Technical and Regulatory Aspects for Molten Salt Reactors

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Abstract

As part of efforts to enhance the NRC's readiness to efficiently and effectively license and regulate a new generation of advanced non-light water reactors (ANLWRs), the NRC is assessing the performance needs and issues for structural materials to be used in ANLWRs, such as molten salt reactors (MSRs). This paper provides a summary of technical analysis used to identify gaps in understanding materials performance, and research activities to better understand and resolve technical issues related to MSRs.

Keywords: molten salt reactors; corrosion; salt purity; graphite; sensors;

1 Introduction

In recent years, there has been increased interest in the use of developing non-light water reactor technologies in the US, including molten salt reactor technologies. Several variations are being proposed, including fluid-fueled (that is, the fissile material is dissolved in the primary coolant salt) and the fluoride salt-cooled high temperature reactor (FHR), and the use of both fluoride and chloride salts for fuel and coolant. To prepare itself for potential license applications for these and other advanced reactor types, the NRC developed a vision and strategy to ensure it does so effectively and efficiently [1].

NRC developed documents which detail the actionable steps and resource requirements necessary to support the NRC's strategic objectives in its vision and strategy document. In Volume 2 [2], several Contributing Activities are listed, which provide the details of how NRC will achieve the goals and objectives stated in the vision and strategy document. The work described in this paper was conducted to support and inform several contributing activities related to the area of Materials and Component Integrity, part of Strategy 2, Acquire/develop sufficient computer codes and tools to perform non-LWR regulatory reviews.

The NRC is also developing new requirements for the licensing and regulation of advanced nuclear reactors and is seeking public input. The new rulemaking, Part 53 in Title 10 of the *Code of Federal Regulations* (10 CFR Part 53), "Licensing and Regulation of Advanced Nuclear Reactors," would adopt technology-inclusive approaches and include the appropriate use of risk-informed and performance-based techniques, to provide the necessary flexibility for licensing and regulating a variety of advanced nuclear reactor technologies and designs.

1.1 MSRs

Molten salt reactor technology is not a new concept: the first reactor came online at Oak Ridge National Laboratory over 50 years ago. The Molten Salt Reactor Experiment (MSRE) operated from June 1, 1965 until December 12, 1969. The MSRE was a "fluid-fueled" reactor, which used fluoride salts for fuel and coolant. The reactor has been described in several papers [3]. Since the MSRE, molten salt reactors have been a focus of research for several decades, both domestically and internationally. Despite the extensive work that has been performed on these reactors, there are still gaps in understanding materials issues pertaining to MSRs. Material selection and qualification are important considerations for the deployment of MSRs. Thus, the most important materials issues need to be considered for licensing MSRs.

2 Technical Gaps in MSRs

Oak Ridge National Laboratory reviewed the current understanding regarding materials issues in MSRs and identify knowledge gaps and research priorities for materials research in support of MSR licensing and regulation [4]. Potential MSR applicants may restrict their designs to use materials currently approved in American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code, Section III, "Rules for Construction of Nuclear Facility Components," Division 5, "High Temperature Reactors" (e.g., 316H), or choose cladding materials that provide adequate corrosion resistance to molten salts. Therefore, the molten salt compatibility of materials currently approved in Division 5, with and without protective cladding, need evaluation. Alternatively, applicants could choose to use non-code qualified materials in their designs; one such example is Hastelloy N, used in the MSRE. Other gaps identified included a need to better understand corrosion data, including better standardization for experimental methods and salt chemistries, developing standards for salt purity, and developing best practices for corrosion testing in molten salts. Reliable data on molten fluorides from the 1960s–1970s exist, but they cover a limited range of salts and alloys and often lack complete salt chemistry analysis.

2.1 Corrosion and Salt Purity

Compatibility of materials with molten salt coolants is one of the more challenging aspects of MSR design. For high temperature applications in oxygen-containing environments, alloys containing elements such as Cr, Al, and Si are used routinely to promote the formation of self-healing protective surface oxide films that act as diffusion barriers and reduce the rate of future oxidation. In molten salt systems, these protective oxide films either do not form or are dissolved by the fluxing action of the chloride or fluoride salts and can't be relied upon for corrosion protection. Alloy corrosion is the key materials compatibility issue that is influenced by salt redox chemistry. Consequently, further technical analysis on corrosion aspects of MSRs was carried out; the resulting report outlines relevant knowledge on measurement, management, and mitigation of corrosion in MSRs [5].

Discussed in the report is how impurities in the salt can affect the salt chemistry; additionally, circulating activity, reactivity characteristics and thermophysical properties of the fluid can also be affected by impurities. Therefore, control of impurities in the salt is critical to maintain proper reactor operation and ensure reactor safety. The major impurities include oxides, structural-metals and sulfur. Salts are extremely hygroscopic, so every effort needs to be taken to exclude water from the salt. The presence of water can result in hydrolysis of fluoride and chloride salts; they release corrosive hydrochloric or hydrofluoric acid byproducts, respectively. These byproducts can react with constituents of vessel materials, such as chromium. In the case of salt-fueled MSRs, the presence of fission products (FPs) and transuranic elements in the fuel salt can also effect salt chemistry. Although this is of great importance to the development of MSRs going forward, the effect of FPs on material degradation in molten salts has received little study since the original MSR research at ORNL.

