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GRAPHITE–MOLTEN SALT CONSIDERATIONS FOR COMPONENTS IN NUCLEAR APPLICATIONS

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ABSTRACT

The new high-temperature reactor (HTR) designs being considered for future Generation IV nuclear reactor deployment include designs using molten salt as the primary coolant. These molten salt–cooled graphite core designs pose new material compatibility challenges that are not considered within the gas-cooled HTR designs that have been previously built and operated. Although early indications from the Molten Salt Reactor Experiment (MSRE) in the 1960s were that molten salts could be considered chemically inert to graphite, recent studies revealed additional physical and thermal interactions that the molten salt imposes that may be just as significant as the chemical reactivity. Specifically, molten salt intrusion into the open pore structure of nuclear graphite grades can cause additional internal stresses within the microstructure, exacerbating the stress accumulation from irradiation-induced dimensional change. Additionally, designs using a molten salt–containing liquid fuel could produce hot spots within graphite structural components, causing local thermal stresses. Abrasion and erosion concerns are magnified with molten salt because of their extremely high density (some salts have higher densities than the structural graphite components). Finally, the graphite–graphite and fuel pebble–graphite tribological behavior are distinctly different within the molten salt from the inert gas environments and must be investigated. These topics and others are currently under investigation within the US Department of Energy Advanced Reactor Technologies graphite program and will be discussed in depth.

Keywords: nuclear graphite, molten salt, HTR

NOMENCLATURE

ART	Advanced Reactor Technologies
FHR	fluoride salt-cooled high-temperature reactor
HTR	high-temperature reactor
MSR	molten salt reactor
MSRE	Molten Salt Reactor Experiment

1. INTRODUCTION

The passively safe high-temperature reactor (HTR) design is one of the primary technologies considered for Generation IV reactors and includes the small modular and microreactor designs. One of the primary benefits of this advanced design is the much higher outlet temperatures achieved compared with conventional light-water reactors, allowing new energy-producing options such as high-temperature heat sources for industrial manufacturing processes, hydrogen production, or high-temperature electrolysis.[1,2,3,4] The thermal-spectrum HTR designs can operate safely at these high temperatures because they use nuclear graphite components and a thermally stable coolant. Typically, HTR designs are designed to use an inert gas coolant (e.g., helium gas); however, as the possibility of using molten salt coolants has become increasingly popular, molten salt reactors (MSRs) have received increased interests. These MSR designs provide several technological and safety advantages over the gas-cooled HTR designs, including lower operational pressure, higher thermodynamic efficiency, and smaller pressure vessel designs. However, there is minimal operational experience using molten salt in these nuclear applications, and a thorough understanding of the potential material issues between the molten salt and graphite components is required before a reactor design can be licensed.[5] For example, initial results from the 1960s indicated that the fueled FLiBe used in the MSRE was chemically inert to the graphite internal core components.[6,7,8] However, more recent results revealed that some chemical interactions may occur.[9,10,11] This paper describes graphite's properties and outlines the current molten salt–graphite material issues and ongoing research efforts to address these issues.

2. NUCLEAR GRADE GRAPHITE

Graphite is an excellent neutron moderator, widely used in MSRs and fluoride salt–cooled HTRs (FHRs). Nuclear grade graphite is a manufactured composite material, fabricated from coke filler particles, a pitch-based binder phase, and a complex network of pores (Figure 1). The shape, size, distribution, and connectivity of the pores are functions of the manufacturing process. Most manufactured graphite has a density between 1.7 and 1.8 g/cm^3, and therefore a total porosity of about 20%.[12]

Depending on the size of the grains or filler particles (which greatly affects the pore size), ASTM D8075[13] classifies nuclear graphite into the following categories: coarse, medium-coarse, medium, medium-fine, fine, superfine, ultrafine, and microfine. Similarly, depending on the molding process, graphite properties may exhibit various levels of anisotropy, as defined in ASTM D7219.[14]

