# Status of Fast Spectrum Molten Salt Reactor Waste Management Practice

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# Abstract

The study described in this report was initiated to evaluate the status of waste management practices associated with fast spectrum molten salt reactors (FS-MSRs). Waste streams specific to variable spectrum MSRs are also considered. Waste management practices for MSRs are fundamentally different from those of their solid-fueled counterparts. To best advance MSR concepts to implementation, these differences warrant fresh thinking on a variety of subject areas, rather than adapting techniques established for solid-fueled reactors. A number of areas are recommended for focused technological research and development. While not exclusive, these target areas are considered to provide the most impact to advancing FS-MSR waste management practice:

- Specific to variable spectrum MSRs, neutron moderator(s) that are tolerant to radiation and high temperatures (alternative to graphite)

- New concepts for remote, long-handled tooling and radiation-resistant electronics

- Salt dehalogenation processes (primarily for fluorides as chlorides have demonstrated options)

- Phosphate and silicate waste form evaluations for dehalogenated salt streams

- Integration of lithium-7 and chlorine-37 recovery and recycle into waste treatment approaches

- Strategies for chlorine-37 isotopic enrichment

- Integrated capture and storage of fission product noble gases (e.g., radiation-tolerant sorbents)

# Summary

The study described in this report was initiated to evaluate the status of waste management practices associated with fast spectrum molten salt reactors (FS-MSRs). Two dimensions of MSR waste management were evaluated:

- Since MSRs represent a significantly different paradigm in their design compared with solid-fueled reactors, there is a concomitant fundamental difference in their operation and waste management approach in the following areas:

  – Fuel management. Used MSR fuel salt will contain actinides, fission products, and activated corrosion products. Molten fuel salt does not experience mechanical radiation damage, so it does not have a mechanically derived lifetime. The reasons to discard fuel salt are degradation in the neutronic efficiency, fuel salt thermophysical properties or solubility of fissile material. Depending on the specific use case for the fuel salt, the degradation may take several decades.

  – Reactor components. The fuel salt is anticipated to have a longer useful lifetime than the salt-wetted components. All of the salt-contacting structures and components will likely be replaced several times over the course of an MSR plant lifetime. As initially considered, radiation damage to the structural alloy while in contact with corrosive salt mixtures appears likely to be the life-limiting phenomenon for most MSR vessels. Other stressors will be important for thin-walled heat exchangers. Graphite has a limited lifetime under fast neutron irradiation in a variable spectrum MSR. Consequently, in-core graphite may be the first material needing replacement in thermal and spatially variant spectrum MSRs and represents a significant volume.

  – Components and concept of operations lessons learned for waste management practice. The containment area around an MSR will have an extremely high radiation environment. Unlike solid-fueled reactors, MSRs lack an unfueled downcomer region and have thin-walled reactor vessels that provide limited shielding. MSRs will require substantial shielding between the fuel salt and the biosphere. Consequently, all components and maintenance activities need to be designed to be performed remotely using long-handled tooling.

  – Operational impacts of off-gas treatment systems on waste management. The off-gas waste products and the separated solids waste products will both represent nontraditional waste forms. The short-lived fission gases will need to be held (weeks to months) for decay while longer-lived fission gases (especially krypton-85) will need to be stored longer-term (decades).

- The options available for stabilizing process waste give rise to considerable ambiguity in how an FS-MSR fuel cycle could be implemented.

  – There is no state-of-the-art approach to treatment and stabilization of used fuel salt, although several options exist at the concept stage. In general, specialty phosphate glass and glass-bonded mineral or ceramic waste forms are common across all MSR fuel cycles and salt types being investigated, and in some cases, demonstrated, especially for chloride salt. Other waste forms such as salt-metal composites have been postulated and have broad applicability but need practical demonstration. Experience with treating waste streams arising from the molten chloride salt in electrorefiners used in pyroprocessing used metal nuclear fuel can be leveraged.

  – Criteria originally used to select the preferred waste form for defense high-level waste are also appropriate for contrasting the options with a view to selecting a consensus preference. However, the criteria should be augmented with the experience gained over several decades and must also consider interim storage and transportation as well as final disposal.

A number of areas are recommended for focused technological research and development. While not exclusive, these target areas are considered to provide the most impact to advancing FS-MSR waste management practice:

- For variable spectrum MSRs, neutron moderator(s) that are tolerant to radiation and high temperatures (alternative to graphite)

- New concepts for remote, long-handled tooling and radiation-resistant electronics

- Salt dehalogenation processes (primarily for fluorides as chlorides have demonstrated options)

- Phosphate and silicate waste form evaluations for dehalogenated salt streams

- Integration of lithium-7 and chlorine-37 recovery and recycle into waste treatment approaches

- Strategies for chlorine-37 isotopic enrichment

- Integrated capture and storage of fission product noble gases (e.g., radiation-tolerant sorbents)

Overall, waste management practices for MSRs are fundamentally very different from those of their solid-fueled counterparts. To best advance MSR concepts to implementation, these differences warrant fresh thinking on a variety of subject areas, rather than adapting techniques established for solid-fueled reactors.

# Acknowledgments

# Acronyms and Abbreviations

| | |
|---|---|
| A | alkali |
| AE | alkali earth |
| Cermet | ceramic-metal composite |
| DOE | U.S. Department of Energy |
| FS-MSR | fast spectrum molten salt reactor |
| Halmet | halide-metal composite |
| MSR | molten salt reactor |
| MSRE | Molten Salt Reactor Experiment |
| RE | rare earth |

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# 1.0  Introduction

The study described in this report was initiated to evaluate the status of waste management practices associated with fast spectrum molten salt reactors (FS-MSRs) and some specific characteristics of variable-spectrum MSRs. Two dimensions of MSR waste management were evaluated:

- The options available for stabilizing process waste give rise to considerable ambiguity in how an FS-MSR fuel cycle could be implemented. This ambiguity is compounded by the potential roles FS-MSRs could play in an advanced fuel cycle and particularly one design option associated with the reactor: that of the choice in halide.

- Since MSRs represent a significantly different paradigm in their design to solid-fueled reactors, there is a concomitant difference in their operation and waste management approach. Today's nuclear waste management infrastructure has been wholly tailored to supporting the operation of solid-fueled reactors. Therefore, MSR waste management potentially represents a fundamental challenge to the established infrastructure and was explored in this study.

This study focuses on the waste management practices and potential waste forms arising mainly from FS-MSR fuel cycles but also from variable spectrum MSRs where specific waste streams are generated. However, thermal spectrum MSR fuel cycles were considered where prior work provides insight to the FS-MSR discussion.  Some potential roles of FS-MSRs necessarily involve processing solid nuclear fuel to separate actinides. The wastes arising from processing solid nuclear fuel are not considered in this report.

