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Thermochemical and Transport Properties Important to Molten Salt Reactor Operation: Off-Gas Performance and the Fission Product Mechanistic Source Term

Joanna McFarlane
Charles F. Weber
M. Scott Greenwood
A. Lou Qualls

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OAK RIDGE NATIONAL LABORATORY
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Nuclear Security and Isotope Technology Division

THERMOCHEMICAL AND TRANSPORT PROPERTIES IMPORTANT TO MOLTEN SALT REACTOR OPERATION: OFF-GAS PERFORMANCE AND THE FISSION PRODUCT MECHANISTIC SOURCE TERM

Joanna McFarlane
Charles F. Weber
M. Scott Greenwood
A. Lou Qualls

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Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831-6283
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ABSTRACT

The source term used in reactor performance and safety analysis requires understanding the chemical speciation and transport behavior of fission and activation products in the primary heat transport system (PHTS) and containment. As a starting condition, the transport models will use the isotopic compositions determined through ORIGEN (Bell 1973) calculations and thermochemistry that describes the speciation of the fuel, the salt, activation products and fission products. However, as changes in phase will be under non-equilibrium conditions, the source terms will also need models for the transport behavior of key compounds in the PHTS under various scenarios: normal operation with and without an off-gas system, maintenance, off-normal events, and severe reactor accidents. This document highlights those mechanistic behaviors for which models are needed. Simulations of reactor behavior require these models to be developed for molten salt reactors (MSRs), especially if not part of the suite used in describing LWR behavior. The document concludes with recommendations how to develop these models based on what is already known about reactor safety and fission product behavior.

1. INTRODUCTION

1.1 MSRs CONSIDERED AS TEST CASES

Several types of molten salt reactors are being considered for testing and commercialization, including those that have fuel salt and those that have ceramic fuel and circulating coolant salt. (Serp et al. 2014) The ceramic fuel-coolant salt type reactors have similarities with high temperature gas cooled reactors, for which accident scenarios have already been considered. Hence, this report will focus on the less-discussed requirements for describing the source terms of salt-fueled reactors where the fuel is circulated through the PHTS and cladding does not contribute to the retention of fission products.

Fluoride-based salt reactors have been operated successfully. Data from the molten salt reactor experiment (MSRE) can provide information on several topics from initial contamination to fission product loading. However, MSRE was never meant to operate as more than an experimental apparatus. Calculations for reactor performance have been done on the molten salt demonstration reactor (MSDR) that was fully designed but never built and operated. The salt for the MSDR PHTS is a mixture of LiF-BeF_2-ThF_4-UF_4 (71.5%-16%-12%-0.5%) (Greenwood et al., 2018).

Specifications for a chloride-based MSR are much more speculative as such a reactor has not reached criticality. Several designs for chloride-based MSRs are available and include a combination of salts: (Holcomb et al., 2011)

- FS-MSR breeder fuel salts, NaCl-KCl-$PuCl_3$, $PuCl_3$-NaCl (40% $PuCl_3$)
- Coolant salts: NaCl-$MgCl_2$, KCl-$MgCl_2$, LiCl-KCl-$MgCl_2$, LiCl-RbCl, LiCl-KCl
- Other diluents: $MgCl_2$, $CaCl_2$, KCl-$SrCl_2$-RbCl

1.1.1 Impurities in Clean Salt

Thermochemical studies indicate that salt impurities must be minimized for reactor performance. The salts are hygroscopic and water needs to be removed before the reactor is loaded. Impurity removal from fluoride MSRs involves sparging the salt with a mixture of HF and H_2 in argon over several days or weeks. Purification of chloride salts is typically done by sparging with a chlorination agent, such as Cl_2, CCl_4, dichloropropane, and $SOCl_2$. (e.g., Rabinowitch and Katz, 1947)

Initially, the impurity load for molten salts can be assumed to follow the specifications established for the MSRE (Shaffer, 1971). These are listed in Table 1 and will be assumed to be the same for both chloride and fluoride salt reactors. More information on impurity levels will be forthcoming with development of different methods for salt purification and understanding of chloride corrosion in the preparation of the salt and during reactor operation. Standard methods for chemical analysis of the purified salt, need to be established, now done generally by ICP-MS or ICP-OES. Chloride salts can be titrated to determine water content through the conversion of $MgCl_2$. Fluoride salt oxygen content can be derived from the amount of H_2/HF needed for purification, or by reaction of the oxide with potassium bromotetrafluoride (Eklund et al. 1999) that is an update from the method developed by Goldberg and colleagues who used a Toepler pump (Goldberg et al. 1960). Residual impurities may react with salt components and affect the redox chemistry in the reactor, thereby enhancing corrosion, or affect fission product chemistry and volatility.

