OAK RIDGE
National Laboratory

Current technical gaps and challenges for nuclear graphite in molten salt reactors

Nidia C Gallego, gallegonc@ornl.gov

ORNL Molten Salt Workshop

November 5-7, 2024

U.S. DEPARTMENT OF
ENERGY

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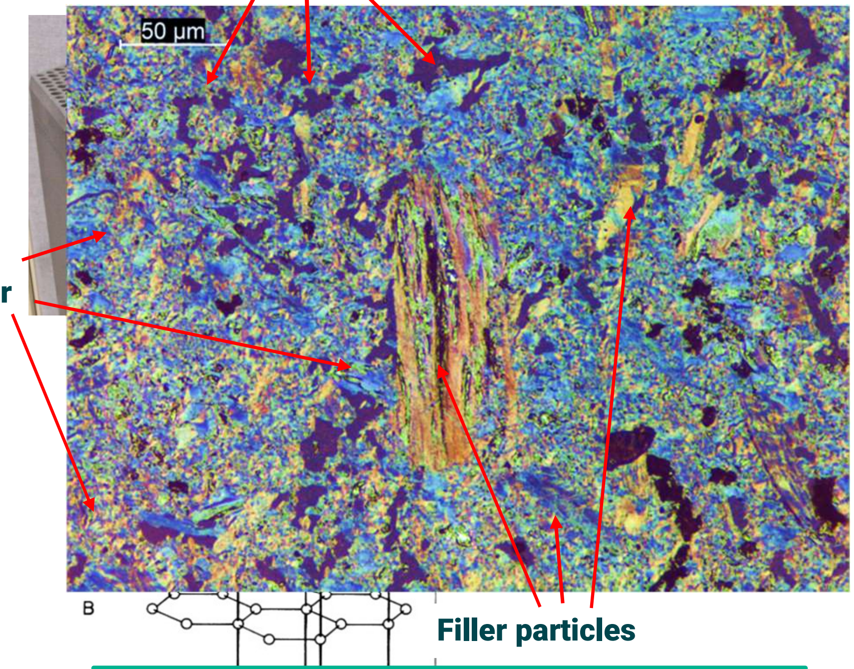
FOR THE US DEPARTMENT OF ENERGY