## 2.0 Potential Roles of FS-MSRs in Advanced Nuclear Fuel Cycles

Nuclear fuel cycles implemented using solid fuel are classically described as either *open* or *closed*. In the open cycle, solid fuel is removed from the reactor at the end of its life and dispositioned with no further processing. All fuel constituents are deliberately retained within the fuel. In the closed cycle, solid fuel is again removed from the reactor at the end of its life but is processed to recover fissile material for manufacture into fuel for recycle.

By their nature, FS-MSRs challenge the conventional definition of open and closed fuel cycles. Specifically, gaseous fission products (primarily noble gases) are not retained in the fuel and they are separated into an off-gas, which is processed to separate the fission products for disposal or decay storage. Additionally, some fission products, primarily noble metals but also others insoluble in the salt, can precipitate from the salt. Whether solids need to be continuously separated from the salt is open to debate in the technical community. There is an argument suggesting these fission products plate onto internal reactor surfaces and provide some protection against corrosion. Having a liquid fuel also allows for periodic or continuous addition of fissile material to MSRs or continuous processing to separate constituents deleterious to performance (e.g. neutron poisons). Taken together, these characteristics indicate conventional fuel cycle definitions are not wholly applicable to FS-MSRs. However, a focus on the fuel salt can provide a definition for an FS-MSR fuel cycle as implied by a previous study (Holcomb et al. 2011). An MSR fuel cycle is considered open for this study if (1) the fuel salt is not processed to remove fissile material (for recycle) or fission products, and/or (2) fissile material is not added to maintain reactor neutronics. Conversely, an MSR closed fuel cycle involves either recovery of dissolved fissile material or fission products from the fuel salt.

FS-MSRs can assume three roles in closed and open advanced fuel cycles (Holcomb et al. 2011):

- *As a breeder*. In this role, fertile material is converted into fissile material, which is recovered from the fuel salt for manufacture into new fuel for either solid-fueled reactors or FS-MSRs operating in an equilibrium mode. A breeder FS-MSR is part of a closed fuel cycle by definition.

- *As a burner*. In this role, actinides separated from solid-fueled reactor fuel are fed to the burner FS-MSR for them to be transmuted into short-lived fission products or actinides. In this role, the burner FS-MSR fulfills a high-level waste management function in reducing geologic repository demand from used solid fuel.

- *As a convertor*. In this role, the FS-MSR is maintained at equilibrium or at a slight positive breeding ratio to primarily produce power. Fissile material is added to the reactor as needed to replenish its fissile inventory.

Operating with a fast neutron spectrum means the FS-MSR can tolerate accumulation of rare earth (RE) fission products better than thermal reactors because the neutron cross-section of the RE fission products is smaller. However, RE fission products cannot be allowed to accumulate to concentrations that depress the solubility of actinides sufficiently that they cannot remain critical. Notwithstanding operational considerations, therefore, FS-MSRs could operate for very long durations, certainly longer than solid-fueled reactors, even in an open fuel cycle. However, it has yet to be determined just how long an FS-MSR could operate before the fuel salt must be replaced or processed to remove constituents deleterious to its operation. The precise identity of those constituents is also yet to be determined but could include RE fission products and noble metal (e.g. technetium, ruthenium, rhodium) solids as already mentioned.

MSRs have distinctive capabilities in their potential to consume actinide wastes. FS-MSRs, as with other fast reactors, can directly burn actinides. However, in an MSR, liquid fuel is not vulnerable to mechanical damage, and thus does not have a mechanically limited lifetime. Consequently, thermal spectrum reactors, which ordinarily would need to discharge damaged solid fuel containing significant amounts of long-lived actinide wastes, can keep the fuel salt in core for much longer periods, eventually consuming actinides that would otherwise have been waste. MSRs also have the potential to employ a spatially variant spectrum. Spatially variant spectrum MSRs use thermal regions to maintain criticality with lower quantities of fissile material while employing fast regions to more efficiently consume heavy actinides. A useful configuration for a spatially varying spectrum MSR is one that uses a thick graphite interior lining for the reactor vessel along with an unmoderated central core region. The graphite both shields the reactor vessel from radiation damage, substantially prolonging its life, and results in a thermal region at the periphery of the core without significantly changing the spectrum of the central region. Alternatively, an exterior moderator could be used at the cost of radiation damage to the reactor vessel.

As mentioned above, an important fundamental design variable for FS-MSRs is the halide of the salt, which is either chloride or fluoride. The criteria for choosing the halide has already been well summarized (e.g., Holcomb et al. 2011) and will not be repeated here. In summary, there is more operating experience with fluoride salt and it proffers a less harsh chemical environment for material of construction. However, chloride salt offers a significant advantage for reactor neutronics in hardening the neutron spectrum important for FS-MSRs. A mixed chloride-fluoride salt has been conceptually considered for FS-MSRs, but not sufficiently to warrant consideration in this report.

Isotopic management of the salt is an important consideration for FS-MSRs, and both chloride and fluoride systems present nuances:

- Chlorine has two stable isotopes, with chlorine-35 being about three times as abundant as chlorine-37 (Holcomb et al. 2011). However, chlorine-35 activates to chlorine-36 in the core. Chlorine-36 presents significant disposal challenges because it is long-lived, an energetic beta emitter, and highly water-soluble. Therefore, there is advantage for waste disposal by isotopically enriching the chloride salt in chlorine-37. One process, liquid-phase thermal diffusion, has been demonstrated to be feasible but insufficiently mature for full-scale implementation.

- One concern with fluoride salts is the use of lithium and the activation of lithium-6 to produce tritium; creating both a waste problem and also a neutronic toll. Tritium is a short-lived and energetically weak beta emitter, but it must be continuously separated in the off-gas system and dispositioned. Lithium-6 constitutes about 7% of natural lithium, and isotopically enriching it in lithium-7 is desirable for tritium management. Lithium isotopic separation has been extensively studied in the context of nuclear fusion.

The choice of halide and the role of the FS-MSR in the fuel cycle significantly influence the range of potential waste streams as well as available waste forms and their technical maturities. These aspects are explored later in this report. First, though, the waste management operations of MSRs are considered with emphasis on the paradigm differences with solid-fueled reactors.

## 3.0 Differences in Waste Management Practice from Solid Fueled Reactors

### 3.1 Fuel Management

Used MSR fuel salt will contain actinides, fission products, contaminants and activated corrosion products. Molten fuel salt does not experience mechanical radiation damage, so it does not have a mechanically derived lifetime. The reasons to discard fuel salt are the neutronic efficiency penalty, the decrease in fissile solubility, or adverse changes in the fuel salt thermophysical properties (e.g., excessive melting point rise or viscosity increase such that the salt can no longer perform its safety or operational functions) due to fission, corrosion, and contamination products accumulating in the salt. Depending on the specific use case for the fuel salt, the degradation may take multiple decades.

