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Graphite–Salt Interactions: Summary of FY23 Activities

Jisue Moon
Nidia C. Gallego
Cristian I. Contescu
Dino Sulejmanovic
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Yuxuan Zhang

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Radioisotope Science and Technology Division
Chemical Science Division
Material Science Technology Division
Neutron Scattering Division

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

This report summarizes the research activities related to graphite–molten salt interactions during FY 2023. It includes results of FLiNaK infiltration experiments under various operating conditions, such as different temperatures, pressures, and times, to understand the effect of each condition on a variety of nuclear-grade graphites.

Six graphite grades with various origins and properties were selected for the intrusion experiments using molten FLiNaK. The effect of intrusion pressure, temperature, and time were evaluated by measuring weight uptake, and the extent of penetration was studied using neutron tomography (n-CT). In addition, the wetting behavior of molten FLiNaK on a graphite surface was studied by measuring the contact angle on various grades of graphite. The results obtained by n-CT and contact angle measurements will help advance the understanding of factors that control the salt penetration in graphite and their relationship with intrinsic structural properties of the various graphite grades.

1. INTRODUCTION

In the 1960s, the Molten Salt Reactor Experiment (MSRE) at the US Department of Energy's Oak Ridge National Laboratory demonstrated that graphite could be used as a moderator in nuclear reactors, particularly with molten fluoride salts, which are used as both coolant and liquid fuel carriers. During this time, the graphite and fluoride salt interactions were investigated. CGB graphite, the graphite grade selected for the MSRE reactor, simultaneously met three requirements: (1) a low intrusion of pressurized salt to avoid thermal stress and the development of hot points via the accumulation of fissionable materials in the voids that naturally exist in nuclear graphite; (2) a low gas permeability to minimize retention of fission products in graphite; and 3) a high-density, isotropic, well-graphitized structure that would minimize structural damage and dimensional changes by fast neutron irradiation and maximize the lifetime of in-core components. However, CGB graphite is no longer available, and the salt intrusion behavior of currently available graphite grades must be investigated.

In continuation of the previous year's studies on molten salt intrusion into graphite using neutron imaging, the team improved the experimental procedure for the n-CT scan by obtaining an image of the graphite sample before the infiltration experiment. Intrusion experiments were performed under various conditions to understand the effects of impregnation pressure, temperature, and time. Additionally, the contact angle of molten FLiNaK on the surface of different grades of nuclear graphite has been measured at different temperatures.

2. EXPERIMENTAL PROCEDURES

2.1 NUCLEAR GRAPHITE SELECTION AND CHARACTERIZATION

Six nuclear-grade graphite samples (IG-110, 2114, ETU-10, NBG-25, PCEA, and NBG-18) were selected for all infiltration experiments, and the physical properties of each sample were measured. The average porosity properties of the graphite samples used in the intrusion studies are listed in Table 1. Individual sample values may vary slightly because of inherent variability within a graphite block. The graphite grades studied can be classified as superfine (IG-110, 2114, and ETU-10), fine (NBG-25), and medium-fine (PCEA and NBG-18) based on the ASTM International Standard Guide for Categorization of Microstructural and Microtextural Features Observed in Optical Micrographs of Graphite (ASTM D8075).

Table 1. Microstructural and average porosity properties of graphite grades used on intrusion studies in this report

Graphite grade	Classification[a]	Grain size[b] (mm)	Average bulk density[c] ($g \cdot cm^{-3}$)	Average skeleton density[d] ($g \cdot cm^{-3}$)	Average specific volume of open pores[e] ($cm^3 \cdot g^{-1}$)	Average specific volume of closed pores[f] ($cm^3 \cdot g^{-1}$)	Average specific total pore volume[g] (cm^3)	Porosity[h] (%)
IG-110	Superfine	10	1.7648	2.0360	0.0754	0.0448	0.1202	21
2114	Superfine	13	1.8304	2.0542	0.0595	0.0404	0.0999	18
ETU-10	Superfine	15	1.7404	2.0858	0.0951	0.0331	0.1282	22
NBG-25	Fine	60	1.8201	2.0499	0.0616	0.0414	0.1030	19
PCEA	Medium-fine	800	1.8129	1.9723	0.0446	0.0606	0.1052	19
NBG-18	Medium-coarse	1,600	1.8470	1.9811	0.0366	0.0584	0.0950	18

