Flow restrictions in helium sparge ▪ Accountability 	5	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, pressure, flow, etc.) ▪ Pressure relief ▪ Secondary containment

Table 3c. Onsite fuel processing hazards during power operations (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
<ul style="list-style-type: none"> ▪ Defueling ▪ Spent fuel removal (small amounts) 	Chlorides and fluorides	2.2.2	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Flow restrictions in sparge ▪ Accountability ▪ Be (if present as BeF₂) 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, pressure, flow, etc.) ▪ Pressure relief ▪ Secondary containment ▪ Recycle/waste stream established prior to operation

Table 3d. Activities during maintenance outages

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
<ul style="list-style-type: none"> ▪ Off-gas with helium sparge of process head space ▪ Possible scrubbers: NaF-MgF₂, KOH-NaOH, zeolite, silver-functionalized packed beds, cryogenic capture, activated carbon, metal-organic framework 	Fluorides, chlorides to reduce fission gas build-up in headspace and reduce emissions	4.4	<ul style="list-style-type: none"> ▪ Flow restrictions/pressure ▪ Very high radiation ▪ Heat 	2	5	<ul style="list-style-type: none"> ▪ Remote, rapid analysis of process variables, scrubbers, hold-up beds ▪ Purge gas pressure relief ▪ Secondary containment
<p>►</p> <ul style="list-style-type: none"> ▪ Online sampling of off-gas 	Fluorides, chlorides	4.4	<ul style="list-style-type: none"> ▪ Flow restrictions/pressure ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in entrained salt aerosols) ▪ Heat ▪ Halogens ▪ Be (if present as BeF₂) 	2	4	<ul style="list-style-type: none"> ▪ Remote handling and rapid online measurements for process variables (temperature, pressure, flow, etc.) ▪ Pressure relief ▪ Secondary containment

Table 3d. Activities during maintenance outages (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment		Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)		
<ul style="list-style-type: none"> ▪ Salt filtering ▪ Maintenance/replacement of filters 	Fluoride, chloride salts	4.5	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in entrained salt) ▪ Heat ▪ Halogens ▪ Be (if present as BeF₂) 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurement of process variables (temperature, pressure, etc.) ▪ Secondary containment 	

Table 3e. Fuel salt processing and conditioning during operations

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment		Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)		
<ul style="list-style-type: none"> ▪ Salt processing online ▪ Actinide recovery, protactinium and FP separation. ▪ Control of redox chemistry if required. ▪ Processing options given in sections below <p>Salt returned to reactor</p>	Fluorides	2.2.3, 4.6.2	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling ▪ Be as BeF₂ ▪ Rad waste generation 	2	5		<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, etc.) ▪ Secondary containment ▪ Shielded waste storage
<ul style="list-style-type: none"> ▪ Salt processing online ▪ Actinide recovery and FP separation ▪ Adding UCl₃ to solubilize metallic FPs ▪ Processing options given in sections below ▪ Salt returned to reactor 	Chlorides	4.6.1	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling ▪ UCl₃, precipitation U metal ▪ Rad waste generation 	2	5		<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, etc.) ▪ Secondary containment ▪ Shielded waste storage

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Table 3e. Fuel salt processing and conditioning during operations (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Salt processing ▪ Electrochemical	Chlorides	4.6.1, 4.7.1	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling ▪ Electrical 	5	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, etc.) ▪ Secondary containment ▪ Shielded waste storage
▪ Salt processing ▪ Electrochemical	Fluorides	4.6.2, 4.7.1	<ul style="list-style-type: none"> ▪ Be as BeF₂ ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides in salt) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling ▪ Electrical 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, etc.) ▪ Secondary containment ▪ Shielded waste storage
▪ Salt processing ▪ Fluorination	Fluorides	2.2.3	<ul style="list-style-type: none"> ▪ F₂, Be as BeF₂ ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP, actinides) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, etc.) ▪ Secondary containment ▪ Shielded waste storage

Table 3e. Fuel salt processing and conditioning during operations (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Salt processing ▪ Reductive extraction	Chlorides	4.6.1	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP) ▪ Precipitation of U metal ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling ▪ Electrical 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, etc.) ▪ Secondary containment ▪ Shielded waste storage
▪ Salt processing ▪ Reductive extraction	Fluorides	4.6.2	<ul style="list-style-type: none"> ▪ BeF₂ ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP) ▪ Heat ▪ Halogens, HF ▪ Corrosive ▪ Off-gas handling ▪ Electrical ▪ Molten metals 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, etc.) ▪ Secondary containment ▪ Shielded waste storage