Many developers propose employing previously used fuel in MSRs. The fuel salt may simply be a batch of fuel previously used at the same MSR plant, or the fuel salt's fissile materials may have been extracted from previously used solid reactor fuel. Additionally, since fission products within the fuel salt can leave or decay, actinides will be added to the fuel salt to compensate for burnup (and neutron absorber accumulation), and additional materials will be added to fuel to adjust its chemistry during operation, both the composition and contents of the fuel salt within a particular MSR will continuously evolve. Consequently, the precise lifetime for fuel salt is indeterminate at the present time. To the extent possible, it is preferable to leave the fuel salt actinides within active fuel salt both to maximize resource utilization and to minimize the creation of long-lived, long-lived plutonium and minor actinides. It would be useful to develop the capability to predict when (or whether) fuel salt would eventually become unusable without more extensive, chemically based separations. Note that all of the fuel salt will become waste following the shutdown of all MSRs, at least the portion not recycled into other reactors.

Solid particles will develop in the fuel salt as a result of fission, corrosion, and contamination. The solids will partially separate from the liquid inherently but much will take the form of plating out onto the salt-wetted surfaces (Kedl 1972). At MSR operating temperatures, the plated-out solids are anticipated to slowly diffuse into and partially react with the structural alloys, forming inter-metallics. Diffusion and solid-state reaction rates with the structural alloy elements are temperature dependent. At less than 700 °C, the fission product bulk diffusion and interaction distance will be thin (of the order of microns) but may include a deeper grain boundary interaction zone. The insoluble surface deposits may reduce the surface corrosion (Robinson 1958). However, tellurium, which has a redox-dependent solubility in fluoride salts, is known to cause surface cracking of nickel-based structural alloys (Keiser 1977). Also, material solubilities are temperature dependent, so limited solubility materials will tend to accumulate at the lowest temperature portions of the fuel salt loops. Accumulating deposits [especially those shown to grow dendritically (Blankenship 1961)] can block flow passages and consequently represent a potentially life-limiting phenomenon for fuel salt loop components if not removed.

### 3.2 Reactor Component Management

The fuel salt is anticipated to have a longer useful lifetime than the salt-wetted components. All of the salt-contacting structures and components will likely be replaced several times over the course of an MSR plant lifetime. Removing the fuel salt and flushing the fuel salt loop is anticipated to be one of the first actions of any in-containment maintenance activity. As initially considered, radiation damage to the structural alloy [especially neutron embrittlement of nickel-based alloys (Martin and Weir 1967)] appears likely to be the life-limiting phenomenon for most MSR reactor vessels, while other stressors (creep fatigue, erosion, etc.) will be important for thin-walled heat exchangers (Briggs 1969). The salt-contacting components will be a nontraditional waste form with significant volume. For example, if the reactor

vessel has an average lifetime of 15 years and the plant has a 100-year lifetime, the plant's waste stream will include multiple highly radioactive (contaminated and activated) reactor vessels. The regulatory classification (whether Low or High Level Waste) of this waste stream is currently indeterminant given the contamination arises from spent fuel.

The contamination remaining on fuel salt components that have been in direct contact with the fuel salt following removal from use will include actinides. Consequently, the wastes will have material control and accountability requirements in addition to radiation safety derived requirements. Over time, however, the fissile actinides in fuel salt will burn out, leaving a very high-burnup fuel salt actinide distribution. Activation of metals (e.g., within pumps, piping, heat exchangers) will be significant due the neutron flux throughout the fuel salt loop potentially resulting in greater than Class C low-level waste or high-level waste, depending on regulatory interpretation. MSRs are expected to generate a larger contaminated/activated waste stream than solid fueled reactors due to the combination of the components comprising the fuel salt boundary, graphite, and the fuel salt and cover gas processing system wastes. As the majority of the fission product and activation wastes have half-lives less than the plant lifetime, the wastes could initially be stored locally for decay and eventually processed as part of decommissioning.

Graphite is the only moderator material that has been demonstrated to be chemically compatible with direct contact with fluoride fuel salts. Even graphite sets the lower redox limits for the fuel salt as uranium fluoride forms uranium carbide in highly reducing conditions. Metal clad moderators reduce the neutronic efficiency of the reactor, resulting in increased enrichment requirements and creating a highly activated cladding waste stream.

Graphite has a limited lifetime under fast neutron irradiation. Consequently, in-core graphite may be the first material that needs to be replaced in thermal and spatially variant spectrum MSRs. Activated, contaminated graphite represents a significant volume thermal spectrum MSR waste stream. Radiation damage to graphite was central to Oak Ridge National Laboratory's decision in 1967 to shift from a dual- to a single-fluid MSR (with its more complex chemical processing) and was a central rationale for halving the power density of the molten salt breeder reactor's conceptual design (Bettis 1967, 1968). A two-fluid MSR would have a much simpler fuel salt processing scheme to achieve net breeding with the Th/U fuel cycle. The waste streams, proliferation, and safeguards characteristics of two-fluid MSRs, however, have received less attention than single-fluid systems due to the implementation challenges arising from graphite's limited displacement damage tolerance.

Graphite that is in contact with fuel salt will become substantially contaminated due to fission gas penetration and subsequent decay in the pores of the graphite, and to a lesser extent direct fuel salt penetration (Compere et al. 1975). The amount and depth of fuel salt penetration into graphite depends on the radiation damage. Opening a reactor vessel to remove and replace contaminated graphite would likely be a complicated operation due to the high residual dose background and the potential for spreading contamination. For this reason, some reactor vendors have indicated that they intend to replace the reactor vessel at the same time as the graphite, so that the vessel can serve as the container for the irradiated graphite waste. Alternatively, exterior moderators have been considered, which makes replacing moderator much easier and allows non-salt compatible moderators at the expense of lower reactor vessel life from radiation damage.

## 3.3 Components and Concept of Operations Lessons Learned for Waste Management Practice

The containment area around an MSR will have an extremely high radiation environment. Unlike solid-fueled reactors, MSRs lack an unfueled downcomer region and have thin-walled reactor vessels that

provide limited shielding. MSRs will require substantial shielding between the fuel salt and the biosphere. The dose rates inside the shielding will be much too high for either personnel or solid-state electronics. Consequently, all components and maintenance activities need to be designed to be performed remotely using long-handled tooling (Holcomb et al. 2018). Developing a concept of operations for how to transfer and package waste will be key to creating realistic layouts for MSRs, much more so than at solid-fueled reactors due to the larger amount of component replacement, lack of personnel access, and the extended distribution of contamination and radiological dose.