Manufactured Graphite and its Porous Structure

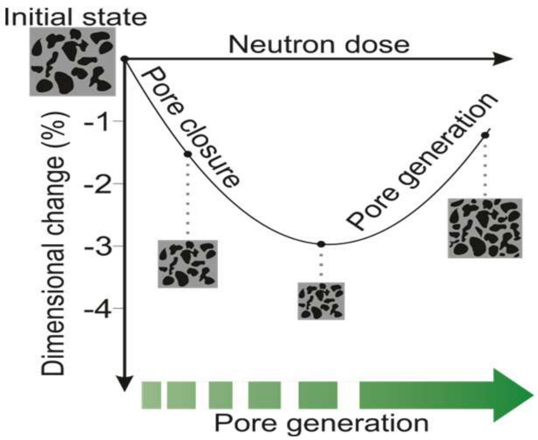


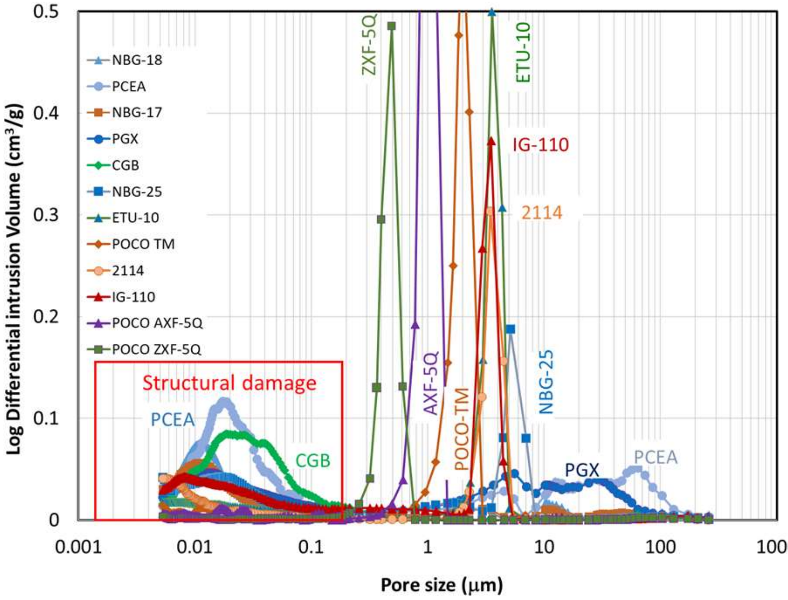
Pores

Pitch binder

Filler particles

Manufactured Graphite has about **20 % porosity**





One carbon, many graphite grades

		Class	Density [g/cm^3]	Country of origin	Irradiation data	Forming process	Availability
AGC-Campaign	**H-451**	Medium	1.71	SGL USA	Low dose	Extruded	🟥
	NBG-17	Medium-fine	1.86	SGL (Germany/ France)	Low dose	Vibro-molded	🟩
	NBG-18	Medium	1.87	SGL (Germany/ France)	Low dose	Vibro-molded	🟩
	PCEA	Medium-fine	1.79	GrafTech (USA)	Low dose	Extruded	🟨
	IG-110	Fine < 100	1.76	Toyo (Japan)	Low dose	Iso-molded	🟩
	IG-430 (dropped)	Fine < 100	1.80	Toyo (Japan)	Low dose	Iso-molded	🟨
	2114 (added)	Superfine < 50		Mersen (France-USA)	Low dose	Iso-molded	🟩
MSRE	**CGB**	Medium	1.86	Union Carbide (USA)		Extruded	🟥
OTHER fine grain graphites	**POCO-ZXF-5Q**	Microfine < 2	1.78	Poco (USA)	Low dose	Iso-pressing	🟩
	POCO-AXF-50	Ultrafine < 10	1.78	Poco (USA)	Low dose	Iso-pressing	🟩
	POCO-TM	Ultrafine < 10	1.82	Poco (USA)	Few data	Iso-pressing	🟩
	G347A	Ultrafine < 10	1.85	Tokai (Japan)	High dose	Iso-pressing	🟩
	IGS743NH	Superfine < 50	1.80	Nippon (Japan)	Low dose	Iso-molded	🟩
	ETU-10	Superfine < 50	1.74	Ibiden (Japan)	Low dose	Iso-pressing	🟩

The different reactor concepts share common challenges to graphite presence in the core.

Effect of fast neutron irradiation and its relationship with microstructure

- ➢ Dimensional changes, structural damage
- ➢ Change in mechanical and thermal properties

Degradation due to Environmental Effects

Gas-cooled reactors

- ❖Chronic oxidation
  - Moisture in coolant will cause slow by continuous oxidation during normal operation – will always happen
- ❖Acute oxidation
  - Air or water ingress (accident conditions) – should never happen

Fluoride salt-cooled reactors

Physical

- ❖ Salt intrusion into graphite pores: how much, how deep, effect on mechanical/ thermal properties; effect of potential heating/cooling cycles; effect of/on irradiation damage; what if salt is fueled
- ❖ Wear and abrasion: pebble on graphite/pebble; pebble on metal surface; dust generation
- ❖ Erosion: flow of salt through graphite channels

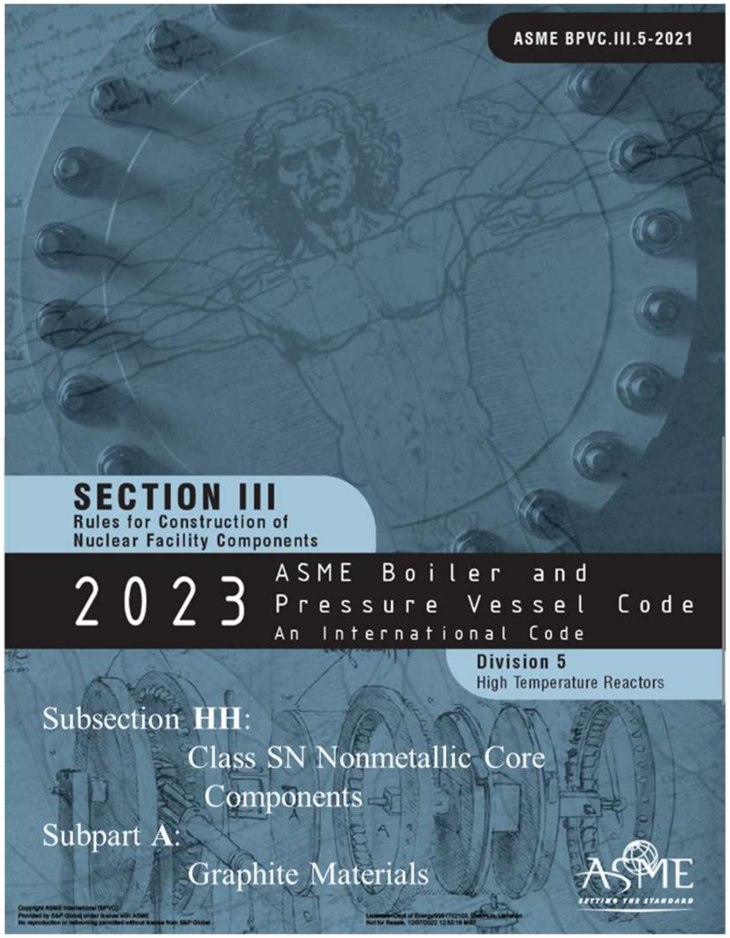
Chemical

- ❖ Chemical Interactions: Fluorination, intercalation, effect on properties of graphite
- ❖ Effect of salt impurities
- ❖ Effect of graphite dust in salt
- ❖ Absorption of fission products
- ❖ Galvanic corrosion

ASME SEC III Division 5
High Temperature Reactors

The current HHA does not address any coolant salt interactions with graphite.