Table 1: Impurity Specifications for MSRE

Contaminant	wppm	Contaminant	wppm
H_2O	1000	Ca	100
Cu	50	Mg	100
Fe	100	K	100
Ni	25	Li (natural)	50
S	250	Zr (natural)	250
Al	150	Cd	10
Si	100	Rare earths	10
B	5	Cr	25
Na	500	N, C	Not specified

Isotopic purity will also affect reactor performance. Fluoride-salt based reactors require isotopically pure lithium-7 as the isotope lithium-6 will more quickly activate to form tritium. Chloride-salt based reactors require chlorine-37 instead of the natural isotopic mixture of chlorine-35:chlorine-37 because of the low neutron cross-section of chlorine-37 and the need to minimize generation of radioactive chlorine-36.

1.1.2 Fission Product Reservoirs under Normal Operation

Fission products from fuel salt reactors, both chloride and fluoride based are presented in Table 2. (Betzler 2017a, 2017b, 2018). Predictions of fission products using ORIGEN are expressed on an isotopic basis; from a chemistry perspective, isotopes of the same element can be assumed to behave identically. Isotopically there are fission product decay chains that produce daughters with quite different phase behavior from their parent in the reactor or in the off-gas system. These include some of the noble gas isotopes. The most important xenon and krypton isotopes include: ^{139}Xe $t_{1/2}$ =39.5 s, ^{90}Kr $t_{1/2}$ =32.3 s, ^{137}Xe $t_{1/2}$ =3.83 min, ^{135m}Xe $t_{1/2}$ =15.3 min, ^{89}Kr $t_{1/2}$ =3.18 min, ^{135}Xe $t_{1/2}$ =9.1 hr, ^{88}Kr $t_{1/2}$ =2.84 hr, ^{133m}Xe $t_{1/2}$ =2.19 d, and ^{133}Xe $t_{1/2}$ = 5.25 d.

Table 2. Elements Generated from Operation of Selected MSRs

Parameter	**Molten Salt Breeder Reactor**	**Thermal Spectrum MSR**	**Fast Spectrum MSR**
Reference	Betzler et al. (2017b)	Betzler et al. (2018)	Betzler et al. (2017a)
Fuel Type	Th/^{233}U	Low-enriched U	U/Pu
Carrier Salt	FLiBe	LiF	NaCl
Fuel Salt	ThF_4, UF_4	UF_4	UCl_3, $PuCl_3$
Operating Temperature (°C)	636	613	750
Salt Volume (m^3)	48.7	46.8	12.3
Fueling Condition	Maintain constant ^{232}Th loading	Add 500 kg/year low-enriched U (5%)	Maintain constant ^{238}U loading
Low Level Processing	No isotopes removed	Ag, H, Kr, Mo, Nb, Pd, Rh, Ru, Sb, Se, Tc, Te, Xe removed.	Ag, Kr, Mo, Nb, Pd, Pu, Rh, Ru, Sb, Se, Tc, Te, Xe removed
High Level Processing	Ag, Ba, Br, Cd, Ce, Cs, Eu, Gd, I, In, Kr, La, Mo, Nb, Nd, Pa, Pd, Pm, Pr, Rb, Rh, Ru, Sb, Se, Sm, Sn, SR, Tc, Te Xe, Y, Zr	Ag, As, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, Fe, Ga, Gd, Ge, H, I, In, Kr, La, Mn, Mo, Nb, Nd, Ni, Pd, Pm, Pr, Rb, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Tc, Te, Ti, V, Xe, Y, Zn, Zr	Ag, As, Ba, Br, Cd, Ce, Cs, Dy, Er, Eu, Gd, Ge, Ho, I, In, Kr, La, Mo, Nb, Nd, O, Pd, Pm, Pr, Pu, Rb, Rh, Ru, Sb, Se, Sm, Sn, Sr, Tb, Tc, Te, Y, Zr