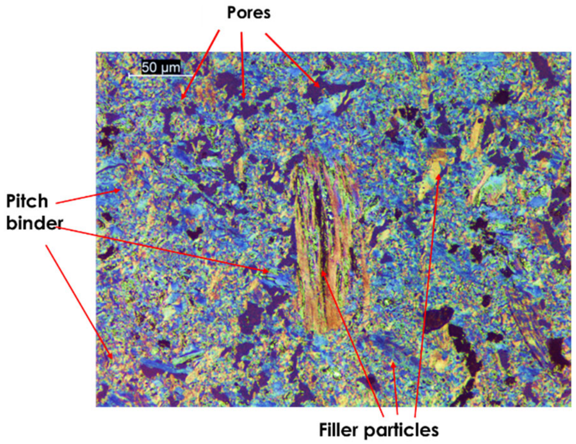


FIGURE 1: OPTICAL MICROSCOPE IMAGE SHOWING THE PRESENCE OF FILLER PARTICLES, BINDER, AND POROSITY IN NUCLEAR GRAPHITE.[12]

Graphite porosity plays a critical role in defining its neutron irradiation–induced material behavior (i.e., strength, stiffness, dimensional change). However, graphite porosity also provides channels for penetration of oxidant species and fission products, with undesired effects on mechanical, thermal, and neutronic properties. When exposed to molten salts (either clean or fueled), partial salt infiltration is expected to occur, causing (still not fully elucidated) additional complicated effects on graphite's structure and properties.

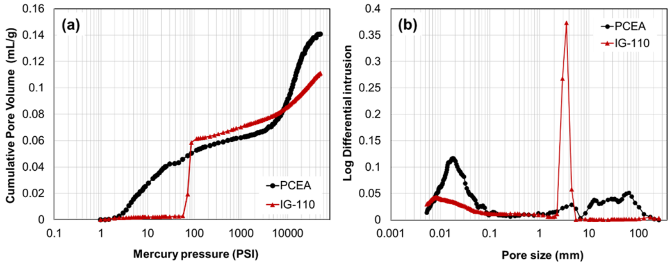


FIGURE 2: (a) CUMULATIVE PORE VOLUME OF MERCURY INTRUSION VS. MERCURY PRESSURE FOR GRAPHITE GRADES PCEA AND IG-110. (b) LOG DIFFERENTIAL PORE VOLUME VS. PORE SIZE.[18]

Nuclear graphite grades exhibit a wide range of porous structures. For example, Figure 2 shows the mercury intrusion and pore size distribution of two graphite grades with significantly different structures, pore size, and pore size distribution: PCEA (extruded, medium-fine grain) and IG-110 (isostatically pressed, superfine grain). The differences between graphite grades translate into different behaviors when exposed to molten salts.

3. GRAPHITE–SALT INTERACTIONS

When graphite is exposed to a molten salt at high temperatures and modest pressures, physical as well as chemical interactions may occur. Physical interactions may include salt intrusion, abrasion, erosion, and wear. Chemical interactions may include fluorination[9,10] or tritium retention.[11] The effects of these interactions on the mechanical or thermal properties may affect graphite's performance in a reactor environment.

3.1 Salt Intrusion into Graphite and its Effects

Ongoing DOE-funded research focuses on quantifying and understanding molten salt intrusion into graphite's porous structure as a function of pressure, temperature, time, and graphite grade. Preliminary results have been documented in several publications.[12,15]

When it comes to salt intrusion into the graphite pore structure, the parameters D_0 and D_t as defined by the ASTM D8091[16] do not provide a complete picture of the intrusion process. Therefore, understanding the effect of salt intrusion on graphite properties requires understanding salt penetration depth and salt distribution across the graphite component.[17]

Recent efforts at ORNL have focused on using neutron imaging techniques for this purpose and have reported some preliminary results from the analysis of FLiNaK-exposed graphite samples that relate the infiltration behavior of several graphite grades with different microstructure.[18]