Salt infiltration and retention as well as wear and erosion (chemical attack ?), aspects need to be incorporated in the design rules.



ASME BPVC.III.5-2021

SECTION III
Rules for Construction of
Nuclear Facility Components

2023 ASME Boiler and Pressure Vessel Code
An International Code

Division 5
High Temperature Reactors

Subsection **HH**:
Class SN Nonmetallic Core Components

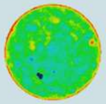
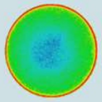
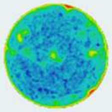
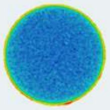
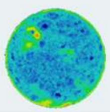
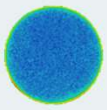
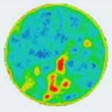
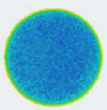
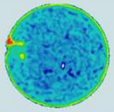
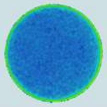
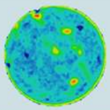
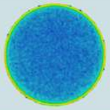
Subpart **A**:
Graphite Materials

Salt intrusion

what we know, challenges & gaps

We know that…

NBG-18, 1023K, 3 bar, 336 hrs

	650°C			750°C			
	12 hrs	2 weeks		12-20 hrs		2 weeks	
		NBG-18	IG-110	NBG-18	IG-110	NBG-18	IG-110
7 bar							
5 bar							
3 bar							

- Salt intrusion into graphite pores may happen, but it is highly dependent on graphite grade, temperature, pressure (and maybe time)
- When it happens, there is usually a ‘distribution’ or ‘gradient’ of salt, that depends on graphite grade, sample size and geometry, and intrusion conditions

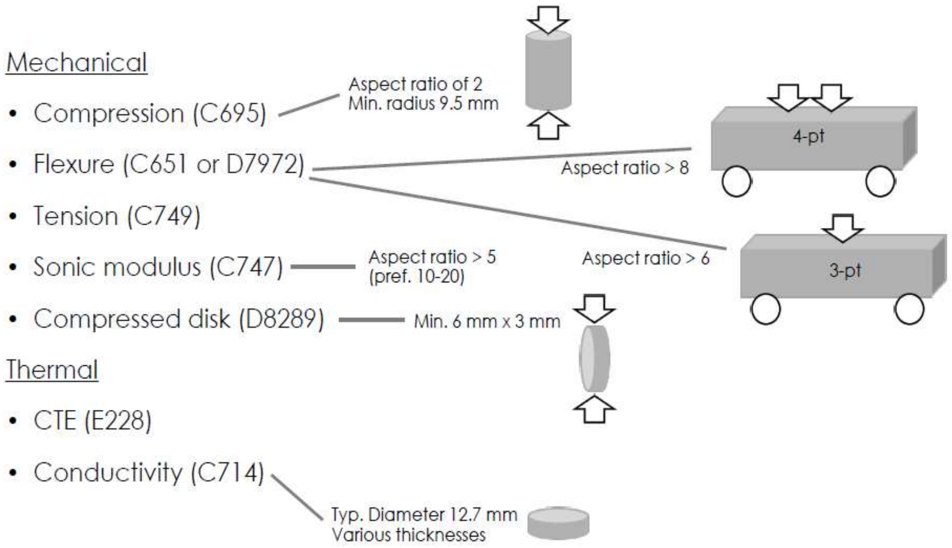
See poster presentation this afternoon

The BIG Challenge / Questions

- If salt intrusion happens, so what ?????
- How can we determine if salt intrusion affects graphite properties?

Challenges, technical gaps

- If we follow current ASTM standards, preparing ‘homogenous’ or ‘representative” samples for various testing is a challenge
- What variable is actually evaluated? Pressure/time, coverage, % pores infiltrated?
- Infiltration happens at high temperature (where salt is molten), but sample is brought back to room temperature
- Do we test at room temperature (salt is solid)? High temperature (salt is molten)?
- Do we remove or keep salt?
- Testing capabilities requires inert environment and possible high temperature



Mechanical

- Compression (C695)
- Flexure (C651 or D7972)
- Tension (C749)
- Sonic modulus (C747)
- Compressed disk (D8289)

Thermal

- CTE (E228)
- Conductivity (C714)

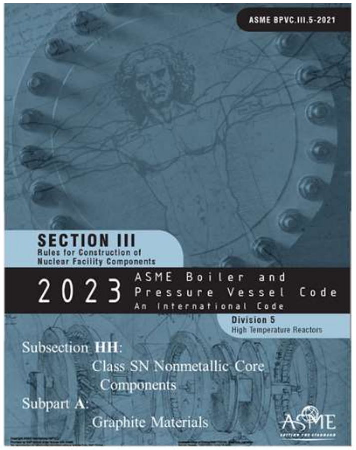
The NEXT BIG Challenge

- Would intrusion behavior change with time, after irradiation damage? Would salt chemistry change over time and affect intrusion??