Cooling water is a potentially significant operational hazard at MSRs, as maintaining low pressure within containment is a central MSR safety argument. Cooling water can flash to steam with a high volumetric change. Consequently, MSR coolants are much more likely to be single-phase materials (e.g., dry nitrogen or other molten salts) that do not change phase upon interacting with fuel salts. Alkali liquid metals can cause molten salts to become sufficiently reducing to plate out fissile materials, so they also may not be suitable for large-scale use near MSRs.

The technology for cleaning up fuel salt spills in containment has not been proven, but some variant of the technology employed to remove the sludge from the Hanford waste tanks has been considered (Robb and Holcomb 2020). One of the key issues with molten salts is their potential to leak from any breach in the fuel salt circuit. Any breach in the fuel salt circuit can result in nearly 100% loss of the contained radionuclides (liquid and gaseous). The containment environment at MSRs will be much too radioactive for personnel access, even without fuel salt spills. Semiconductor-based electronics will not survive long at likely dose rates near spilled used fuel salts. Technologies and concept of operations necessary to clean up and package spilled fuel salt would provide confidence that a breach in a salt line would not result in permanent plant shutdown. MSRs that include drain tanks will likely slope any catch pans to drain into the fuel salt drain tanks to minimize the containment cleanup required and simplify decay heat rejection.

## 3.4   Off-gas Treatment and Solids Separation Systems Operational Impacts on Waste Management

MSRs have two primary cover gas system design variants: (1) a combination of mechanical filters, a 2-hour delay tank, and a series of activated carbon beds or (2) a caustic scrubber followed by one or more activated carbon beds. Options for capturing off-gas products have been covered elsewhere (e.g., McFarlane et al. 2020). The cover gas waste products and the separated solids waste products will both represent nontraditional waste streams. The longer-lived fission gases (especially krypton-85) will need to be held for decay storage.

The off-gas treatment systems must have near 100% availability as they need to be in operation any time the plant is at power. As a result, some portions of the off-gas treatment system (such as filter banks) may be designed in parallel to enable maintenance and replacement activities while the plant remains on-line. For the first few hours, the fission gases provide a substantial amount of decay heat. The off-gas total decay heat production for the molten salt breeder reactor (2250 $MW_{th}$) was estimated to be 21.3 MW, with roughly 9% entrained as aerosols or mists, almost 80% of the gaseous heat load generated in the first hour following release, and much less than 1% of decay heat remaining in the gas stream after 2 days (Smith and Bell 1969). Consequently, an MSR's off-gas treatment system will require substantial passive decay heat removal capability for the first few hours. The need for reliable, safety-grade cooling can interfere with ease of access for maintenance. Also, off-gas treatment filters will become highly contaminated and will require both shielding and cooling following removal.

Suspended solids that do not plate out from the fuel salt will need to be purposely removed to minimize erosion. The most advantageous method to remove the solids has yet to be determined. However, many of

the separations will depend on the density difference between the solids and the fuel salt. Suspended materials that are less dense than the fuel salt can be removed through flotation-based methods. Similarly, more dense materials can be removed by settling or centrifugal methods. Particles with densities similar to the fuel salt can be removed by mechanical filtering; fiber metal filters have been recommended (Lindauer and McGlothlan 1969). Solid material separation can be performed on a side stream of the fuel salt during operation or periodically during shutdowns on the full volume of the salt. The selected equipment, methods, and procedures for separating solids from fuel salts have not been disclosed by developers to date. In general, the separation techniques are anticipated to be traditional, with reliable side stream pumping having the largest remaining technology development hurdles.

The complex, multicomponent solubilities of fission products in fuel salts are not well known, so the required frequency of processing and the lifetime of the salt cannot be confidently predicted at this time. At one extreme, the fuel salt on the Molten Salt Reactor Experiment (MSRE) was only filtered as part of the transition to the uranium-233 fuel cycle following fluorination to convert the uranium tetrafluoride to uranium hexafluoride when larger quantities of suspended corrosion products were generated (Lindauer 1969).

The filters arising from off-gas treatment and solids separation will likely be the most challenging waste streams from reactor operations. These filters can be processed by traditional means to size-reduce them by compaction rather than any form of chemical stabilization. However, the regulatory classification (whether Low or High Level Waste) of these waste streams is currently indeterminant given the contamination arises directly from fuel constituents.

# 4.0 Status of Waste Forms Available for FS-MSR Waste Management

This section describes the outcome of one of the primary purposes of the study to assess the status of the waste forms available for FS-MSR waste management. Information from two primary references (Riley et al. 2018, 2019, 2020) was distilled into flowcharts to provide the waste form options structure and consolidate in some cases highly technically detailed information for programmatic decision-making purposes. The flowcharts and discussion are not intended to be exhaustive for all potential waste treatment processes and forms. Instead, notable examples are provided to illustrate concepts and indicate options of potentially greatest technical value.