2.2 Standardization of Corrosion Measurements

Research is being conducted on standardization for molten salt experimentation. It is difficult to compare studies performed at different institutions due to a lack of standards for salt purity and experimental setup. To produce meaningful, evidence-based standards, data must be collected in a systematic fashion to determine the effects of specific impurities so standards can be set regarding maximum concentrations.

To date, work is being conducted on a number of topics related to standardization of corrosion data. One set of experiments is looking at a potential specimen surface area to volume ratio effect, and if there is a need to apply a qualitative “correction factor” to corrosion data, based on this ratio. Another effort is looking at the effect of capsule material on corrosion test results for both fluoride and chloride salts. Data obtained to date suggests that capsule materials strongly affect corrosion test results. Despite small efforts aimed at comparing containment materials, a more complete effort is needed to evaluate how common capsule materials compare to each other. For this task, the most common metallic and ceramic containment materials are being evaluated.

2.3 Graphite Compatibility and Infiltration

Graphite is the most commonly proposed moderator material for thermal reactors. Carbon also is a proposed outer-layer material for fuel pebbles in the solid-fueled FHR design. Structural graphite is generally understood to have good compatibility with fluoride salts, exhibiting minimal mass loss. However, fluorination is a concern because it can lead to chemical changes in the graphite [6]. Tang et al. exposed several grades of graphite to molten FLiBe and observed that graphite grades with higher porosity experienced greater fluorine penetration than grades with lower porosity. This is especially concerning for fuel salts, as infiltration of fissile isotopes may affect core neutronics. It is noted that the fine-grained graphite grade used in the MSRE is no longer available. Most current research on graphite focuses on grades proposed for High Temperature Gas-cooled Reactor (HTGR), which tend to be larger grained grades with larger pores, which have better dimensional stability under irradiation.

Research on graphite infiltration as a function of pressure and pore size is needed to properly assess graphite behavior and to select and approve a graphite grade that balances fluoride salt hermeticity with radiation stability. Chloride salt data are not needed at this time, as chloride reactors are generally fast-spectrum reactors that do not require moderation.

2.4 SiC and Ceramic Components

Little data exists on the compatibility of SiC and other ceramics with molten salts. Ceramic materials have not been widely adopted for use in MSRs, but limited data suggests they may have merit in some applications but may not be compatible with all salts. Ceramic matrix composite materials may be proposed as structural materials, and ceramic components have been explored in a limited capacity for pump components, sealing components, and heat exchangers. For a system with both ceramic and metal components, the potential for dissimilar material corrosion also should be evaluated.

2.5 Irradiation-corrosion

There presently are few data on the effects of radiation on corrosion. There are gaps in the current understanding of the effect of irradiation on salt properties, and of how irradiating salt might affect its corrosive properties. Further, understanding of the effect of radiation on salt-material interfaces is incomplete for both structural alloys and moderator materials. The effect of irradiation on corrosion in molten salts is a knowledge gap as it may have a significant impact on reactor performance.

3 Other Technical Considerations

3.1 Advanced Sensors for Chemistry, Tritium, and Off-gas Control

A better understanding of the application of advanced sensors, such as its use in chemistry, tritium, and off-gas control, and structural health would be helpful to monitor performance of reactor systems and components. .

3.1.1 Electrochemical Monitoring

As discussed earler, the redox potential is an important diagnostic for MSRs and directly influences corrosion. There has been no sensor technology developed for direct corrosion indication or corrosion tracking in a molten salt environment [7]. Electrochemical sensors, which can measure redox potential, have been identified as potential in-situ reactor measurement tools. Measuring the redox potential online would allow for material lifetimes to be predicted more accurately, and chemical issues to be diagnosed. For example, ANL is developing an in-situ voltammetry technique that can be used to monitor redox potential and actinide concentrations in MSRs [8].

3.1.2 Tritium Control and Monitoring

Tritium (^3H) is produced in fuel salts that contain beryllium (Be). The predominant pathway is through the nuclear reaction of lithium (Li)-6. The use of Li-7 (smaller neutron capture cross section) can mitigate the production of ^3H, but nonetheless, some will be present in the salt.

Tritium can react with fluoride (F-) ions in solution to form hydrogen fluoride (^3HF). Redox control agents can be added to the coolant to convert ^3HF to $^3H_2$, since HF is highly corrosive. However, the $^3H_2$ can diffuse through the hot metals of the reactor. Typically, tritium migration in FLiBe is dependent upon the partial pressure of hydrogen or HT in the blanket gas, since this affects the chemical form of the tritium produced. Higher partial pressures can result in greater HT formation. The monitoring of tritium both inside and outside the reactor is needed to measure the full tritium inventory [9]. Detection approaches, such as optical spectroscopy and Raman spectroscopy, have also been proposed as possible techniques for the monitoring of tritium in the off-gas stream [10].