How about Abrasion and Erosion

How about Abrasion and Erosion

- ASME code said this was just applicable to GCR
- Erosion only an issue a gas flow velocities > 100 m/s



ASME BPVC.III.5-2021

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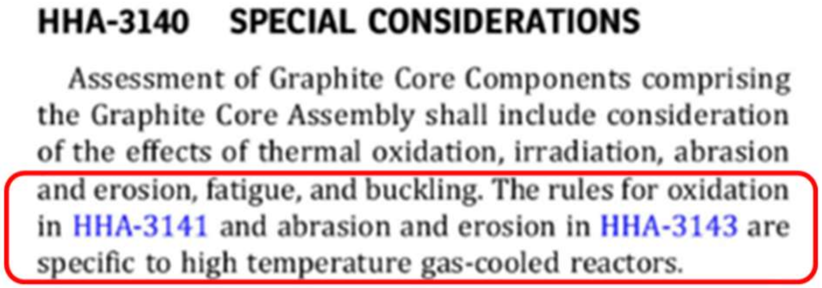
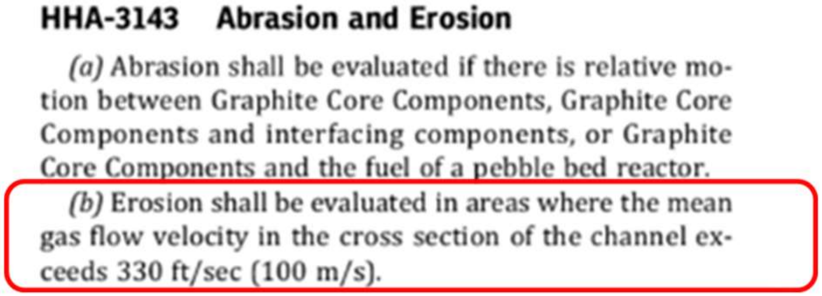
ASME



HHA-3140 SPECIAL CONSIDERATIONS

Assessment of Graphite Core Components comprising the Graphite Core Assembly shall include consideration of the effects of thermal oxidation, irradiation, abrasion and erosion, fatigue, and buckling. The rules for oxidation in HHA-3141 and abrasion and erosion in HHA-3143 are specific to high temperature gas-cooled reactors.



HHA-3143 Abrasion and Erosion

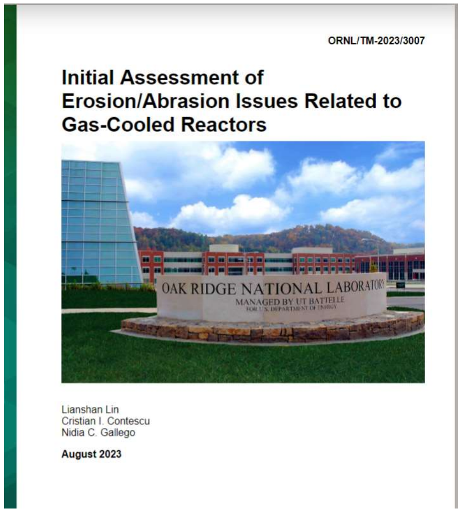
(a) Abrasion shall be evaluated if there is relative motion between Graphite Core Components, Graphite Core Components and interfacing components, or Graphite Core Components and the fuel of a pebble bed reactor.

(b) Erosion shall be evaluated in areas where the mean gas flow velocity in the cross section of the channel exceeds 330 ft/sec (100 m/s).

Erosion

Record 23-2484 submitted and approved

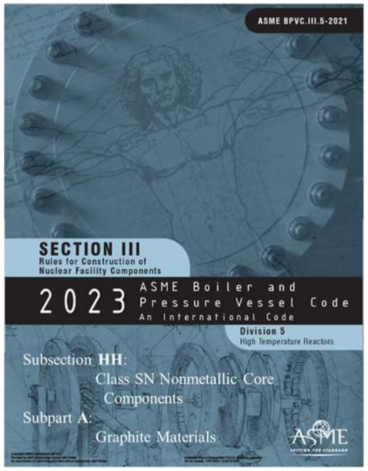
Proposal to edit sections HHA-3140 and HHA-3143 to address applicability of the sections to MSRs