Table 3e. Fuel salt processing and conditioning during operations (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Salt processing ▪ Vacuum distillation	Chlorides	4.6.3	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (volatile FP, actinides) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling 	4	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, pressure, vacuum, flow ...) ▪ Secondary containment ▪ Shielded waste storage
▪ Salt processing ▪ Vacuum distillation	Fluorides	4.6.3	<ul style="list-style-type: none"> ▪ Be as BeF₂ ▪ Very high radiation ▪ Very high contamination (volatile FP, actinides) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling 	6	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Rapid online measurements for process variables (temperature, pressure, vacuum, flow...) ▪ Secondary containment ▪ Shielded waste storage
▪ Salt processing ▪ Oxidative precipitation	Chlorides	4.6.4	<ul style="list-style-type: none"> ▪ O₂ (combustion/explosion) ▪ 750°C ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP) ▪ Heat ▪ Halogens ▪ Corrosive 	2	5	<ul style="list-style-type: none"> ▪ Pressure relief ▪ Flow monitoring ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation

Table 3e. Fuel salt processing and conditioning during operations (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
<ul style="list-style-type: none"> ▪ Salt processing ▪ Melt crystallization 	Chlorides	4.6.5	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination (leakage of volatile FP) ▪ Heat ▪ Halogens ▪ Corrosive ▪ Salt transfer and handling 	5	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Accountability for solid isotopes

Table 3f. Activities after shutdown

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment		Qualitative severity judgment Rank: 1 (low) to 5 (high)	Mitigation strategies
				TRL: 1 (low) to 9 (high)			
▪ Online sampling of off-gas	Fluorides, chlorides	4.4	<ul style="list-style-type: none"> ▪ Flow restrictions/pressure ▪ Very high radiation ▪ Heat 	2	3	<ul style="list-style-type: none"> ▪ Remote and rapid measurements for rad and process variables (temperature, pressure, flow, etc.) ▪ Purge gas pressure relief ▪ Secondary containment 	
<ul style="list-style-type: none"> ▪ Core unloading ▪ Spent fuel removal by pressurization 	Chlorides and fluorides	Shutdown	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive ▪ Pressure ▪ Be (as BeF₂ if present) 	2	5	<ul style="list-style-type: none"> ▪ Pressure relief ▪ Flow monitoring ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation 	
▪ Removal from containment/drain tanks	Spent salt, fluorides and chlorides	Shutdown	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive ▪ Be (as BeF₂ if present) 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation 	

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Table 3f. Activities after shutdown (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment		Qualitative severity judgment Rank: 1 (low) to 5 (high)	Mitigation strategies
				TRL: 1 (low) to 9 (high)			
▪ Onsite storage	Spent salt, fluorides and chlorides	Shutdown	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive ▪ Be (as BeF₂ if present) ▪ F₂ and other fluorine-bearing species from radiolysis ▪ U metal precipitation upon remelting 	2	3		<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation
▪ Packaging and transportation to off-site facility	Spent salt, fluorides and chlorides	Shutdown	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive ▪ Be (if present as BeF₂) 	2	4		<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation

Table 3g. Waste form preparation

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Waste form preparation and processing ▪ Actinide recovery by pyroprocessing (volatile FP removed in front-end process)	Chloride salt	4.6.1	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive 	5	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation and processing ▪ Actinide recovery by pyroprocessing (volatile FP removed in front-end process)	Fluoride salt	4.6.2	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive ▪ Be 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation and processing ▪ Actinide recovery by hydrofluorination (volatile FP removed in front-end process)	Fluoride salt	3.1.2	<ul style="list-style-type: none"> ▪ H₂/HF, Be ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling 	5	4	<ul style="list-style-type: none"> ▪ Pressure relief ▪ Flow monitoring ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation and processing ▪ Actinide recovery by electrochemical deposition (volatile FP removed in front-end process)	Fluoride salt	4.6.2, 4.7.1	<ul style="list-style-type: none"> ▪ Be ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation

Table 3g. Waste form preparation (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Waste form preparation and processing ▪ Actinide recovery by dissolution in acid (volatile FP removed in front-end process)	Fluoride salt	4.7.1	<ul style="list-style-type: none"> ▪ Be ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive ▪ Off-gas handling 	8	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation and processing ▪ Actinide recovery by roasting with Ca(OH) ₂ (volatile FP removed in front-end process)	Fluoride salt	4.7.1	<ul style="list-style-type: none"> ▪ Be ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation and processing ▪ Actinide recovery by heating with NaOH (volatile FP removed in front-end process)	Fluoride salt	4.7.1	<ul style="list-style-type: none"> ▪ Be ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation and processing ▪ Actinide recovery by silicate roasting (volatile FP removed in front-end process)	Fluoride salt	4.7.1	<ul style="list-style-type: none"> ▪ Be, SiO₂ ▪ Very high radiation ▪ Very high contamination (volatile FP) ▪ Heat ▪ Halogens ▪ Corrosive 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation

Table 3g. Waste form preparation (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Waste form preparation, ${}^7\text{Li}$ recovery (volatile FP removed in front-end process)	Fluoride salt	3.1.1	<ul style="list-style-type: none"> ▪ Be ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation ▪ ${}^{37}\text{Cl}$ recovery (volatile FP removed in front-end process)	Chloride salt	3.1.1	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Halogens ▪ Corrosive 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation ▪ Dehalogenation	Chloride salt	4.7.2	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Volatile chlorides ▪ Corrosive 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation ▪ Dehalogenation	Fluoride salt	4.7.2	<ul style="list-style-type: none"> ▪ Be ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Volatile fluorides ▪ Corrosive 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation ▪ Recycle/waste stream established prior to operation
▪ Waste form preparation ▪ Glass ceramic	Pyroprocessed dehalogenated salt residue	4.7.3	<ul style="list-style-type: none"> ▪ Be (if relevant) ▪ Very high radiation ▪ Very high contamination ▪ Heat 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation

Table 3g. Waste form preparation (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
▪ Waste form preparation ▪ Oxide	Pyroprocessed dehalogenated salt residue	4.7.3	<ul style="list-style-type: none"> ▪ Be (if relevant) ▪ Very high radiation ▪ Very high contamination ▪ Heat 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation
▪ Waste form preparation ▪ Phosphate glass	Salt residue	4.7.2	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat ▪ Corrosive ▪ Be, NH₄Cl (g) (if relevant) ▪ Phosphoric acid, etc. 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation
▪ Waste form preparation ▪ Borosilicate glass	Dehalogenated salt residue	4.7.3	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation
▪ Waste form preparation ▪ zeolites	Dehalogenated salt residue	4.7.2	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation
▪ Waste form preparation ▪ Glass composite	Salt glass	4.7.3	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Heat 	2	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation
▪ Waste form preparation ▪ Glass material oxidation and dissolution system (GMODS)	Metals and ceramic waste	4.7.3	<ul style="list-style-type: none"> ▪ Pb ▪ Heat ▪ Very high radiation ▪ Very high contamination 	2	5	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation

Table 3g. Waste form preparation (continued)

Physical or chemical process	Salt type and process objective	Relevant report sections	Key hazards	Qualitative assessment	Qualitative severity judgment	Mitigation strategies
				TRL: 1 (low) to 9 (high)	Rank: 1 (low) to 5 (high)	
<ul style="list-style-type: none"> ▪ Waste form preparation ▪ Tritium removal 	Graphite (fluoride salts)	4.7.3	<ul style="list-style-type: none"> ▪ Very high radiation ▪ Very high contamination ▪ Be ▪ Graphite fines 	5	3	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation
<ul style="list-style-type: none"> ▪ Waste form preparation ▪ Washing to remove FPs 	Structural metals	4.7.3	<ul style="list-style-type: none"> ▪ Very high contamination ▪ Very high radiation 	7	4	<ul style="list-style-type: none"> ▪ Remote handling ▪ Secondary containment ▪ Online instrumentation

6. SUMMARY

This report provides a review of the hazards associated with liquid-fueled MSR fuel-processing operations. Fuel salt processing involves a wide range of hazards depending on the fuel salt, processing operation, fissile material concentration, radiation level, and presence of other toxic or hazardous materials. The hazards are summarized in a set of tables that include a relative ranking of the hazards and references to sections of the report which provide additional information and context. The steps in MSR fuel processing operations are substantially different from those for solid uranium oxide fuel fabrication and handling. A distinctive feature of MSRs is their ability to quasi-continuously refuel and adjust the fuel salt chemistry. Hence, fuel processing for liquid-fueled MSRs is more closely connected to reactor operations than would be the case for solid fueled systems.

MSR designs are not yet fully mature; nor are the designs for the primary and ancillary support systems for the synthesis and treatment of molten salt fuel. An estimate of the relative maturity (TRL score) of the processes is also included in this report's hazard table. The overall requirements for fuel processing operations, however, are reasonably well known, and the report provides overviews of likely fuel salt processing steps.

An important limitation of this report derives from the fact that only two relatively small MSR test reactors have ever been operated. Some systems and activities can be extrapolated from prior small-scale MSRs, and some can be extrapolated from non-nuclear, larger scale halide salt use. Large-scale fuel-salt facilities, however, may involve equipment and hazards not seen at smaller scales. Also, key reactor-specific hazards such as inadvertent criticality while performing initial fuel transfer into the reactor vessel have no direct antecedents in solid fueled reactors.

Liquid MSR fuel processing includes steps that are more closely coupled with reactor operations than steps used for fuel processing in solid fuel reactors. Consequently, fuel processing hazards are not as distinct from reactor safety as they are in solid fuel reactors, and this report includes some overlap with reactor accidents.

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