

Graphite-Molten Salt Interactions

Dr. Nidia Gallego

Oak Ridge National Laboratory, USA

24 May 2023



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Meet the Presenter

Dr. Nidia Gallego, Distinguished Research Scientist in the Physical Sciences Directorate at Oak Ridge National Laboratory (ORNL). She earned her MSc and PhD in Materials Science and Engineering from Clemson University (Clemson, SC) and joined ORNL in December 2000. Her research interests include, among others, physical and chemical properties of carbon materials, effects of neutron irradiation on graphite and carbon materials for use on space power systems. Currently, Nidia is the ORNL Technical Lead for the graphite activities for both the GCR and MSR campaigns funded by the US DOE Advanced Reactor Technologies (ART) Program, and the Task Lead for Production of Carbon-Bonded Carbon Fiber (CBCF) components as part of the Radioisotope Power Systems Program funded by NASA.



Email: gallegonc@ornl.gov

Webinar Invite

Join us on April 5, 2023 8:30 a.m. EDT

Overview of Nuclear Graphite R&D in Support of Advanced Reactors

As arguably the very first nuclear reactor core material, graphite has been utilized in a variety of nuclear applications since Enrico Fermi first stacked up bricks of graphite in a university squash court. But why? Graphite is not the first material that comes to mind when considering the extreme environment anticipated within a nuclear core. Materials with high strength, toughness, hermeticity, and hardness are traditional material choices for this demanding application. Graphite exhibits only moderate, or even low, values for these material properties. This presentation will address these issues and attempt to demonstrate that graphite is nearly the perfect material choice for these (Very) High Temperature Reactor designs. The latest information on graphite's unique crystal structure and bulk microstructure which provide the desired properties, the (baffling) irradiation behavior, the expected response to anticipated degradation, and how the nuclear graphite community is establishing the operational safety envelop of the core components within these new advanced reactor designs will be discussed. We'll finish up with a short demonstration of why nuclear graphite cannot burn (No, Chernobyl graphite fires did not happen).

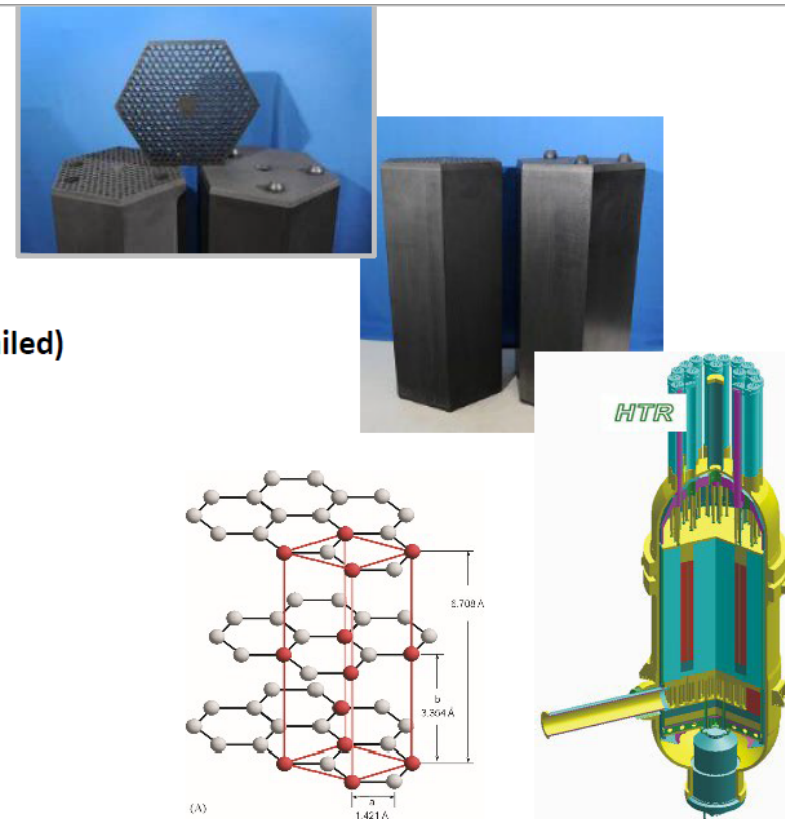


Dr. Windes has over 35 years' experience in extreme materials research with the majority being in nuclear materials. His material interests range widely from solid oxide fuel cell development to space nuclear propulsion systems to spent nuclear fuel issues. However, his focus for the past 20 years has been in the areas of nuclear graphite and carbon-based composite materials for the new High Temperature Reactor design. As the Advanced Reactor Technologies graphite program technical lead, he has overseen the large Advanced Graphite Creep (AGC) irradiation experiment at INL, developed one of the largest unirradiated nuclear graphite material property databases, is the current chair in developing ASME graphite code, and has numerous interactions with the NRC, international organizations, and commercial HTR vendors on graphite related issues. Dr. Windes holds a doctorate in Material Science from the University of Idaho and a Master and Bachelor in Nuclear Engineering from the University of Illinois and UC Santa Barbara, respectively.