1.1.3 Fission Product Inventory versus Burnup

In situations where the fissile isotopes do not change, the fission product inventory is expected to increase monotonically with burnup. If fissile isotopes are created (i.e. “breeding”), the fission product distribution will shift with burnup from the initial charge of fissile material to that generated from activation of the initial charge of fertile material. In the case of MSRs, there are also plans by some vendors to do online fuel upgrade (“bleed and feed”) in which a side stream of fuel salt is periodically removed and replaced with fresh fuel to maintain power density. Online processing has implications for fission product inventory and for safeguards concerns.

In some reactor designs, volatile fission products may be removed continuously through an off-gas system, reducing their inventory in the reactor core. Tritium comes from the activation of fluoride salts, particularly those containing lithium fluoride. (Harrison et al. 2016). Even without active removal, tritium is expected to reach an equilibrium concentration because of its high permeability through structural metals, including the high surface area heat exchanger. Hence, active tritium removal will be necessary to reduce the levels emitted during normal operation of a fluoride-based salt reactor.

1.1.4 High-Dose Locations Outside the Core Coming from Delayed Neutrons

Like all reactor designs, MSRs will need to be shielded to protect personnel including operators. However, because the fuel salt passes outside the core and through the heat exchangers, shielding from delayed neutrons will be needed outside of primary containment and on the secondary side of the reactor. Off-gas systems in direct contact with the salt headspace will need shielding, as will secondary systems of scrubbers or decay tanks. Salts that require online processing at an adjacent facility will have additional shielding requirements throughout the purification or separation processing facility. Transfer of the salt from the reactor to the processing facility and back will have to be done with automation and the loop components, pumps, valves, electronics, and monitoring equipment will all require shielding.

2. FISSION PRODUCT, ACTIVATION PRODUCT, AND REACTOR MATERIALS THERMOCHEMISTRY AND REACTION RATES

Fission product abundance can be predicted from models such as SCALE (Betzler et al. 2017b) knowing the neutron flux and energy as well as the fissile atom content in the core. Fission product chemistry at the temperature of normal operation , ~650°C, can be described by thermochemical models, such as the Gibbs free energy minimization routine Thermochimica (Piro et al. 2012). The solubility of the fission products and their chemical stabilities will come from these calculations. Various categories of fission product and activation product compounds are listed below.

2.1 SALT SOLUBLE FISSION PRODUCTS

Most of the fission products will have high solubility and will be entrained in the salt as it circulates through the PHTS. These will include the high dose consequence cesium and strontium, as well as lanthanides and actinides. Tritium, as TF, will also have a high solubility, but a fraction will escape the PHTS as a form of hydrogen.

2.2 VOLATILE FISSION PRODUCTS AND DAUGHTERS

Volatile fission products that will not be retained by the salt to any great extent include isotopes of xenon and krypton. Understanding the source term arising from these gases includes two areas of large uncertainty. One is how the gases bubble through the salt and where will they be collected. Reactor designs include a headspace in which the gases are assumed to accumulate but understanding the transport of entrained gases and bubbles through the entire PHTS is of interest. The second area of concern regarding the noble gases is their decay products, some of which will change form and phase in the off-gas system or headspace. This decay needs to be understood for the design of the off-gas system and the dose experienced by off-gas materials. Radiolysis is not expected to have a large impact on the salt itself, aside from the formation of activation products, because of the high rate of recombination expected at temperatures of normal operation. However, the off-gas operates at temperatures, 200°C or lower, where radiolysis may become an important consideration for materials performance and degradation.