The open cycles, applicable to actinide burners and convertors, are considered first. Figure 4.1 depicts the waste form options applicable to permanent stabilization of actinide burner and convertor fuel salt with delineation between fluoride and chloride salts. There are no waste forms experimentally proven for MSR fluoride salt. For chloride salt, benefit is taken of the similarity with the treatment and stabilization of pyrochemical electrorefiner salt. For instance, defluorination has not yet been demonstrated with MSR-relevant fluoride salt mixtures using the ultrastable H-Y zeolite process for chloride salts (Wasnik et al. 2019). Notwithstanding differences in technical maturity, there are several commonalities between the salts, notably the glass-bonded sodalite ceramic waste form and the phosphate glass waste form following dehalogenation of the salt. The ceramic-metal composite (cermet)-style (halide-metal composites are specifically known as 'halmets') waste form (encapsulating salt or salt-loaded ceramics into a metal such as copper) is common on both sides but is not demonstrated for salt waste.
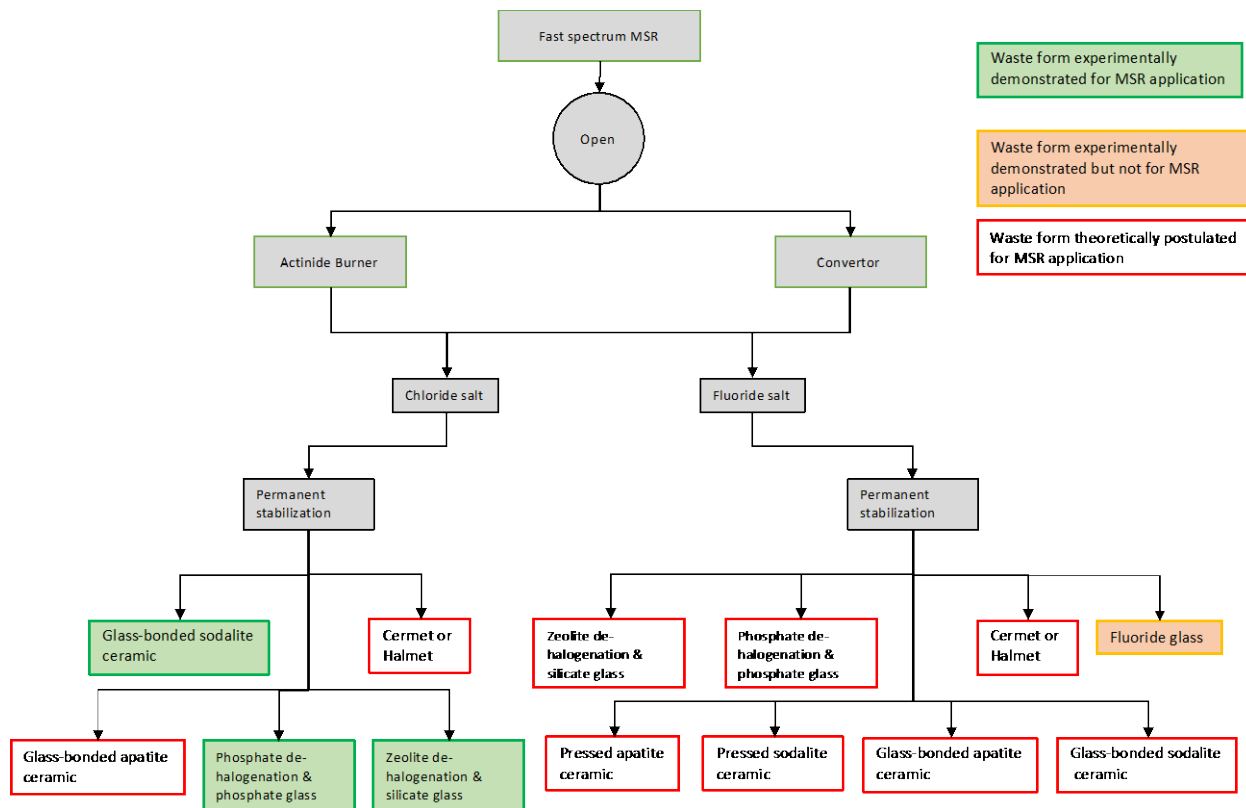


Figure 4.1. Waste Forms Applicable to Permanent Stabilization of Used Fuel Salt in an MSR Open Cycle

Interim stabilization of used fuel salt in an open cycle could be beneficial, similar to the approach for used light water reactor fuel. For this scenario, the options considered at Oak Ridge National Laboratory for managing de-fueled coolant fluoride salts from the Molten Salt Reactor Experiment (Bechtel Jacobs Company LLC 2010) are applicable. As shown in Figure 4.2, allowing the de-fueled fuel salt to freeze and continued monitoring is the only demonstrated approach, and then only for fluoride salt. With fluoride salt there is the concern of fluorine gas generation, and so re-melting the salt and adding a getter has been discussed. That option is translated generically as a "chemical" for chloride salt. Notably, reheating the fluoride salt is problematic. Reheating uranium tetrafluoride to 200 °C in the presence of fluorine generated uranium hexafluoride, which is highly mobile through the system. Reheating was a key step in the issue with the MSRE stored fuel salt.
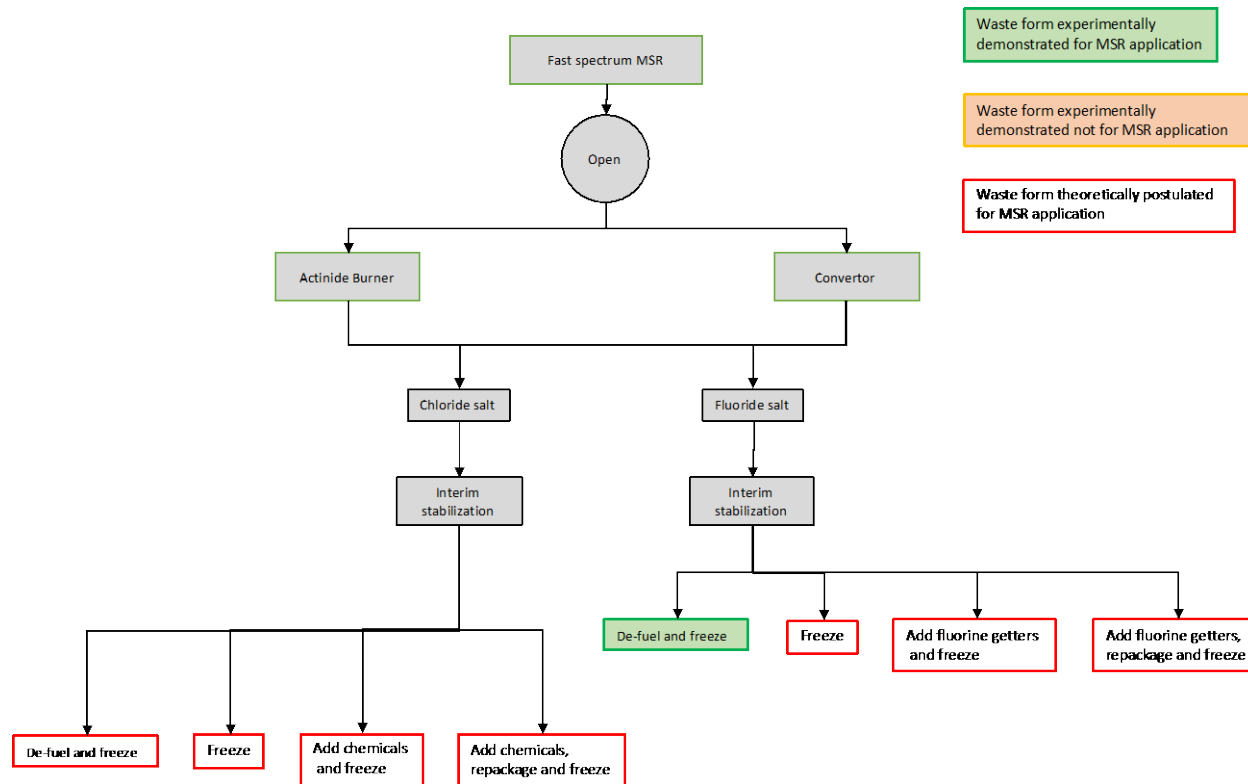


Figure 4.2. Waste Form Options Applicable to Interim Stabilization of Used Fuel Salt in an MSR Open Cycle