For more information, please contact Patricia Paviet at patricia.paviet@pnnl.gov or visit the GIF website at www.gen-4.org

Discussion Points

- Why are we talking about graphite?
- What makes graphite tick?
 - Graphite crystal and microstructure (not too detailed)
 - Anisotropy and pores
 - Engineered composite
- Graphite behavior
 - Irradiation
 - Oxidation
- Some speculation on graphite behavior
 - Interesting irradiation mechanisms
 - Why graphite can not, will not burn
 - Molten salt interactions (a prelude)



Hiroki Hayashino, JAEA, Japan;
Patrick Alexander, TerraPower,
USA; Ron Omberg, PNNL, USA

26 July 2023, Off-gas Xenon
Detection and Management in
Support of MSR, Dr. Hunter
Andrews, ORNL, USA; Dr.
Praveen Thallapally, PNNL, USA

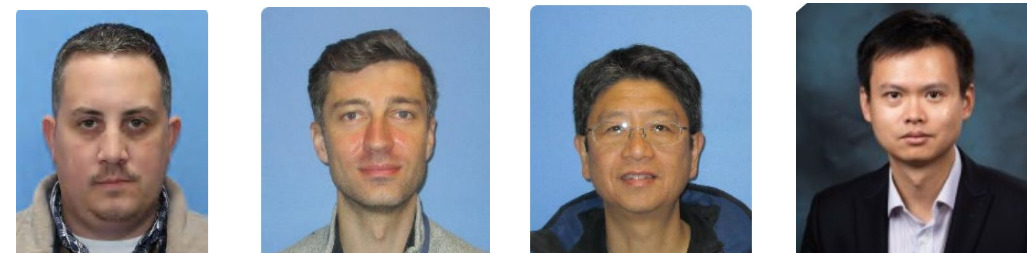
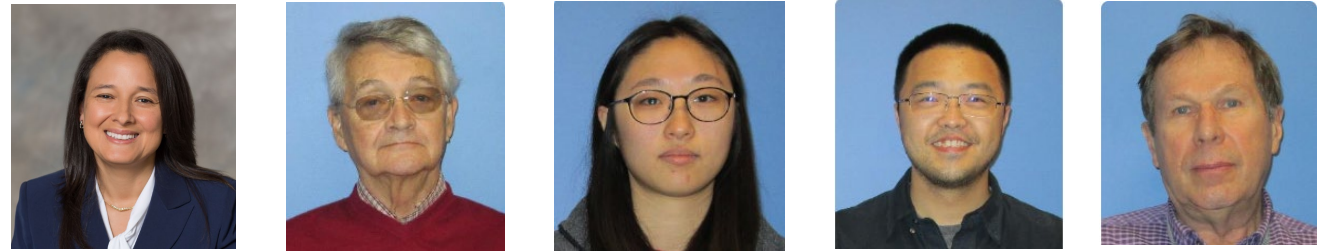
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A recording of the presentation and the slide deck is available from the GIF website (https://www.gen-4.org/gif/jcms/c_82831/webinars).

Team Effort – ORNL Contributors

Nidia Gallego
Cristian Contescu
Jisue Moon
Yuxuan Zhang
Jim Keiser
Adam Willoughby
Dino Sulejmanovic
Jun Qu
Xin He

Many others around ORNL and other collaborators at INL and other organizations



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Advanced Reactor Technology Program