Tritium and iodine are examples of elements that will have a highly soluble chemical form in the salt but will also have significant volatility. Tritium will escape the salt as T_2 or HT, depending on the form of chemical redox control used in the reactor design. Iodine, being a halide, will have a high solubility in the salt, but ICl has a boiling point (bp) of 97.4°C and, thus can escape the salt. Several stable iodine fluoride compounds can form, IF_5 (bp 97.85°C) and IF_7 (bp 4.8°C). IF will decompose to I_2 (bp 183°C) and IF_5. The volatility of cesium will depend on its chemical form in the salt. (Capelli et al. 2018)

2.3 PRECIPITATES

Noble metals are expected to plate-out into the system and thus represent a static, growing, and distributed source term. It is anticipated that they may be transported from hotter areas to cooler areas of the PHTS, certainly affecting dose distribution but also affecting the hydraulic diameter of certain areas of the PHTS. Hence, where they plate-out and if and when they relocate from a surface needs to be understood. The five noble metals associated with solid fuels are Mo, Rh, Ru, Pd, and Tc.

Graphite fines are another class of solids that may be transported within the PHTS. Radiation damage and fission product recoil will slowly degrade graphite structures in the reactor producing small particles of carbon. These are light materials and will accumulate at the vapor/fluid interface in the PHTS. The graphite is not going to contribute to the dose, however, small graphite particles may become airborne and transport with other solids as an aerosolized salt mist into the headspace. In addition, a significant loading of graphite in the PHTS may affect radiation transport and other bulk properties of the fuel salt.

2.4 CORROSION OF METAL PIPING

Halide salts are highly corrosive and even though alloys have been chosen for reactor operation that show high resistance to corrosion, no alloy is completely inert. It is expected that some level of corrosion and release of chromium compounds will occur, with a form of chromium chloride or fluoride circulating within the PHTS. The rate of chromium extraction from stainless steel and nickel alloys is continuing and is an example of where reaction kinetics may play an important role in PHTS chemistry. The choice of construction alloy is a matter of ongoing discussion because questions of durability to corrosion over reactor lifetime have not been fully addressed.

2.5 RADIOLYSIS

Radiolysis of salt components has been discussed as a precursor to tritium production. Other gases can be formed in fluoride salts, including nitrogen and oxygen. Radiolysis is not expected to affect reactor performance because of rapid recombination in the PHTS. However, radiolysis may play an important role in the performance and integrity of off-gas equipment and off-line processing, where temperatures will be lower and volatile halides may be generated.

2.6 OFF-EUTECTIC DRIFT

Often salt formulations are chosen to be eutectics because these have congruent behavior and minimized melting points. However, salt composition will change over time with burnup. The salt itself may decompose with radiolysis, the fission product inventory will increase for those isotopes that are not released into the off-gas system, and the actinide inventory may shift from burning to breeding. These effects are not expected to have a significant change on the bulk properties of the fluid, viscosity, thermal conductivity, or heat capacity, unless there is a significant shift from the eutectic point. Salt redox chemistry may change depending on the production of reactive gases and the measures taken to maintain redox stability. These dynamic effects could change fission product speciation and the source term.

3. TRANSPORT PROPERTIES NEEDED TO DESCRIBE FISSION PRODUCT INVENTORY UNDER NORMAL OPERATING CONDITIONS

Fission products and activation products are generated in the salt that is pumped through the PHTS. As these constituents will be a small fraction of the overall salt chemistry, they will be carried along by the salt, either in solution or swept through as a separate phase. Thus, fluidic properties of the salt itself will provide an initial condition for source term assessment, along with salt thermochemistry mentioned earlier. Physical properties of interest that describe the flow and pumpability of the salt include density and viscosity, and their dependence on temperature. A recent review of the thermophysical properties of molten salts by Serano-López and colleagues (2013) discusses where data are available and where data are lacking for eight representative salts. None of these salts have an actinide as a major component.

3.1 HEAT TRANSFER IN SALT

The thermal properties of the salt will determine the temperature profile in various elements of the PHTS. These will include heat capacity and thermal conductivity. Optical properties of the salt, such as its absorption spectrum in the infrared will also be needed, as this will determine radiative heat transfer.