Salt treatment to remove fission products dissolved in the fuel salt that are deleterious to operation is introduced for the closed cycle. Presently it is unclear whether separation of RE, alkali (A), and/or alkali earth (AE) fission products would be an economical way to extend the longevity of the salt or whether simply implementing an open cycle would provide the greater benefit. Nonetheless, Figure 4.3 illustrates the waste treatment and waste form options for closed actinide and convertor fuel cycles. Notable here is the greater number of process options compared to waste forms, some of which have only been postulated. As before, similarities between the chloride salts used in MSRs and pyrochemical electrorefiners offer some commonality for waste treatment and waste forms. The pressed or glass-bonded monazite or xenotime minerals are the only common waste forms between chloride and fluoride salts, but there appears to be considerable opportunity to develop others for the treatment processes.
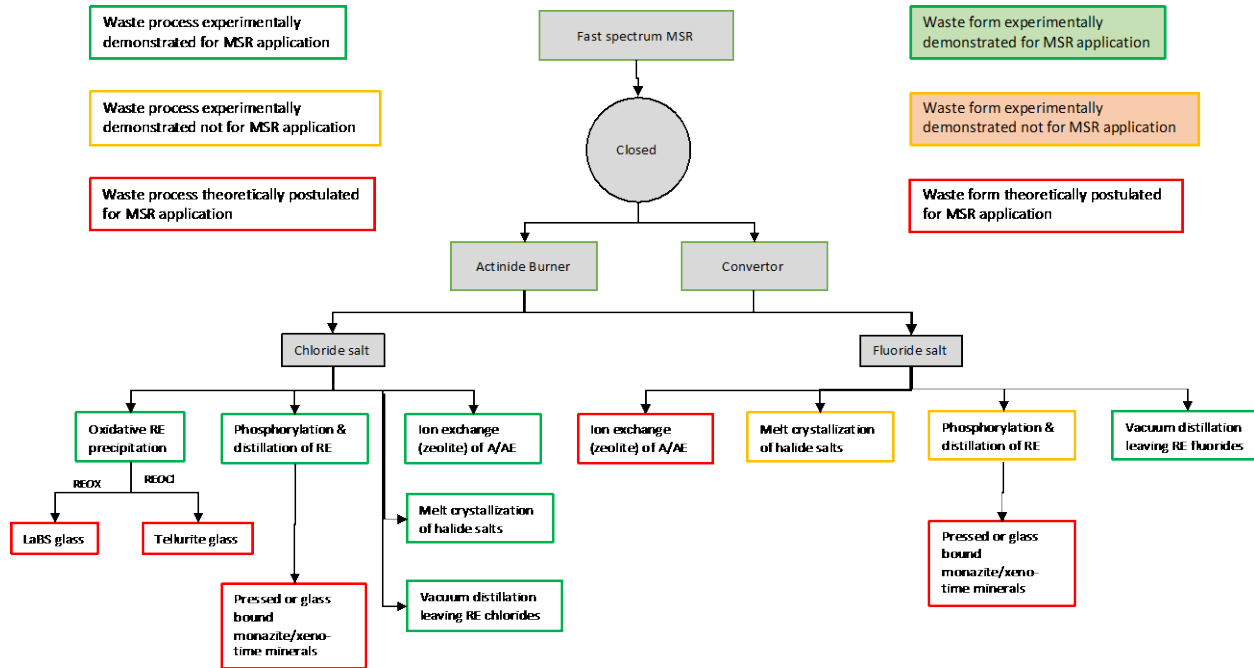
Figure 4.3. Waste Treatment and Waste Forms Applicable to Actinide and Convertor MSR Closed Cycles

Figure 4.4 identifies four processes applicable to separating actinides from fuel salt for the breeder MSR with reductive separation applicable to both salts. These processes enable separation of fission products from the fuel salt incidental to the actinides. The specific processes for fission product separation and stabilization shown in Figure 4.3 are also applicable for the breeder FS-MSR. The pyrochemical process has been amply demonstrated for chloride salt. Capture of fission products within zeolite ion exchange media has been demonstrated for the pyrochemical process, while they are separated as salts in the reductive separation process. In the latter case, a final waste form is likely available but needs to be explicitly identified. Fluoride distillation and oxide precipitation are applicable to the fluoride salt and have been demonstrated (McNeese et al. 1972) but not pursued beyond small laboratory studies.
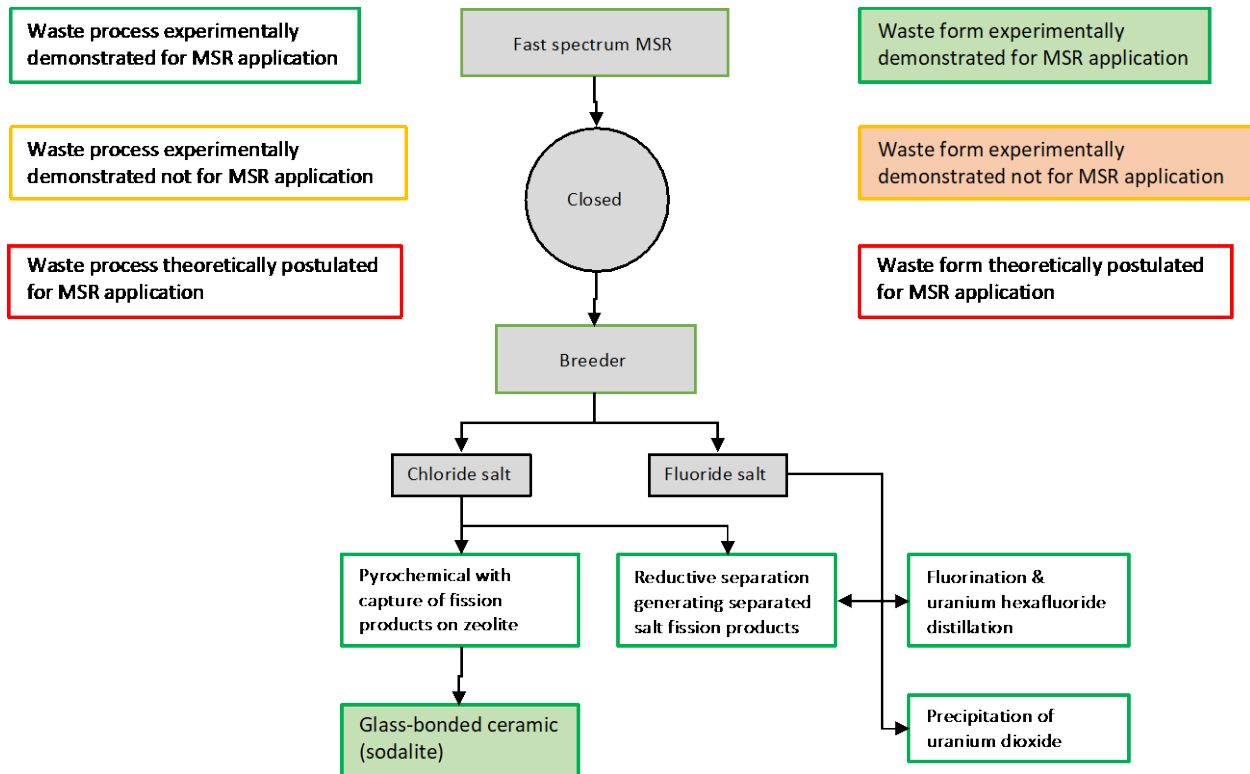
Figure 4.4. Salt Processing and Waste Forms Applicable to the Breeder MSR Fuel Cycle