ORNL/TM-2023/3007

Initial Assessment of Erosion/Abrasion Issues Related to Gas-Cooled Reactors

Lianshan Lin
Cristian I. Contescu
Nidia C. Gallego

August 2023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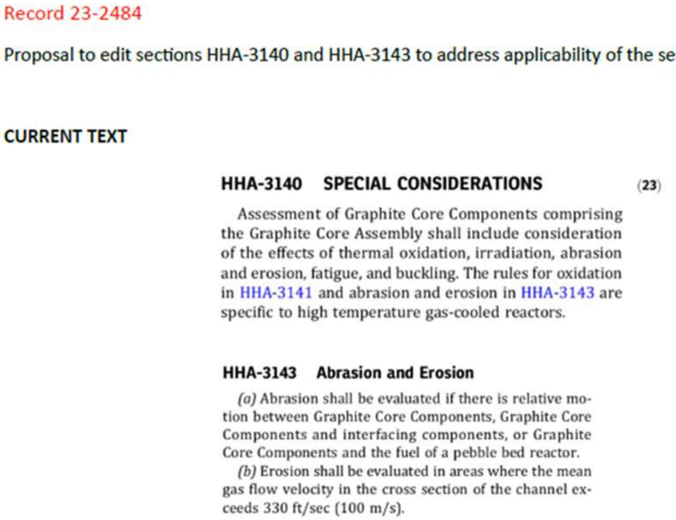
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CURRENT TEXT

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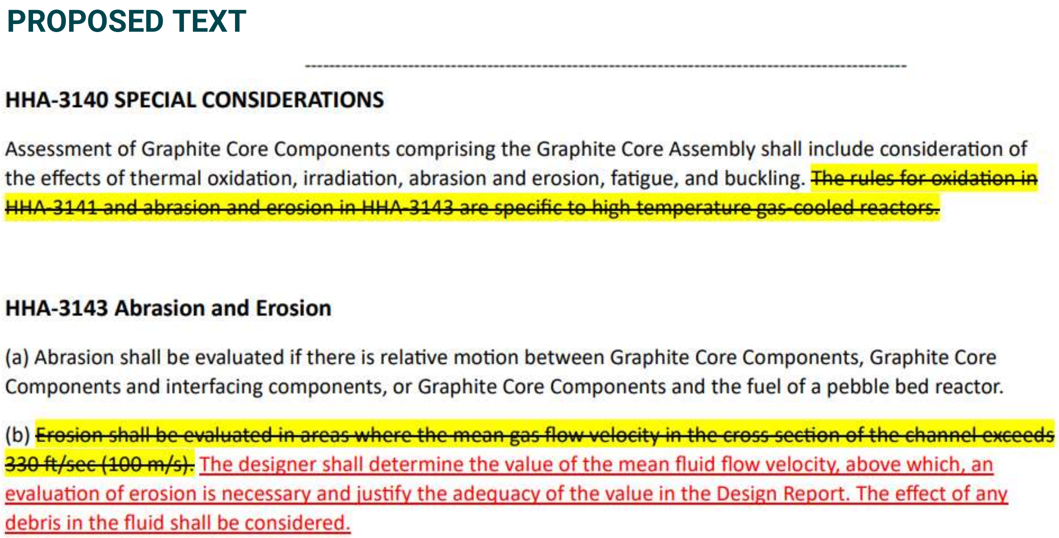
PROPOSED TEXT

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(b) ~~Erosion shall be evaluated in areas where the mean gas flow velocity in the cross section of the channel exceeds 330 ft/sec (100 m/s).~~ The designer shall determine the value of the mean fluid flow velocity, above which, an evaluation of erosion is necessary and justify the adequacy of the value in the Design Report. The effect of any debris in the fluid shall be considered.

Abrasion and wear

- Concerns:
  - Degradation
  - Dust generation
  - Damage to pebbles
- A few reports in the literature, but information is still limited
- Additional research is needed

See poster presentation this afternoon


Wear 522 (2023) 204706

Contents lists available at ScienceDirect

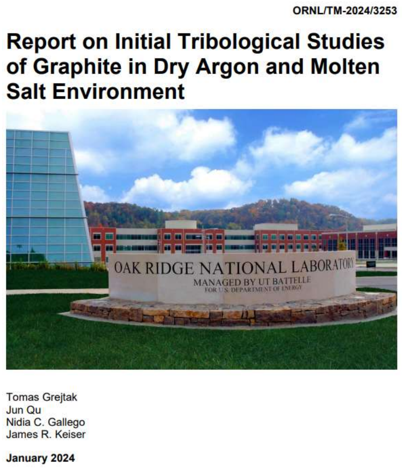
Wear

journal homepage: www.elsevier.com/locate/wear

Tribocorrosion of stainless steel sliding against graphite in FLiNaK molten salt☆

Xin He[a], Chanaka Kumara[a], Dino Sulejmanovic[a], James R. Keiser[a], Nidia Gallego[b], Jun Qu[a,*]

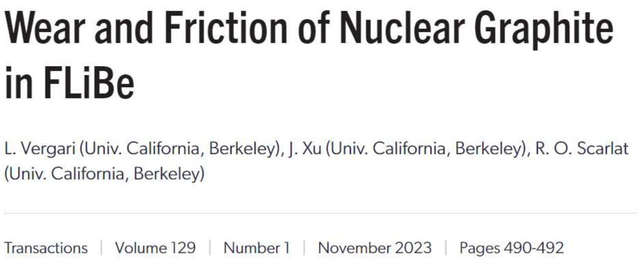
[a] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA
[b] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA


ORNL/TM-2024/3253

Report on Initial Tribological Studies of Graphite in Dry Argon and Molten Salt Environment

Tomas Grejtak
Jun Qu
Nidia C. Gallego
James R. Keiser

January 2024

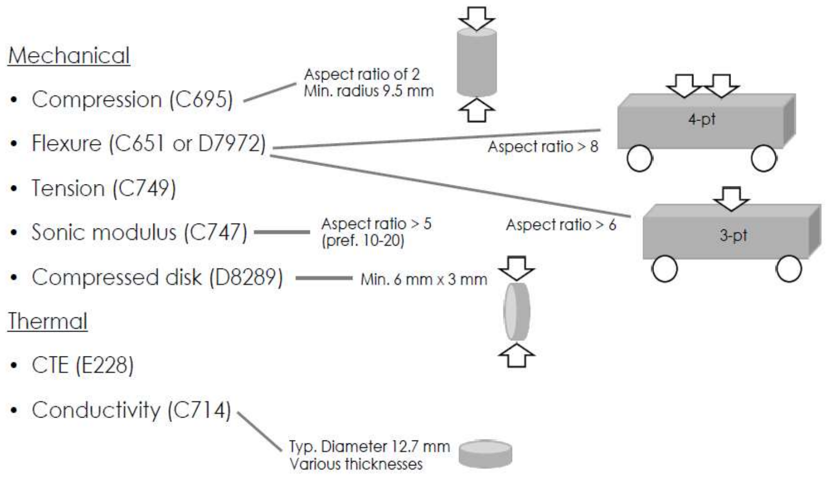

Wear and Friction of Nuclear Graphite in FLiBe

L. Vergari (Univ. California, Berkeley), J. Xu (Univ. California, Berkeley), R. O. Scarlat (Univ. California, Berkeley)

Transactions | Volume 129 | Number 1 | November 2023 | Pages 490-492

ASTM – where do we stand?

- Large collection of ASTM documents was built over time for characterization of HTGR graphites
- Development of Standard Guides for MSR/FHR graphite has started
  - ASTM D8091 – pressurized salt intrusion and quantification
  - ASTM D8377 – mechanical properties testing at high temperature



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- Flexure (C651 or D7972)
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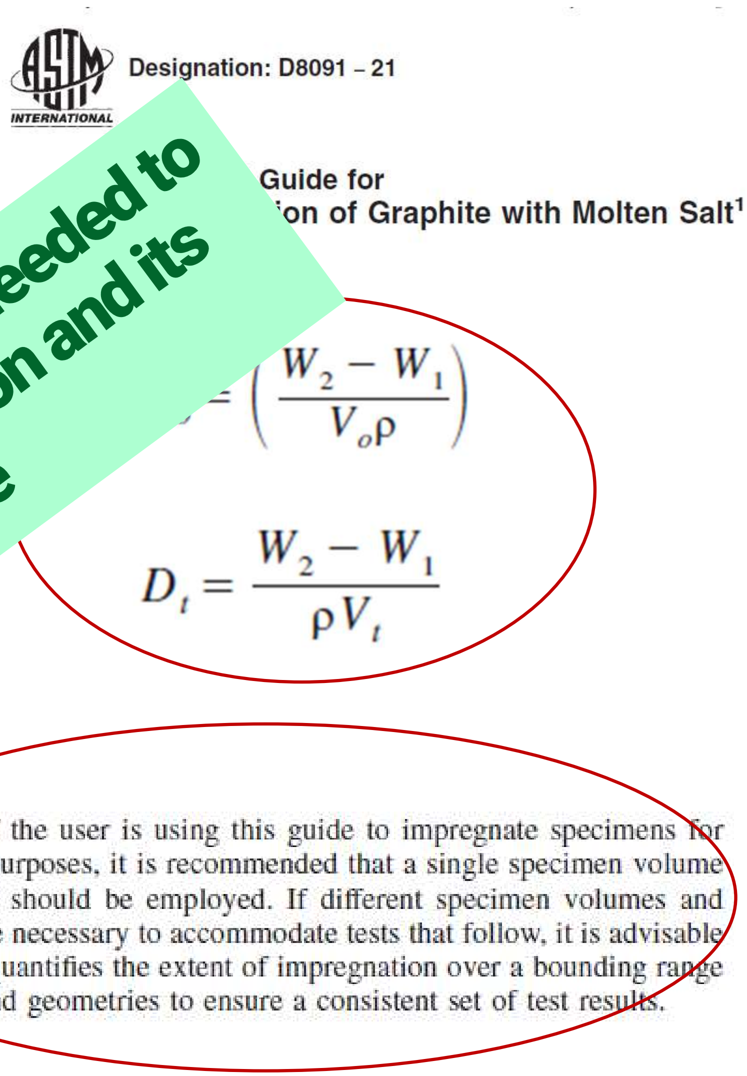
Thermal