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

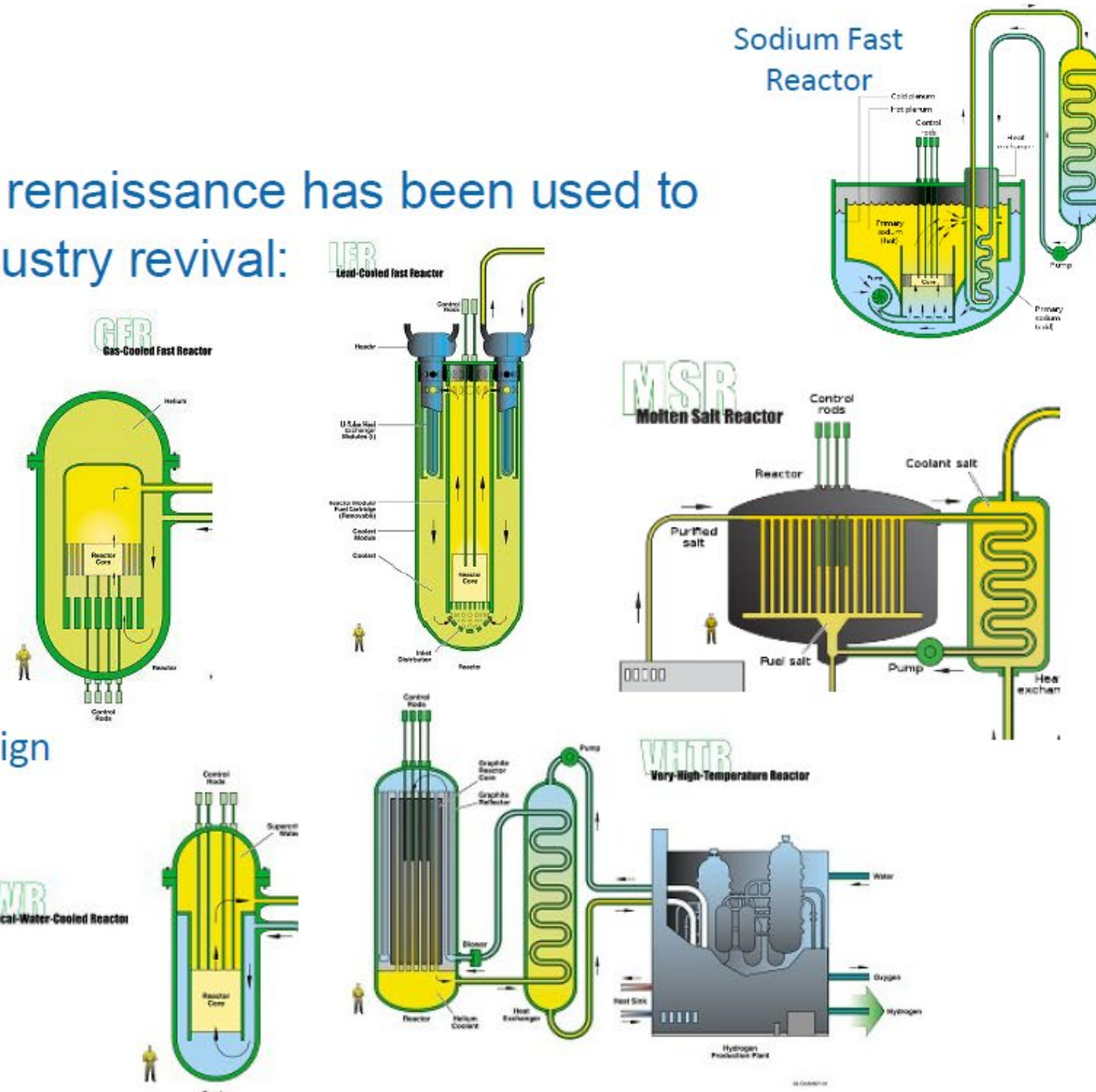
The Nuclear Renaissance

(Since about 2001) the term nuclear renaissance has been used to refer to a possible nuclear power industry revival:

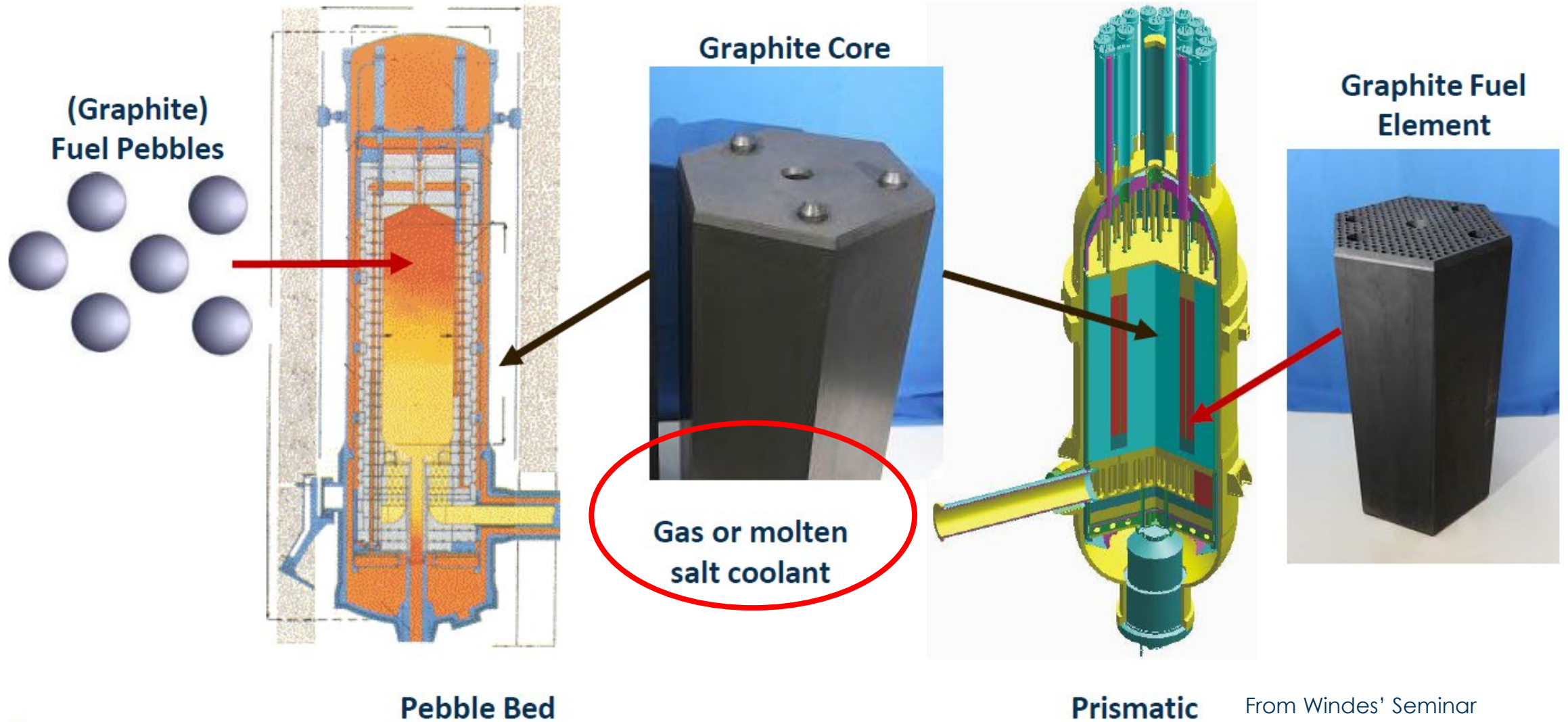
- Rising fossil fuel prices
- Limiting greenhouse gas emission

Generation IV reactor designs

- Inherently & Passively safe
 - Natural shutdown and cooling from design
- New designs = new uses
 - Process heat
 - Small modular designs
 - Variety of coolants and fuels



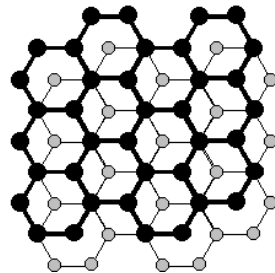
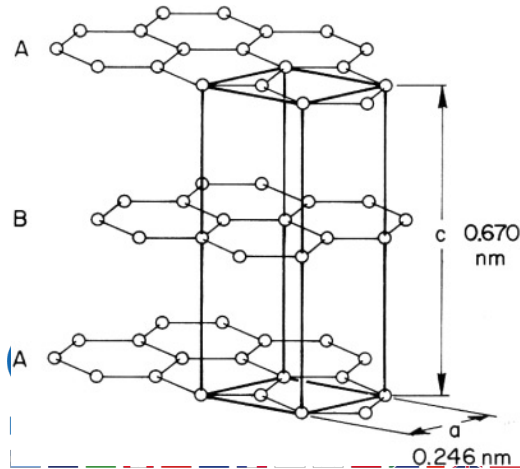
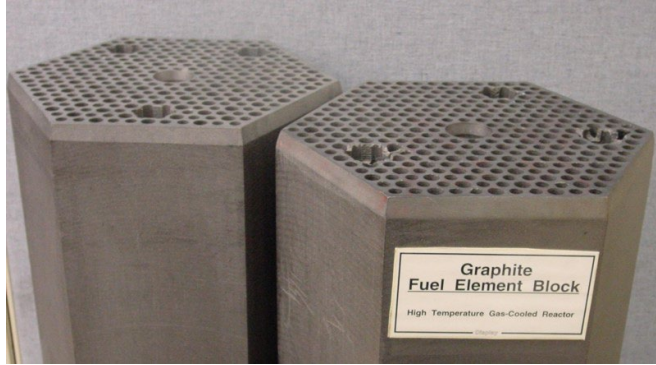
(Very) High Temperature Reactor (HTR)