In general, across all fuel cycles and salt types, specialty phosphate glass, or glass-bonded minerals or ceramic waste forms are common and, in some cases, demonstrated, especially for chloride salt. Other waste forms such as cermet have been postulated and have broad applicability but need practical demonstration. The variety of waste treatments and waste forms considered for MSR fuel cycles reflects, to an extent, the versatility and design variation of this type of reactor. Nonetheless, it also indicates the lack of technical consensus on a preferred alternate or selection of alternates. In the context of that gap, the next section describes an approach for reaching a technical consensus using vitrification and borosilicate glass for stabilizing defense high-level waste as the case study.

# 5.0 Approach for Technical Consensus on Waste Treatment and Waste Form

The quest for technical consensus on the preferred waste form for stabilizing the high-level waste stored at the U.S. Department of Energy (DOE) Savannah River Site started in 1979 (Alternative Waste Form Peer Review Panel 1979). The technical consensus reached for the Savannah River Site high-level waste then essentially set the standard for the waste stored at the West Valley and Hanford sites. In that year, a peer review panel was convened, composed of eight scientists and engineers representing independent, experts from industry, government, and universities and the disciplines of materials science, ceramics, glass, metallurgy, and geology. Eleven alternative waste forms were considered using data and reports provided by the DOE project teams. Each member of the panel rated each waste form on nine "scientific merits" or criteria:

1. Potential for minimizing leachability

2. Potential for achieving a uniform product

3. Suitability for prediction of long-term behavior

4. Sensitivity of properties to radiation

5. Sensitivity to thermal and mechanical history

6. Potential for favorable geologic interactions

7. Potential for quality assurance for licensing and regulation

8. Sensitivity to waste composition

9. Thermal conductivity

The individual rankings were then consolidated by consensus in 1980 and the panel's critique and recommendations were outlined in two further reports (Alternative Waste Form Peer Review Panel 1980, 1981). Importantly, the panel's consensus decision also had implications for the high-level waste generated from any recycling of commercial used nuclear fuel because it would also likely have been dispositioned in the federal geologic repository at Yucca Mountain. As it was, the same alternate (borosilicate glass) was selected for the high-level waste stored at West Valley. In this regard, the panel leveraged the work already proceeding and well-advanced in France.

Together, the nine criteria describe waste form technical maturity, and data must exist in each for a judgment to be made on a waste form's applicability for a waste stream. Notably, the nine criteria cover not only the waste form performance and properties and their long-term predictability important for repository design and licensing, but also the performance of the process to stabilize the waste. This delineation is illustrated in Table 5.1.

Table 5.1. Delineation of Waste Form Decision Criteria

| Waste Form Properties and Performance | 1. Potential for minimizing leachability |
| --- | --- |
| | 3. Suitability for prediction of long-term behavior |
| | 4. Sensitivity of properties to radiation |
| | 5. Sensitivity to thermal and mechanical history |
| | 6. Potential for favorable geologic interactions |
| | 9. Thermal conductivity |
| Waste Stabilization Process Performance | 2. Potential for achieving a uniform product |
| | 7. Potential for quality assurance (control) for licensing and regulation |
| | 8. Sensitivity to waste composition |

The nine criteria above worked well for identifying suitable waste forms (the radioactive waste and any encapsulating or stabilizing matrix) for managing waste streams at the time, and as noted above, technical maturity was an overall consideration. Much has been learned in the ensuing decades from operational experience related to storage and transportation of high-level radioactive waste and spent nuclear fuel as well as development of geologic disposal systems. This suggests the nine criteria above might deserve to be modified or supplemented as new and novel nuclear reactor discharges begin to be defined from the emerging advanced reactor fuel cycles that might be deployed in the first half of the 21st century.

As no waste form or matrix is technically mature for this application, the concept of technical maturity of the process would exclude most reasonable options. Instead, consideration for technical viability should be considered. As discussed in Section 3.0, remote operations using long-reach tooling is a challenge that must be faced while processing waste salts and potentially some of the by-products of salt treatment. Processes that are adaptable to remote operations, with minimal reliance on electronic controls, and minimal handling steps should naturally be favored. Meanwhile options that include multiple mechanical processes, particularly those using fine radioactive dust should be avoided.

Prospects for near-term storage, long-term storage, subsequent transportation, as well as the importance of waste handling and stability are certainly better understood than they were four decades ago. Meanwhile, the disposal design parameters and environment within which the waste forms will reside are currently not fully established and will vary with the detailed waste package design, engineered barrier design, repository design, and repository layout. The following considerations are outlined for specific waste form and package design criteria for interim storage, transportation, and final disposal:

- Containment and confinement: *Containment* refers to the retention of radioactive material in such a way that it is effectively prevented from becoming dispersed into the environment or is only released at an acceptable rate. *Confinement* refers to the segregation of radionuclides from the human environment and the restriction of their release into that environment in unacceptable quantities or concentrations. Consideration should be given to conditioning waste streams to ensure waste forms that are solid, generally monolithic, and not readily dispersible particulates (including avoiding the formation of colloids when undergoing dissolution in groundwater) (IAEA 1990). Having the waste form itself perform containment and confinement functions supports defense-in-depth for storage and transportation as well as the multiple barrier approach for disposal.

- Criticality control for storage, transportation, and disposal: Precluding criticality during handling, storage (10 CFR 72), and transportation (10 CFR 71) is required and highly desirable after disposal. Development of waste forms with integral criticality control should be considered. This could include a combination of managing of the mass and distribution of fissile material within the encapsulating and stabilizing matrix; placement and longevity of neutron absorbers; and strategies for the waste form performing a moderator exclusion or moderator displacement function.

- Chemical and physical durability: Consideration should be given to the waste form's ability to withstand the effects of chemically induced processes such as corrosion, dissolution, and phase transformations (IAEA 1990), as well as to maintain its configuration under expected mechanical loads during storage, transportation, and disposal.