3.2 DIFFUSION OF FISSION PRODUCTS AND MINOR CHEMICAL SPECIES THROUGH SALT

Fission and activation will occur throughout the PHTS, thus, to a first approximation one can assume that fission products will be created throughout the circulating salt volume. If fission is enhanced in certain volumes by changes in the neutron profile and critical mass, concentration gradients in fission product profile may occur. Losses of fission products to the headspace and to the walls of the PHTS will also create concentration gradients. The behavior of fission products in these gradients, which may be located very close to the walls of the vessel, can be described by diffusion. In addition, there will diffusion along temperature gradients, which may be particularly important in describing fission product behavior in the heat exchanger.

3.3 LOSS OF FISSION PRODUCTS TO THE HEAD SPACE

Certain fission products will be volatile at reactor operating conditions, including iodine and the noble gases as mentioned in earlier sections. While vapor pressures can be measured using an instrument such as the Netzsch TGA Skimmer, volatility and escape from the salt will depend on transport properties such as the rate of diffusion through the salt fluid to the head space, and the formation and coalescence of bubbles in the salt. Reactive fission products such as iodine will react with other salt components, fluorine, chlorine, or tritium, and so speciation will depend on the redox conditions in the salt. This chemistry can become very complex, such as that of ruthenium in fluoride systems. (e.g., Sakurai and Takahaski 1978). Both chemical kinetics and physical models of bubble formation will be needed to describe the volatility of certain fission products.

3.4 PRECIPITATION OF SOLID FISSION PRODUCTS IN COOLER AREAS OF THE PHTS

Fission product transport to surfaces within the reactor will depend on the thermal profile of salt flow through the loop, which can be described knowing the Reynolds number, and mass and thermal transport properties. Salt loop temperature is expected to vary from a maximum exiting the core to a minimum at the exit of the heat exchanger. Interactions of noble metals with surfaces will be the most important at the cooler end of the high-surface area heat exchanger and may be described with thermochemistry coupled with models of the wetting behavior of the salt on the surface. Wetting will change with changes in the surface properties, deposition of fission products or scaling and corrosion. The precipitation rate of noble metals will be enhanced under conditions of reduced flow and in cooler locations, with redistribution becoming a possibility if deposits reach a critical size.

3.5 GRAPHITE DEGRADATION

Graphite within the reactor is subject to degradation throughout the lifecycle of the reactor. The process is thought to arise from a combination of neutron bombardment and fission recoil, the latter because fission products have been observed in the graphite by post-irradiation examination. Out-of-reactor exposure to neutrons was observed in the charcoal filters at MSRE, where uranium compounds that had relocated to the off-gas filters provided enough dose to cause a reaction to form volatile carbon fluoride compounds. (Bettis 1972) Besides chemical effects, physical degradation of the graphite will produce fines that are lighter than the salt and are likely to accumulate at the salt/gas interface, such as in the headspace. They may be volatilized through turbulent flow, as discussed in the next section. Thus, understanding the mechanism for graphite performance in the reactor and its impact on fission product behavior will be important in predicting the source term.

3.6 AEROSOL FORMATION FROM MECHANICAL BREAKUP OF THE SALT

Salts have very low vapor pressures under normal operating conditions, but some salts are expected to be volatile and will be entrained in the off-gas because of mechanical breakup of the surface of the salt in the headspace. Once formed, the salt particles will transport under physical phenomena used to describe aerosol physics, particularly thermophoresis, diffusiophoresis, and agglomeration. (Compere et al. 1975) These mechanisms have been used to describe the transport of particles formed under LWR PHTS severe accident scenarios and depend on the turbulence of the flow and the thermomechanical properties of the fluid. The nature of the salts and the environment into which aerosols would be released are quite different for an MSR.

3.7 REACTIVITY FEEDBACK

Key information in describing reactor behavior, and thus the fission product source term, are the reactivity feedbacks for the salt system (Wooten and Powers, 2018). This includes knowing the coefficient of thermal expansion of the salt, which will affect the density, heat transfer, and the reactor physics. The void coefficient is also of concern, particularly regarding the effect of entrained fission gas bubbles throughout the PHTS. Sodium coolant in fast breeder reactors is a neutron absorber and so that reactor design has a positive void coefficient. Reactivity feedback scenarios have been reviewed by Cammi and colleagues (2011).