3.1.3 Off-gas System

The off-gas system will need to be designed to handle volatle FPs, activation products, particulates, and mists generated from the salt. Off-gas monitoring will supportdemonstrating correct reactor operation and ensuring that any radionculide releases are within regulatory limits. Online sampling methods for fission product compounds such as the use of optical spectroscopy are being considered. Laser-induced breakdown spectroscopy (LIBS) and laser-induced fluorescence analyses have been shown to be effective in determining metals loading in industrial environments such as in exhaust stack emissions [11]. In addition to LIBS, several other elemental analysis techniques exist that could potentially be applied to MSR off-gas systems. Mass spectrometry and gamma spectroscopy are two analytical techniques that will likely be used in tandem with LIBS for elemental (and isotopic) analysis of MSR off-gas streams [12].

3.2 Salt Processing

It appears that some of the advanced reactors, particularly liquid fueled MSRs, may involve at-reactor irradiated fuel processing. The at-reactor fuel processing may be limited to removing and treating volatile/entrained FPs in an MSR off-gas system. It could also involve more extensive processing for the purpose of fissile material recovery or fission product removal.

Chemical processing will most likely be conducted on a continuous basis, with the online chemical processing of a salt stream that is continuously withdrawn from the bulk-inventory of salt circulating through the reactor. Processing options for the salts include electrorefining, separations through volatility differences or distillation, melt crystallization and precipitation, filtration, and redox chemistry. For thermal-spectrum systems, it may be more important to remove the FPs from the salt to minimize the parasitic neutron capture that results from FPs with large capture cross sections, whereas in a fast-spectrum system, these parasitic losses are lower since the fission product capture cross sections are lower in the fast-spectrum energy range [13].

3.3 MSR Fuel Cycle

Operation of MSRs presents distinct technical issues associated with fuel processing operations, including front-end activities related to the enrichment, mixing, transportation, treatment and storage of the fissile and fertile materials and carrier salts. The enrichment and fabrication of feed material (e.g., high-assay low-enriched uranium in the forms of uranium tetrafluoride or uranium trichloride) or fuels (e.g., tristructural isotropic particle fuels) may require NRC licensing activities under 10 CFR Part 70, “Domestic Licensing of Special Nuclear Material”. Further, the transportation of feed material and fuels may require NRC licensing activities under 10 CFR Part 71, “Packaging and Transportation of Radioactive Material”. 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. To date, no large-scale fuel salt production facilities have been licensed or built. Therefore, NRC is sponsoring research to assess the potential hazards and safety impacts associated with these operations through a review of prior experience from the Aircraft Reactor Experiment (ARE) and the MSRE, and the current state of knowledge on Department of Energy (DOE) and commercial vendor plans and fuel compositions. The fuel and coolant salts for both prior operating reactors were produced in the uranium processing facilities at the Y-12 National Security Complex in Oak Ridge, Tennessee. Fissile materials were obtained from existing US Atomic Energy Commission stockpiles and did not necessitate the use of commerical transportation packages. The design and operations of new facilities and transportation packages will require consideration of technical and safety implications of these fuels, including their corrosivity and need for adequate removal of moisture, sulfur and oxygen from commercial grade salts and precursor chemicals. The increased enrichments of the feed and fuel materials will also necessitate revised safety analyses to demonstrate subcriticality at fuel cycle facilities and during conditions of transport.

Efforts are being undertaken to identify necessary research to support long-term storage of spent fuel and high-level waste forms from MSRs, including the necessity for back-end separations and new designs for dry storage to be licensed under 10 CFR Part 72, “Licensing Requirements for the Independent Storage of Spent Nuclear Fuel, High-Level Radioactive Waste, and Reactor-Related Greater Than Class C Waste”. MSRs will require the management of novel waste streams and likely necessitate chemical separations to minimize the yield of high-level waste. Unlike solid fuel, fluid-fueled MSRs will not sequester the gaseous and volatile FPs; therefore these will need to be managed for the most part in the off-gas system. Additionally, salts will require immobilization due to their hygroscopic nature.

3.4 Modeling and Simulation

There is a need for better predictive capabilities for materials compatibility and long-term performance, which would avoid extended experimental campaigns for new materials; design changes; and transient, off-normal, or accident conditions. Models validated by selected experiments would be very useful to designers, operators, and regulators to show how design choices impact reactor lifetime and safety.

4 Conclusion

In summary, MSRs pose unique materials challenges; in particular, structural material corrosion is a key concern. Understanding the chemical behavior in these reactor systems is imperative for corrosion mitigation. Additionally, monitoring programs, materials compatibility, and the effects of salt purity need to be understood. MSRs also have the potential for unique fuel cycle attributes, including the transportation of fuel, potential salt processing operations and novel waste form types.

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