- CTE (E228)
- Conductivity (C714)

Standards:
D02.F0 on Manufactured Carbon and Graphite Products

ASTM D8091-16 and revised in 2021

- Guideline for apparatus and procedure for producing graphite specimens impregnated with molten salts
- Introduces two quantification parameter intrusion:
  - Fraction of *open pore* volume intrud
  - Fraction of *total pore* volume in
- Guide does not specify s size
- Guide does not spe conditions
- There is no mention of distribution within sample



Designation: D8091 – 21

INTERNATIONAL

Guide for

ion of Graphite with Molten Salt[1]

$$\left(\frac{W_2 - W_1}{V_o\rho}\right)$$

$$D_t = \frac{W_2 - W_1}{\rho V_t}$$

NOTE 3—If the user is using this guide to impregnate specimens for comparative purposes, it is recommended that a single specimen volume and geometry should be employed. If different specimen volumes and geometries are necessary to accommodate tests that follow, it is advisable that the user quantifies the extent of impregnation over a bounding range of volumes and geometries to ensure a consistent set of test results.

Improved or new Standards are needed to better understand salt intrusion and its effect on graphite

ASTM D8377-21

Designation: D8377 – 21a

Standard Guid
High Temp
Impreg

surements of Graphite

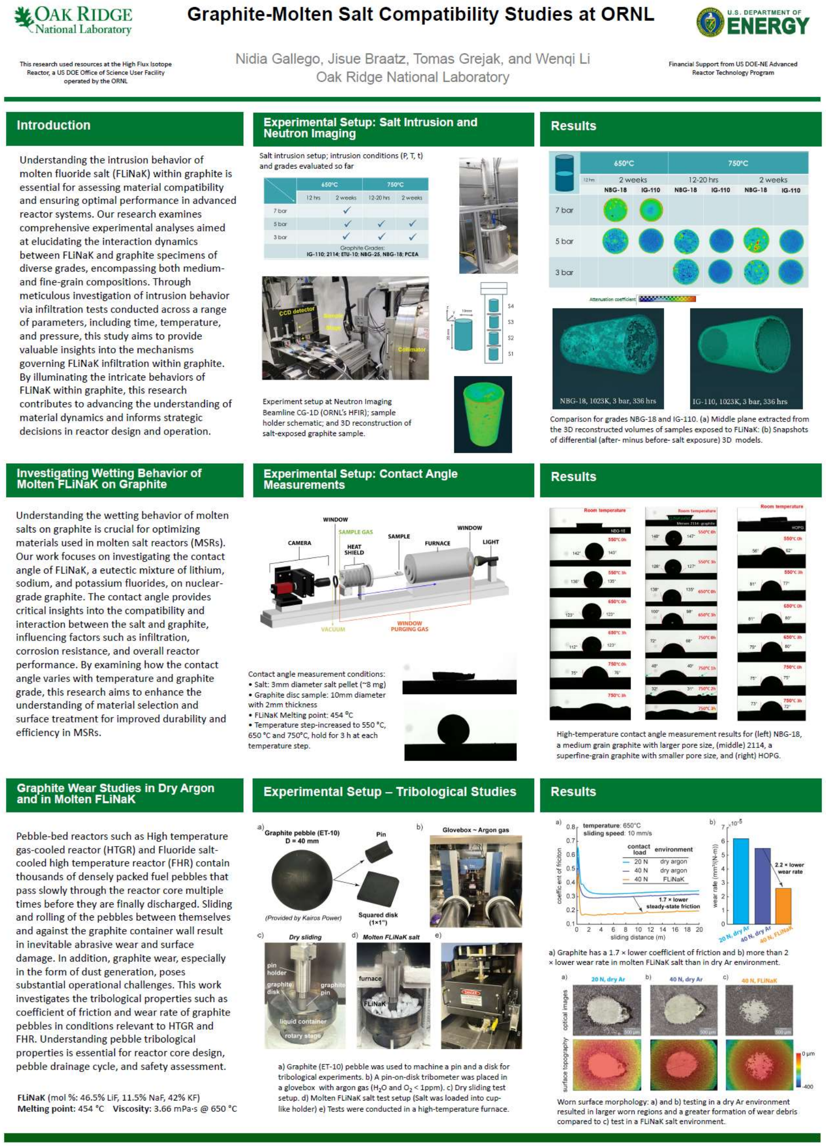
- Sample shape and size should be prepa with the corresponding ASTM:
  - Flexural – ASTM C651
  - Compressive – ASTM 695
  - Tensile – ASTM C749
  - Split disc – ASTM D
- Impregnation – tored samples in glovebox
- Testing of graphit s done at high temperature with retained salt

Do we really need to do testing at high temperature, or can we find a way to employ current standards?

ASTM - Challenges

- Development of Standard **Procedures** requires Round Robin tests"
  - Community may be limited and may not have enough interested participants to afford development of Standard Test Methods
  - Specialized equipment must be custom designed, built, operated at difficult conditions
  - Interlaboratory study (ILS) must have at least 5 participants

Visit our poster presentation this afternoon to learn more about our research activities.