Preliminary neutron imaging results for two graphite samples exposed to FLiNaK at 750°C and 5 bar pressure for 12 h are shown in Figure 3. The pore structures of the two graphite samples are shown in Figure 2. As shown in Figure 3, these two different porous structures lead to dramatically different salt distribution patterns between graphite grades PCEA and IG-110, although both samples were exposed to the same conditions of pressure, temperature, and time.[18]

Molten salt intrusion into the open pore structure of nuclear graphite grades could generate additional internal stresses within the microstructure if subjected to cooling-heating cycles, exacerbating the stress buildup from irradiation-induced dimensional change. Understanding the salt intrusion behavior (penetration depth) as a function of intrusion conditions and graphite grade is a first step. However, the analysis of the effect of salt intrusion in graphite properties possess some challenges, such as determining whether testing should be done at room temperature (where salt is solid) or at higher temperatures (where salt is liquid) or whether the salt should be removed after exposure and before testing. An analysis of these challenges has been summarized elsewhere.[17]

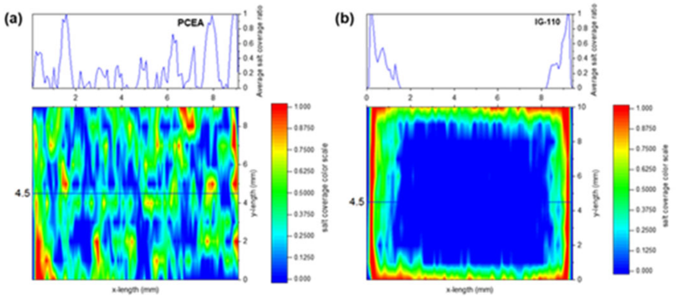


FIGURE 3: PRELIMINARY NEUTRON IMAGING RESULTS SHOWING SALT COVERAGE COMPARISON BETWEEN GRAPHITE SAMPLES (a) PCEA AND (b) IG-110 EXPOSED TO MOLTEN FLiNaK AT 750°C AND 5 BAR FOR 12 H.[18]

3.2 Graphite Wear, Erosion, and Abrasion in Molten Salt

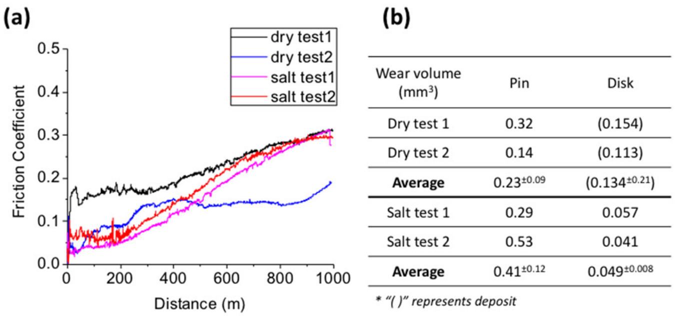
In addition to salt intrusion and its effects on graphite properties, wear, erosion, abrasion, and degradation caused by physical and chemical interactions must be fully understood.

The unique physical and thermal considerations from the salt coolants may affect the safe operation of an MSR design. Furthermore, the graphite–graphite and fuel pebble–graphite tribological behavior are distinctly different within the molten salt and inert gas environments and must be investigated.

Preliminary results[15] shown in Figure 4 indicate a significant difference between the tribological behavior of a graphite pin against a stainless-steel flat surface when immersed in molten FLiNaK vs. similar materials in an inert environment (dry conditions). The dry sliding test results are used as a baseline to understand the chemical (i.e., corrosion) and mechanical (i.e., lubrication) effects of the molten salt. In dry sliding tests, the graphite pin experienced wear loss (i.e., abrasion), whereas the stainless-steel square showed material deposition on the contact area. The deposit was later identified as carbon-based, likely material transfer from the graphite pin and accumulation of graphite wear debris.

In the case of sliding in the molten salt, the initial value of friction coefficient was lower than that measured in dry sliding, likely because the liquid salt at the pin-disc interface reduced adhesion. Unlike in dry sliding, the stainless-steel square had wear loss in the molten salt sliding possibly caused by a combination of abrasion and corrosion. The graphite pin wear in molten salt was more extensive than that in dry sliding, possibly because the wear-roughened stainless-steel surface became more abrasive and/or the graphite pin's mechanical properties degraded in molten salt.