3.8 HEADSPACE GAS SPARGING AND OFF-GAS SYSTEM

Related to Section 3.3, physical models are needed for the off-gas system. Unlike other reactor designs, MSRs may use off-gas recovery of fission products as part of normal operation, reducing the source term due to noble gases and iodine. Off-gas systems have been reviewed by Riley et al. (2018) and designs often involve several stages, including particulate capture by zeolites or hydroxide scrubbers, charcoal beds, metal organic frameworks, and driers. The processes driving these complex systems need to be included in a reactor performance model, starting with the headspace gas purge or sparge through to the release to the environment or capture and storage. Off-gas systems can be considered chemical plants unto themselves, and the physics and chemistry of each unit operation needs to be part of the model. As these systems will be running at lower temperatures than the PHTS, radiolysis through the entrainment of fission products and salt aerosols needs to be included in the model.

4. ACCIDENT SCENARIOS POTENTIALLY ALLOWING FISSION PRODUCT RELEASE OR CONTAMINATION OF INTERNAL SYSTEMS

As a starting point, a reactor analysis will build upon the experience of LWR and sodium fast reactor source term models. However, there will be situations that are unique to MSRs because delayed neutrons will be produced in the PHTS outside of the core and the chemistry of the halide salts is very different from other reactor designs. Some scenarios generating a fission product source term that may be considered are listed in this section, but this is not meant to be a definitive list of off-normal and accident events. These events are generally classified as an unprotected loss of heat sink (ULOHS), unprotected loss of flow (ULOP), unprotected overcooling accident (UOC), and unprotected transient overpower (UTOP) (Guo et al. 2013, Fiorina et al. 2014).

4.1 SCENARIOS LEADING TO BREECH IN PHTS

Equivalent to a loss of coolant accident in an LWR, a rupture in the primary vessel in an MSR would lead both to loss of coolant (ULOHS) and fuel failure (ULOF). However, just as in the LWR, there are classes of LOCA that have different outcomes depending on assumptions about operator intervention or the application of secondary safety systems. The suggested advantage of an MSR is that the fuel salt will solidify in place should a break occur in the PHTS, which should mitigate fission product release and dose consequences. The effect of decay heat has been found to be negligible (Fiorina et al. 2014).

4.1.1 Salt Leak

A small salt leak in the PHTS may be that which is undetected over an extended time and so does not lead to an immediate shut down of the reactor but produces a slow extrusion of salt material into the immediate containment. Thus, monitoring and instrumentation to measure slow increases in activity or losses in salt inventory outside the core are needed to handle this scenario.

4.1.2 Crack in PHTS Headspace

The reactors are not pressurized, and so a small crack in the headspace may lead to air bleeding into the reactor, slowly adding oxygen or water vapor into the PHTS. A variation on this scenario is loss of integrity of the inert sweep gas, introducing contaminants into the headspace. Thus, the vessel surrounding reactor operation may need to be purged with argon or another inert gas. Both the inert cover gas in the containment vessel and the sweep gas in the PHTS headspace would require activity, oxygen and moisture analyzers.

4.1.3 Failure of Heat Exchanger

Failure of the heat exchanger may occur because of corrosion after an extended period of operation, causing a ULOHS incident. In this event, primary salt would mix with the secondary coolant salt allowing activity transport to the secondary side of the plant. Analysis of the Molten Salt Actinide Recycler and Transmuter (MOSART) facility in Russia shows that although temperatures are expected to increase during an ULOHS, they will not exceed 720°C in the salt itself, because of negative reactivity feedback with increasing temperature (Guo et al. 2013). Hence, although this would be a catastrophic event for the power plant, the activity would be contained within a second structure and the fission product release to the environment may not be significant. However, the possibility of this event necessitates adequate shielding on the secondary side of the power plant to protect operators.

Heat exchanger failure could also permit tritium transport into the secondary side, which may occur preferentially at the high surface area and thin walled heat exchanger. Various methods have been suggested to mitigate this possibility, including a three-walled heat exchanger with an internal helium sweep gas to remove any tritium that may permeate through the wall of the PHTS.