[a]Classification according to ASTM D8075-16
[b]Based on manufacturer's information.F
[c]Data from physical measurement of volume and weight according to ASTM C559-16
[d]Data from helium pycnometry
[e]Calculated as $[1/\rho_{bulk} - 1/\rho_{skeleton}]$
[f]Calculated as the difference between total pore volume and open pore volume
[g]Calculated as $[1/\rho_{bulk} - 1/2.24]$
[h]Calculated as $V_t \times \rho_{bulk} \times 100\%$

2.2 MOLTEN SALT INFILTRATION EXPERIMENT AND NEUTRON IMAGING

The salt infiltration rig has been presented in detail in a previous report along with information on the infiltration procedure.[1] The initial graphite samples used to demonstrate the neutron imaging technique had a 10 mm square cross section and 15 mm height. Additional graphite specimens used for infiltration measurements were machined as cylinders with dimensions of 10 mm ø × 20 mm height, each weighing about 3 g. Individual samples were engraved for identification. Before salt intrusion experiments, the selected graphite samples were cleaned, dried, and outgassed for 8 h at 1,200°C to clean the surfaces and remove moisture; the samples were then transferred to a glovebox. The samples were loaded into the aluminum cans while inside the glovebox to maintain an inert environment within the aluminum can; the cans with the graphite samples were then taken to the High Flux Isotope Reactor (HFIR) Multimodal Advanced Radiography Station (MARS) beamline at Oak Ridge National Laboratory (ORNL)[2] to obtain images of fresh graphite samples for comparison with the images after infiltration. Once the samples from the initial n-CT scan were released from HFIR, salt infiltration tests were conducted using an ORNL's molten salt intrusion system. After salt exposures at the targeted temperature, pressure, and time, graphite samples were quickly transferred to an argon glovebox for weighing and loading into aluminum cans and then transferred to MARS beamline again to measure n-CT. After the experiment, an in-house tool based

[1] N. C. Gallego, C. I. Contescu, and J. Keiser, Progress report on graphite-salt intrusion studies, ORNL/TM-2020/1621 (2020)
[2] L. Santodonato, et al. The CG-1D neutron imaging beamline at the oak ridge national laboratory high flux isotope reactor., Phys. Proc. 69 (2015) 104

on Algotom[3] and TomoPy[4] was used to perform normalization, noise filtering, ring artifact removal, and volume reconstruction. The reconstructed sample volume was loaded into Amira[5] for volume analysis.

2.3 CONTACT ANGLE MEASUREMENTS

The contact angle of molten FLiNaK over a graphite surface was measured using a LINSEIS high-temperature optical dilatometer. Graphite samples were machined into discs of 10 mm diameter and 3 mm thickness. The graphite discs were cleaned, dried, and kept under vacuum before measurements. The FLiNaK salt was pressed into 3 mm diameter pellets to control the initial shape and weight of the molten salt and to accurately measure the salt volume during the experiment. The salt was handled and pellets were made inside a glovebox, and pellets were stored in an inert environment before testing. The system was programmed to measure the contact angle at 550°C for 3 h, 650°C for 3 h and 750°C for 3 h.

3. RESULTS AND DISCUSSION

3.1 DEMONSTRATION OF NUCLEAR COMPUTED TOMOGRAPHY FOR INFILTRATION STUDY

The n-CT method is uniquely suited to study the infiltration of molten FLiNaK salt into the graphite structure because of the sensitivity of neutrons to lithium (from FLiNaK) and the high penetration of neutrons through graphite. The neutron imaging and tomography measurements in this study were performed at the MARS beamline at HFIR. The MARS neutron imaging facility provides a polychromatic beam of cold neutrons with a peak wavelength of 2.6 Å and spatial resolution of approximately 75 μm to perform radiography and n-CT.

Each sample was initially weighed and compared with the weight after infiltration. The samples' volume properties were compared using ASTM parameters D_0 and D_1. A detailed experimental setup and analysis method can be found in the literature[6]. The graphite samples used for the initial n-CT analysis were infiltrated with molten FLiNaK salt at 750°C and 5 bar for 12 h.