Additionally, reactor designs using a molten salt-containing liquid fuel could produce hot spots within graphite structural components causing local thermal stresses. The abrasion and erosion concerns are therefore magnified with molten salt because of their extremely high density (some salts have higher densities than the structural graphite components).



Wear volume (mm³)	Pin	Disk
Dry test 1	0.32	(0.154)
Dry test 2	0.14	(0.113)
Average	$0.23^{\pm 0.09}$	$(0.134^{\pm 0.21})$
Salt test 1	0.29	0.057
Salt test 2	0.53	0.041
Average	$0.41^{\pm 0.12}$	$0.049^{\pm 0.008}$

** "( )" represents deposit*

FIGURE 4: (a) FRICTION COEFFICIENT TRACES OF THE GRAPHITE PIN AGAINST 316L STAINLESS STEEL IN DRY AND FLUORIDE SALT AT 650°C; (b) WEAR VOLUME ON THE PIN AND DISC AFTER CLEANING.[15]

4. ASME CODE RULE CONSIDERATIONS

The ASME Boiler Pressure and Vessel Code (BPVC) Section III Division 5 for HTRs[5] addresses the rules for graphite core components in the general requirements. The technical design and material requirements are addressed under subsection HA subpart B (HAB) and subsection HH subpart A (HHA), respectively. The code was originally written for HTR gas reactors and did not consider the environmental effects of MSRs. However, according to article HAB-1000, the graphite and composite rules are different from the metallics code in that it considers the deterioration from environmental effects that may occur when in service.[5]

Therefore, the technical rules on design and material under subsection HHA must address the in-service considerations relevant to MSRs. This requirement is partially fulfilled as the code considers the irradiation effects of graphite, but it circumvents any discussion related to graphite deterioration caused by coolant salt–graphite interaction. It dictates conditions for abrasion and erosion excessive to MSRs and does not accommodate salt coolant conditions (with or without fuel). Nonmandatory appendix HHA-B provides some nonmandatory information on expected environmental effects and briefly mentions salt coolant–graphite interactions. It states that for salt–graphite interactions, salt intrusion into the graphite, porosity, buildup of tritium gas, and property changes should be considered. Moreover, additional consideration should be given to salt coolant that contains fuel because it has the potential to create hot spots in the graphite.

Despite it being referenced in the nonmandatory appendix, the mandatory rules[5] do not make provision for any property changes or design consideration because of the salt–coolant interactions.

Ultimately, MSR designs are intended for commercial application therefore, licensing and applicable code rules must be considered. Unfortunately, specific code rules for these unique molten salt coolant designs are absent from the ASME BPVC.[5] A special Molten Salt Task Group has been formed within the ASME Working Group for Nonmetallic Design and Materials to establish any rules necessary to ensure the safe operation of these molten salt designs. All material issues discussed within the previous sections will be considered, and potential modifications to the code will be implemented in the next version of the ASME BPVC.

5. CONCLUSION

The new molten salt–cooled HTR designs being considered for future Generation IV nuclear reactor deployment pose new material compatibility challenges. Although historical results from the MSRE demonstrated minimal chemical degradation between graphite and molten salts, several novel physical, chemical, and thermal issues are considered significant and are currently under investigation by the nuclear graphite community. Many of the phenomena being investigated stem from nuclear graphite's large pore defect microstructure, which can provide opportunities for salt intrusion into the interior microstructure. Unfueled (clean) molten salt intrusion may increase the internal stress distribution, whereas fueled salts may induce localized hot spots. Chemical interactions may include fluorination, intercalation, or tritium absorption. Finally, because of the high density exhibited in molten salts, issues surrounding abrasion, erosion, and wear in core components are concerns.