4.2 FAILURE OF CHEMISTRY CONTROL

An MSR is a chemical plant, and so off-normal chemical conditions will affect reactor performance and safety. Periodic perturbations are possible (Cammi et al. 2011) as well as scenarios due to reactor degradation or failure of chemistry control, some of which are listed below.

4.2.1 Corrosion Leading to Failure of PHTS Piping

Corrosion has been discussed in several places in this report. Corrosion rates will be governed by the redox potential of the salt. However, the corrosion process itself will be described using models of chemical kinetics, the rates of diffusion of vulnerable metal constituents such as chromium through the alloy to active surface sites, and the diffusion of reagents in the salt. Corrosion may also depend on radiolysis.

4.2.2 Failure of On-line Salt Processing

In some reactor designs, online salt processing is proposed to maintain power density throughout the lifetime of the reactor (Betzler et al. 2017b). Suggestions include removing a small amount of salt through a slipstream to the PHTS, processing it and adding clean salt back into the system. Such an online process is likely to be complicated as it must be operated at high temperatures, in a harsh chemical environment, with irradiated material. Failure of the system may expose workers to fission products at some distance from the reactor itself. Failure may also impair reactor operation as online injection of fresh salt may perturb the local reactivity profile (Fiorina et al. 2013).

4.2.3 Failure of Off-Gas Removal System

Removal of fission gases through an off-gas system is a design feature in many MSRs. The off-gas system of the archetypical MSR had difficulties in an otherwise successful experiment (Bettis 1972). The off-gas clogged, with the source being carbonized pump oil that collected in the charcoal filters. Although this lesson has been learned, it is important that the off-gas system be carefully monitored as it is an integral part of safe reactor operation. Should the pressure drop increase, or conversely, the system develop a leak, then the reactor itself will have to be shut down unless a backup off-gas loop is available.

4.3 SCENARIOS LEADING TO FLOW IRREGULARITIES

4.3.1 Clogged Heat Exchanger

The heat exchanger is the part of the reactor with the highest surface area and most tortuous pathways. Deposition of noble metal fission products and relocation of corrosion products may lead to a reduction or blockage in flow. This would have severe consequences as the heat of the reactor could no longer be rejected. Mitigation would involve monitoring of the physical condition of the heat exchanger during operation, surface characteristics and chemical buildup, as well as the temperature profile and pressure drop.

4.3.2 System or Component Malfunctions

System failure could arise from several events that might include: a pump outage resulting in flow failure or flow transients, loss of power, loss of instrumentation and control, or failure of the secondary and ternary loops that would affect salt temperatures at the core inlet. Some of these transients have been reviewed by Guo and collaborators (2013) and Cammi and collaborators (2011). The desire for an MSR is that it would be "walk away safe", so that should such a transient occur, there would be no dose to the public. This may require automatic shutdown systems to handle decay heat, or a reactor design that prioritizes passive safety. Designs for such systems will depend on the thermochemical and transport models outlined in this report.

5. SAFEGUARDS

Safeguards to prevent tampering or loss of inventory need to be considered for MSRs as for any reactor type. The listing below of activities related to safeguards is a suggested starting point for an activity that will need assessment of the reactor itself, secondary systems that may experience dose and activation, and on-site and off-site processing of fuel salt.

5.1 ASSESS THE NEED

The highly radioactive nature of the salt will make tampering with it difficult and dangerous, but there may be less deterrence in the case of consumables, such as off-gas components or replacement graphite structures. Tritium may be of value, particularly if it is loaded onto absorbents and removed. Thus, waste streams may be the most important consideration in safeguards.

5.2 METHODS FOR MONITORING INVENTORIES

Because of the importance of MSR chemistry, it is likely that the PHTS and secondary processes will be highly instrumented with detectors for various isotopes and changes in salt inventories. Monitoring requirements may be met using detectors for normal reactor operation. This will need to be assessed in the context of safeguards. Small amounts of removal may occur that could not be detected with a high radiological background.