Initial measurements confirmed that, at the experimental conditions used for the salt intrusion experiments, FLiNaK penetrated the graphite porous microstructure. The results also showed that the FLiNaK penetration was nonuniform in most superfine grain graphites, limited to the first few millimeters below the graphite's surface, and localized around the perimeter of the sample cross section. By contrast, for the medium-fine-grain graphite, which has larger pores than superfine-grain graphite, the salt penetrated deeper into the material and fully covered the area of the sample cross section (see Figure 1). More detailed information can be found in a recently published article.[6]

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[3] Vo, N.T., Atwood, R.C., Drakopoulos, M. and Connolley, T., "Data processing methods and data acquisition for samples larger than the field of view in parallel-beam tomography," Optics Express, 29 (12), 17849 –17874 (2021). https://doi.org/10.1364/OE.418448
[4] D. Gürsoy, F. De Carlo, X. Xiao, and C. Jacobsen, "Tomopy: a framework for the analysis of synchrotron tomographic data," J. Synchrotron Radiat. 21(5), 1188–1193 (2014)
[5] D. Stalling, M. Westerhoff, H.C. Hege, The Visualization Handbook Amira: A Highly Interactive System for Visual Data Analysis, Elsevier Butterworth Heinemann, 2005
[6] J. Moon, N. C. Gallego, C. I. Contescu, J. R. Keiser, D. Sulejmanovic, Y. Zhang, E. Stringfellow, "A neutron tomography study to visualize fluoride salt (FLiNaK) intrusion in nuclear-grade graphite, Carbon 213 (2023) 118258

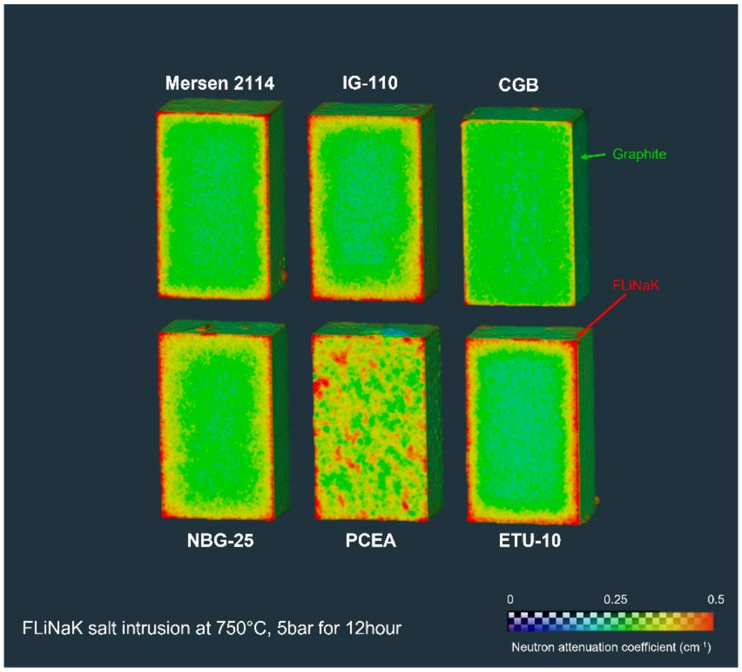

Figure 1. 3D reconstructed view of the graphite samples exposed to FliNaK at 750°C, 5 bar, 12 h. Higher attenuation coefficient regions (red areas) indicate the presence of FLiNaK.

These results prove that neutron imaging can serve as a nondestructive method for understanding the penetration behavior of FLiNaK in the graphite structure. After these initial results, neutron radiography has been used to study the effect of other infiltration parameters such as temperature, pressure, and infiltration time. A summary of that work is presented briefly in the following sections.

3.1.1 The Effect of Infiltration Time at Low Pressure

To understand the effect of infiltration time under low-pressure conditions, two sets of six graphite samples (grades IG-110, 2114, ETU-10, NBG-25, PCEA, and NBG-18) were exposed to molten FLiNaK at 750°C and 3 bar. The first set was exposed at these conditions for 12 h, and the second set was exposed for 2 weeks (336 h). At this temperature and pressure, the weight changes for all superfine and fine-grain graphites, regardless of exposure time, were negligible, whereas some small weight changes were observed for the medium-fine-grain graphites (PCEA and NBG-18), and slightly larger weight changes occurred for the samples exposed for 2 weeks than for the samples exposed for 12 h. The n-CT data on these samples showed that most of the intruded salt in the graphite was located in the larger pores that were open to the surface, as shown in Figure 2. These results are currently being prepared in a manuscript for publication.