Graphite-Molten Salt Compatibility Studies at ORNL

This research used resources at the High Flux Isotope Reactor, a US DOE Office of Science User Facility operated by the ORNL

Nidia Gallego, Jisue Braatz, Tomas Grejak, and Wenqi Li
Oak Ridge National Laboratory

Financial Support from US DOE-NE Advanced Reactor Technology Program

Introduction

Understanding the intrusion behavior of molten fluoride salt (FLiNaK) within graphite is essential for assessing material compatibility and ensuring optimal performance in advanced reactor systems. Our research examines comprehensive experimental analyses aimed at elucidating the interaction dynamics between FLiNaK and graphite specimens of diverse grades, encompassing both medium- and fine-grain compositions. Through meticulous investigation of intrusion behavior via infiltration tests conducted across a range of parameters, including time, temperature, and pressure, this study aims to provide valuable insights into the mechanisms governing FLiNaK infiltration within graphite. By illuminating the intricate behaviors of FLiNaK within graphite, this research contributes to advancing the understanding of material dynamics and informs strategic decisions in reactor design and operation.

Experimental Setup: Salt Intrusion and Neutron Imaging

Salt intrusion setup; intrusion conditions (P, T, t) and grades evaluated so far

	650°C		750°C	
	12 hrs	2 weeks	12-20 hrs	2 weeks
7 bar		✓		
5 bar		✓	✓	✓
3 bar		✓	✓	✓
	Graphite Grades: IG-110; 2114; ETU-10; NBG-25, NBG-18; PCEA			

Experiment setup at Neutron Imaging Beamline CG-1D (ORNL's HFIR); sample holder schematic; and 3D reconstruction of salt-exposed graphite sample.

Results

Comparison for grades NBG-18 and IG-110. (a) Middle plane extracted from the 3D reconstructed volumes of samples exposed to FLiNaK: (b) Snapshots of differential (after- minus before- salt exposure) 3D models.

Investigating Wetting Behavior of Molten FLiNaK on Graphite

Understanding the wetting behavior of molten salts on graphite is crucial for optimizing materials used in molten salt reactors (MSRs). Our work focuses on investigating the contact angle of FLiNaK, a eutectic mixture of lithium, sodium, and potassium fluorides, on nuclear-grade graphite. The contact angle provides critical insights into the compatibility and interaction between the salt and graphite, influencing factors such as infiltration, corrosion resistance, and overall reactor performance. By examining how the contact angle varies with temperature and graphite grade, this research aims to enhance the understanding of material selection and surface treatment for improved durability and efficiency in MSRs.

Experimental Setup: Contact Angle Measurements

Contact angle measurement conditions:
- Salt: 3mm diameter salt pellet (~8 mg)
- Graphite disc sample: 10mm diameter with 2mm thickness
- FLiNaK Melting point: 454 °C
- Temperature step-increased to 550 °C, 650 °C and 750°C, hold for 3 h at each temperature step.

Results

High-temperature contact angle measurement results for (left) NBG-18, a medium grain graphite with larger pore size, (middle) 2114, a superfine-grain graphite with smaller pore size, and (right) HOPG.

Graphite Wear Studies in Dry Argon and in Molten FLiNaK

Pebble-bed reactors such as High temperature gas-cooled reactor (HTGR) and Fluoride salt-cooled high temperature reactor (FHR) contain thousands of densely packed fuel pebbles that pass slowly through the reactor core multiple times before they are finally discharged. Sliding and rolling of the pebbles between themselves and against the graphite container wall result in inevitable abrasive wear and surface damage. In addition, graphite wear, especially in the form of dust generation, poses substantial operational challenges. This work investigates the tribological properties such as coefficient of friction and wear rate of graphite pebbles in conditions relevant to HTGR and FHR. Understanding pebble tribological properties is essential for reactor core design, pebble drainage cycle, and safety assessment.

FLiNaK (mol %: 46.5% LiF, 11.5% NaF, 42% KF)
Melting point: 454 °C **Viscosity:** 3.66 mPa·s @ 650 °C

Experimental Setup – Tribological Studies

a) Graphite (ET-10) pebble was used to machine a pin and a disk for tribological experiments. b) A pin-on-disk tribometer was placed in a glovebox with argon gas (H_2O and O_2 < 1ppm). c) Dry sliding test setup. d) Molten FLiNaK salt test setup (Salt was loaded into cup-like holder) e) Tests were conducted in a high-temperature furnace.

Results

a) Graphite has a 1.7 × lower coefficient of friction and b) more than 2 × lower wear rate in molten FLiNaK salt than in dry Ar environment.

Worn surface morphology: a) and b) testing in a dry Ar environment resulted in larger worn regions and a greater formation of wear debris compared to c) test in a FLiNaK salt environment.

THANK YOU!

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