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REFERENCES

[1] Alonso, G., R. Ramirez, E. de Valle, and R. Castillo. "Process heat cogeneration using a high temperature reactor," *Nucl. Eng. Des*. 280, pp. 137–143, 2014.

[2] Harvego, E. A., S. M. M. Reza, M. Richards, and A. Shenoy. "An evaluation of reactor cooling and coupled hydrogen production processes using the modular helium reactor," *Nucl. Eng. Des.* 236, No. 14, pp. 1481–1489, 2006.

[3] Geschwindt, J. R., Lommers L. J., Southworth F. H., and Shahrokhi F. "Performance and optimization of an HTR cogeneration system," *Nucl. Eng. Des.* 251, pp. 297–300, 2012.

[4] Patterson, M. W. "Cogeneration of electricity and liquid fuels using a high temperature gas-cooled reactor as the heat source," *Nucl. Eng. Des.* 329, pp. 204–212, 2018.

[5] ASME BPVC.III.5. *American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code (BPVC), Section III, Rules for the Construction of Nuclear Facility Components, Division 5, High Temperature Reactors*, New York, 2021.

[6] Briggs, B., Cook W. H., and Taboada A. *Modifications to Specifications for MSRE Graphite*. CF-63-2-18, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1963. doi: 10.2172/1334752.

[7] Briggs, R. B. *Molten-Salt Reactor Program Semiannual Progress Report for Period Ending February 28, 1962*. ORNL-3282, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.

[8] McCoy, H. E. and Weir J. R. *Materials development for molten salt breeder reactors*, ORNL-TM-1854, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1967.

[9] Yang, X., Feng S., Zhou X., Xu H., and Sham T. K. "Interaction between nuclear graphite and molten fluoride salts: A synchrotron radiation study of the substitution of graphitic hydrogen by fluoride ion," *J. Phys. Chem. A* 116, pp. 965–989, 2012.

[10] Wu, H., Carotti F., Gakhar R., Patel N., and Scarlat R. O. "Fluorination of nuclear graphite IG-110 in molten 2LiF-BeF2 (FLiBe) salt at 700 °C," *J. Fluorine Chem.* 211, pp. 159–170, 2018.

[11] Vergari, L. and Scarlat R. O. "Thermodynamics of hydrogen in graphite at high temperature and the effects of oxidation, irradiation and isotopes," *J. Nucl. Mater.* 552, pp. 152797, 2021.

[12] Gallego, N. C., Contescu C. I., and Keiser J. *Progress Report on Graphite-Salt Intrusion Studies*. ORNL/TM-2020/1621, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 2020.

[13] ASTM D8075-16. *Standard guide for categorization of microstructural and microtextural features observed in optical micrographs of graphite*, ASTM International.

[14] ASTM D7219-19, *Standard specification of isotropic and near-isotropic nuclear graphites*, ASTM International, West Conshohocken, Pennsylvania, 2020.

[15] Gallego, N. C., Contescu C. I., Keiser J., Qu J., He X., and Myhre. *FY21 Progress Report on Graphite-Salt Interaction Studies*. ORNL/TM-2021/2247, Oak Ridge National Laboratory, Oak Ridge, Tennessee 2021.

[16] ASTM D8091. *Standard guide for impregnation of graphite with molten salt*. ASTM International, West Conshohocken, Pennsylvania, 2021.

[17] Gallego, N. C., Contescu C. I., and Paul R. M. "Evaluating the Effects of Molten Salt on Graphite Properties: Gaps, Challenges, and Opportunities," in *Graphite Testing for Nuclear Applications: The Validity and Extension of Test Methods for Material Exposed to Operating Reactor Environments*, ed. A. Tzelepi and M. Metcalfe (West Conshohocken, Pennsylvania: ASTM International, 2022), pp. 201–221.

[18] Moon, J., Gallego N. C., et al. *Understanding FLiNaK Salt Intrusion Behavior on Nuclear- Grade Graphite via Neutron Tomography*. ORNL/TM-2022/2688. Oak Ridge National Laboratory, Oak Ridge, Tennessee, 2022.