  - Inert with respect to environmental conditions on both on the earth's surface and subsurface. One of the challenges of managing the handling, storage, and transportation of the spent nuclear fuel discharges from the current fleet of commercial reactors is that the fuel must always be managed and moved either under cover of water or in an inert environment to maintain its configuration and integrity. The undesirable behavior of commercial spent nuclear fuel in air when the fuel is at an elevated temperature is well documented (Hanson et al. 2008). Developing waste forms that are relatively stable in air could simplify the handling and enhance the overall nuclear safety aspects of storage, transportation, and disposal.

  - Chemical hazards: Waste forms should not contain hazardous materials in quantities that would be subject to the Resource Conservations and Recovery Act (OCRWM 2008).

  - Pyrophoricity: Waste forms should not contain pyrophoric or combustible materials (OCRWM 2008).

  - Organics: The amount of organic material contained in the waste form should be limited (OCRWM 2008).

- Thermal considerations: The thermal power output of the packaged waste forms should be limited (1) so as to allow handling, storage, and transportation operations when required and (2) such that any associated detrimental changes to physical, chemical and mechanical properties of the waste form, storage and transportation system components, waste package components, other engineered barriers and repository components can be addressed and mitigated as part of the waste management system design process.

# 6.0 Recommendations for Further Research and Development

## 6.1 Waste Management Practice

Compared to solid-fueled reactors, MSRs present fundamentally different waste management challenges, mainly arising from the much higher dose rates and neutron exposures. There are several areas of waste management practice that warrant systems engineering development:

- A concept of operations for how to transfer and package waste will be key to creating realistic layouts for MSRs, much more so than at solid-fueled reactors due to the larger amount of component replacement, lack of personnel access, and the extended distribution of contamination and radiological dose.

- Ideally, MSR wastes should only have to be packaged once in a way suitable for interim storage (if needed), transportation and final disposal. Such a packaging system requires development.

- The filters associated with the off-gas system and solids separation system and activated metal reactor components will benefit from mechanical processing (e.g., size reduction) for disposal. These wastes will be contaminated and activated with radionuclides not currently encountered in these types of wastes and their handling processes will need development.

Two specific areas where technological research and development could yield significant benefits for waste management practice are recommended:

- Replacement of irradiated graphite presents particular challenges for variable spectrum MSRs. Therefore, improving capabilities for rapidly replacing irradiated graphite while minimizing the potential for spread of contamination would be valuable. However, to really significantly reduce this challenge, an alternate radiation and high-temperature tolerant neutron moderator compatible with uranium fluoride salts should be developed and demonstrated. An improved moderator material would also decrease the volume of other radioactive waste streams by decreasing the amount of fuel salt in use and the size of the replaced reactor vessels.

- The dose rates inside the shielding will be much too high for either personnel or solid-state electronics. Consequently, Holcomb et al. (2018) explain that all components and maintenance activities need to be designed to be performed remotely using long-handled tooling. Developing new concepts for remote, long-handled tooling and radiation-resistant electronics specific for MSRs, instead of adapting what is already available, would have safety and economic benefits for plant layout and waste management.

## 6.2 Waste Treatment Process and Waste Forms

The foregoing discussion has demonstrated the wide range of waste treatment processes and waste forms considered and evaluated for FS-MSR waste streams. This section presents recommendations for what are arguably considered the most impactful research and development to advance the treatment processes and waste forms. None of the options are considered sufficiently mature to present a "state of the art" for FS-MSRs, and this observation compounds the problem of evaluating the options against one another. However, there are some key principles that point the way to an effective program.

From a waste form standpoint, halide content is the primary issue with FS-MSR fuel salt. Halide-rich salt waste loading must necessarily be low for a waste form to be judged effectively against the criteria outlined in Section 5.0. Initial dehalogenation of the salt therefore introduces significant flexibility in the

adoption of a variety of treatment processes and waste forms. Dehalogenation also simplifies interim stabilization of the salt waste in avoiding the long-term generation of halide gases. For example, dehalogenation and stabilization in a phosphate glass offers several factors of improvement in waste loading over the direct use of glass-bonded sodalite. Zeolite dehalogenation and phosphorylation are the most promising approaches considered for further research and development of dehalogenation processes to advance their technical maturity.

The two dehalogenation processes introduce two different potential waste forms. The phosphorylation process would make phosphate glass attractive while using zeolite opens the possibility of a silicate glass. The advantage of the latter process is that it can potentially leverage the work already completed for use of borosilicate glass to stabilize defense high-level waste. Therefore, the phosphate glass waste form is recommended for further research and development. For the silicate glass, applicability of the current database should be evaluated to optimally design the research program.

The purity of key isotopes in either fluoride or chloride salt FS-MSRs is a significant technical and economic factor. Therefore, dehalogenation processes integrated with recycle of lithium-7 and chloride-37 should be matured to maximize the economic opportunities for FS-MSRs. Furthermore, effective and economic means of enriching chlorine in chlorine-37 need maturation to minimize disposal impacts from chlorine-36.

Finally, conceptually unique to MSRs compared to solid-fueled reactors is the need to actively manage fission product noble gases. Management of noble gas fission products is relatively immature for this reason and the fact that the advantages and disadvantages of these radionuclides are short lived. The advantage is that a durable long-term waste form is not required; however, an economic and safe means of capture and interim storage is needed. The state-of-the-art is arguably cryogenic distillation and storage in pressurized gas cylinders based on early work in the context of reprocessing used nuclear fuel from light water reactors. However, approaches that integrate the capture and storage functions provide economic and technical advantages. Initial work on such approaches has already been completed as described by Riley et al. (2019), but further maturation is needed to facilitate their consideration for implementation.

# 7.0 Conclusions

Waste management practices for MSRs are fundamentally very different from those of their solid-fueled counterparts. To best advance MSR concepts to implementation, these differences warrant fresh thinking on a variety of subject areas, rather than adapting techniques established for solid-fueled reactors.

There is no state-of-the-art approach to the treatment and stabilization of used fuel salt, although several options exist at the concept stage. Criteria originally used to select the preferred waste form for defense high-level waste are also appropriate for contrasting the options with a view to selecting a consensus preference. However, the criteria should be augmented with the experience gained over several decades and must also consider interim storage and transportation as well as final disposal.

A number of areas are recommended for focused technological research and development. While not exclusive, these target areas are considered to provide the most impact to advancing FS-MSR waste management practice:

- Neutron moderator(s) that are tolerant to radiation and high temperatures (alternative to graphite) for application in variable spectrum MSRs

- New concepts for remote, long-handled tooling and radiation-resistant electronics

- Salt dehalogenation processes (primarily for fluorides, as chlorides have demonstrated options)

- Phosphate and silicate waste form evaluations for de-halogenated salt streams

- Integration of lithium-7 and chlorine-37 recovery and recycle into waste treatment approaches

- Strategies for chlorine-37 isotopic enrichment

- Integrated capture and storage of fission product noble gases (e.g., radiation-tolerant sorbents)

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