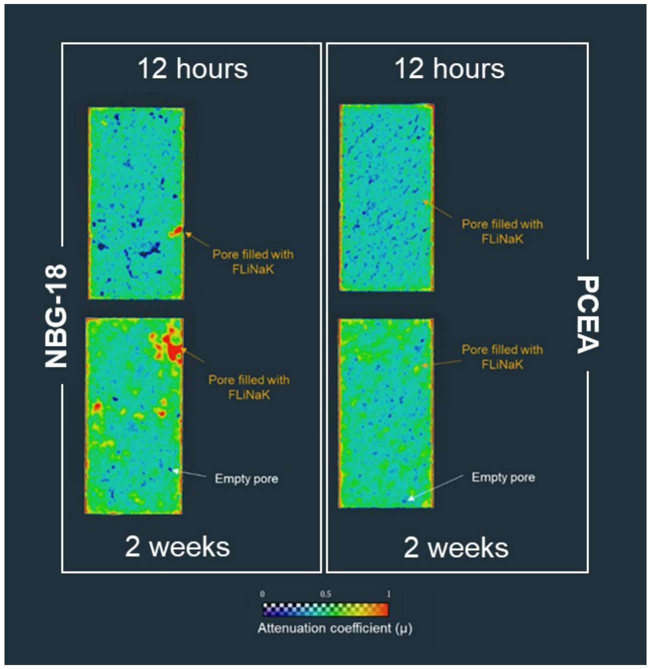

Figure 2. The *yz*-plane extracted from an n-CT scan of (left) NBG-18 and (right) PCEA after infiltration at 3 bar, 750°C for (top) 12 h and (bottom) 2 weeks.

3.1.2 The Effect of Infiltration Temperature

To understand the effect of infiltration temperature, two sets of six graphite samples (grades IG-110, 2114, ETU-10, NBG-25, PCEA, and NBG-18) were exposed to molten FLiNaK at 5 bar pressure for 2 weeks (336 h). The first set was exposed at 750°C, and the second set was exposed at 650°C.

As expected, at the higher temperature, the salt uptake increased by approximately twofold, except for NBG-25, which experienced an increase in salt uptake at the higher temperature of about seven times higher than that at lower temperature. The results from the neutron imaging are still being processed, but hopefully they will help to explain these differences and to elucidate the differences in salt distribution as a function of intrusion temperature.

3.1.3 Ongoing Experiments

Additional experiments are planned to continue to explore the effect of various intrusion variables (temperature, pressure, time) as a function of the structural properties of the various graphite grades, primarily investigating penetration depth and salt distribution. Whether other interactions occur between the salt and the graphite may also be explored, investigating whether reactions are occurring between the salt components, such as Li or F, and the graphite. Other analytical techniques are being explored for this study, including Raman spectroscopy. Furthermore, developing predictive models for intrusion behavior is important. Therefore, another research focus is the wetting behavior of the salt over the graphite surface. These efforts are described in the following section.

3.2 FLINAK CONTACT ANGLE MEASUREMENTS ON NUCLEAR GRAPHITE

Salt impregnation behavior can be estimated by mercury intrusion. However, it is important to have a good knowledge of the wetting characteristics of the salt over the graphite surface as well as of the salt properties such as surface tension. To address these variables, an effort has been initiated to measure the contact angles on different graphite grades as a function of temperature.

To obtain a more accurate contact angle for different grades of graphite, we measured the contact angle of FLiNaK over two different types of graphite: PCEA (medium-grain graphite) and 2114 (superfine-grain graphite). To control the initial shape, 3 mm diameter pellets of FLiNaK salt were prepared in the glovebox and then transferred to the high-temperature optical dilatometer to perform the measurements.

As shown in Figure 3, after its melting point, FLiNaK salt exhibited a nonwetting behavior on both graphite grades (PCEA and 2114). The measured contact angles were 130°–140° and were relatively stable at 550°C after 3 h at temperature. However, as the temperature increased to 650°C, the contact angle was stable for approximately 2 h and then started to decrease to close to 90° for 2114. This trend was more pronounced at temperatures over 700°C as the salt behavior transitioned from nonwetting to wetting. Additionally, some small salt drops appeared near the main salt drop. Based on the volume decrease of the main drop, at the higher temperatures as salt becomes wetting, small amounts of the molten salt may go into graphite pores and then resurface at adjacent, connected pores; however, additional research is needed to better understand this behavior.