5.3 SECURING THE PHTS

As stated earlier, penetration of the PHTS or tampering with the reactor loop itself is highly unlikely because of the high fields, unless a complete reactor shutdown was the goal. However, auxiliary components, such as consumable scrubbers or getters, could be a target for unauthorized processing.

5.4 SECURING ON- OR OFF-LINE SALT PROCESSING

Salt processing may take place some distance from the reactor itself to establish a physical distance between the reactor and the chemical plant. As mentioned earlier regarding salt purification, reactor operation will not want proximity to hydrogen, chlorine or other dangerous gases. However, the transportation of the salt to the chemical process, be it online or off-line, may present a safeguards vulnerability (Gat and Engel, 2000).

5.5 PROTECTION OF NUCLEAR WASTE

MSRs may be run in several different configurations. In some cases, the MSR will be loaded with fuel and run continuously for seven to eight years until the actinide fuel is spent and the reactor is permanently shut down. Other configurations suggest loading the reactor with fertile material and a small amount of fissile material at start up. In either case, the fuel value of the nuclear waste will be minimal at the end of the reactor lifetime. Spent nuclear waste will be stored on site until it has reached an activity level allowing it to be transported to a permanent repository.

Transportation of the spent fuel and permanent disposal that may pose the greatest risks for interception. Although the fissile actinide inventory may be minimal, radioactive fission products could be captured from the salt by simple dissolution and could be used for unlawful purposes.

6. RECOMMENDATIONS

Safety analysis for MSRs is just beginning. As a starting point, the reactor analysis will build upon the model of a sodium fast reactor source term. Source term modeling will inform and couple with the off-gas and monitoring activities, which will be developing the means to monitor fission products in situ and remediate the off gas during reactor operation.

The following studies should be undertaken in the near term:

(i). Thermodynamic scoping calculations for key areas of the PHTS need to be carried out for representative fission and activation products of interest (e.g., noble metals, cesium, strontium, iodine, tritium, rare earths) and corrosion products (such as chromium).

(ii). Based on the thermodynamic calculations, the vapor pressures or important fission product species need to be measured. Key volatiles and their vapor pressures can be measured in a thermogravimetric apparatus coupled with a mass spectrometer. One such apparatus, the Netzsch Skimmer, is on order and will be installed in late 2018.

(iii). In light water reactor (LWR) reactor safety analysis many fission products can be grouped into classes such as the noble metals for example, to simplify the safety analysis. MSRs will approach fission products in a similar manner, but characteristics of typical behavior for each group need to be established. This activity will also identify out outliers, fission products that have behavior that deviates from the group that affects the source term.

(iv). Differences between the MSR source term and the established LWR and the fast reactor source terms will be identified. This activity will show where model development is most needed.

- Perform a literature review of chemical transport in non-equilibrium conditions. For instance, in addition to temperature, phase change rate will depend on natural circulation and convective currents in the headspace, as well as turbulence and flow rate in the salt. This information will inform model development.

- Experimentally investigate the volatility of a non-radioactive fission product compound (e.g., iodine chloride) from a molten chloride salt under various head space conditions, e.g. gas sparging rates. The work will support model development and validation for volatile species transport at the vapor-liquid interface.

(v). Existing reactor performance models for normal reactor operation will need to be extended to include off-gas performance and graphite interactions. This can be done for different simulation platforms, i.e., for TRANSFORM (e.g., Rader et al. 2018) and Melcor (e.g., Grabaskas et al. 2017), which will allow a rigorous a cross-code comparison.

(vi). The off-normal and accident scenarios proposed in this report are highly speculative. The fission product source term work package needs to coordinate with safety and licensing activities to identify scenarios for off-normal performance and the possible effects on source term. These events could include the following:

- Maintenance outage

- Small leak in PHTS

- Design basis accidents
- Severe accident

(vii). The effect of radiolysis in the primary system and subsystems such as the off-gas scrubber system needs to be assessed, resulting in models or proposed experiments.

(viii). As with the reactor accident scenarios, the safeguards implications in MSRs listed earlier is highly speculative. Safeguards assessment can build on the source term evaluation and physical-chemical models describing fission product transport. Monitors can be developed that can track fission product and actinide transport.

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