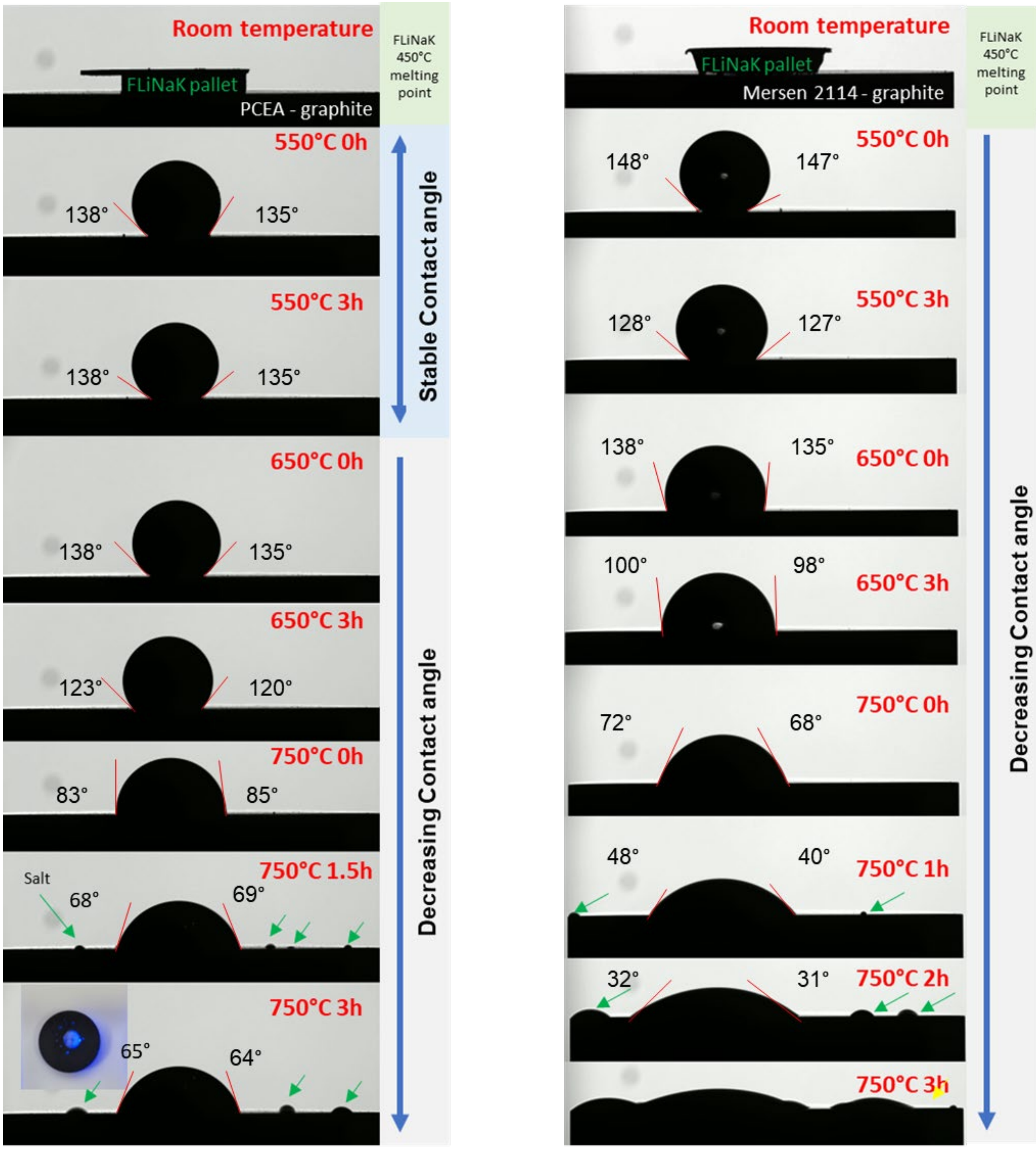

Figure 3. High-temperature contact angle measurement results for (left) PCEA, a medium-fine grain graphite with larger pore size, and (right) 2114, a superfine-grain graphite with smaller pore size. FLiNaK salt pellets with 3 mm diameter were located on the graphite sample, and the temperature increased to 750°C for 3 h to monitor contact angle change.

4. SUMMARY AND ONGOING WORK

This report summarizes the research activities conducted during FY23 to investigate the salt infiltration behavior of graphite under different experimental conditions such as temperature, pressure, and time. Six graphite grades were selected for infiltration tests using FLiNaK. The results indicate that the degree of infiltration increases with temperature. The n-CT technique provided valuable data regarding salt penetration depth and salt distribution within the graphite samples. Several additional experiments at other intrusion conditions are ongoing.

To develop predictive models for the FLiNaK infiltration, an effort has been initiated to understand the salt's wetting behavior. For this effort, measurements of contact angle on different grades and various temperature conditions are underway.

The results presented in this report and future results obtained with this system are expected to help advance the understanding of variables that control the degree of salt penetration in graphite and its relationship with the intrinsic structural properties of various graphite grades. Together, correlating the direct measurement results and graphite structural properties should allow a predictable model to be developed that could be used to select optimal graphite grades.