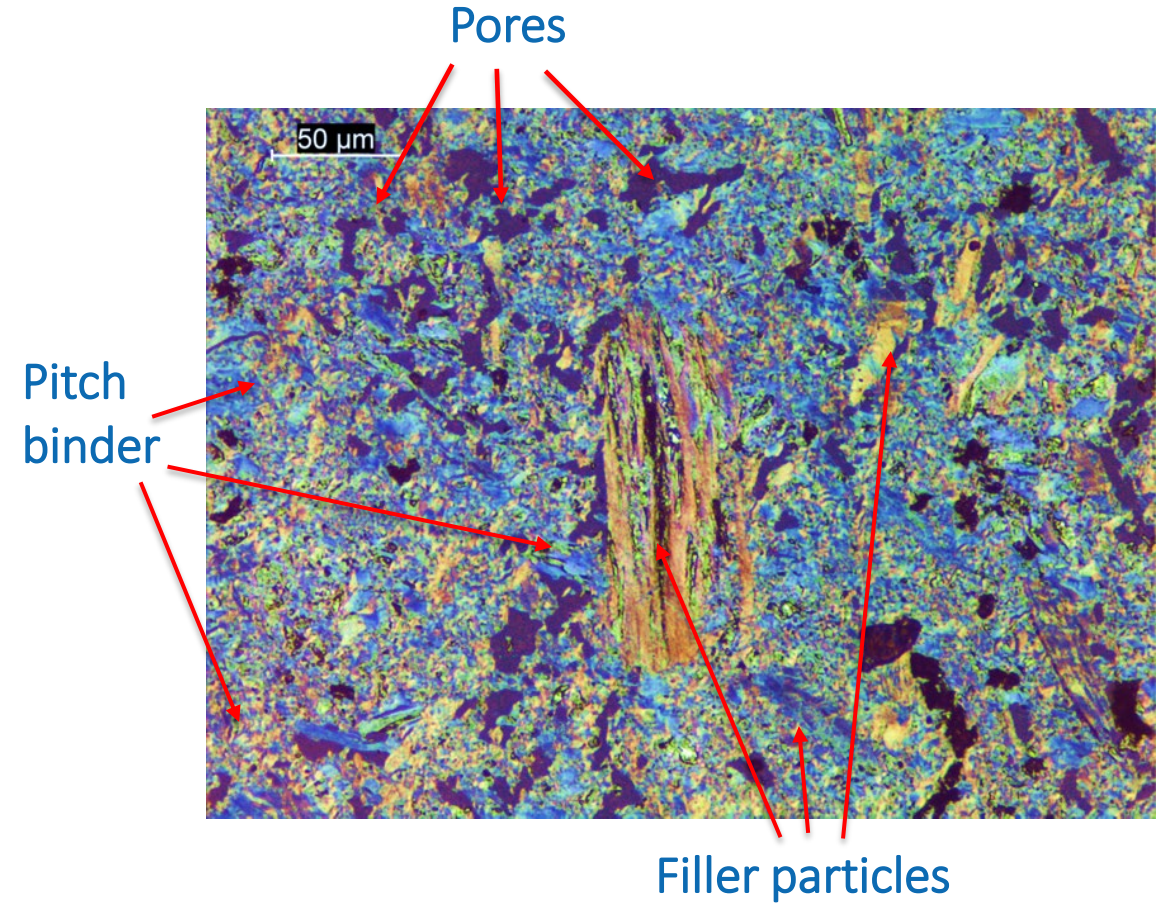
Outline

- Review of Nuclear Graphite and its Microstructure
- Graphite salt intrusion studies
 - Effect of temperature, pressure and time
 - Neutron imaging studies to understand salt penetration depth and distribution
 - Contact angle measurements for the development of predictive models
- Graphite wear behavior in molten salt
 - Wear behavior of graphite pin on stainless steel flat
 - Effect of temperature, sliding speed and environment.
- Summary and On-going Activities

Understanding Manufactured Graphite



- Upper layer (A)
- Lower layer (B)

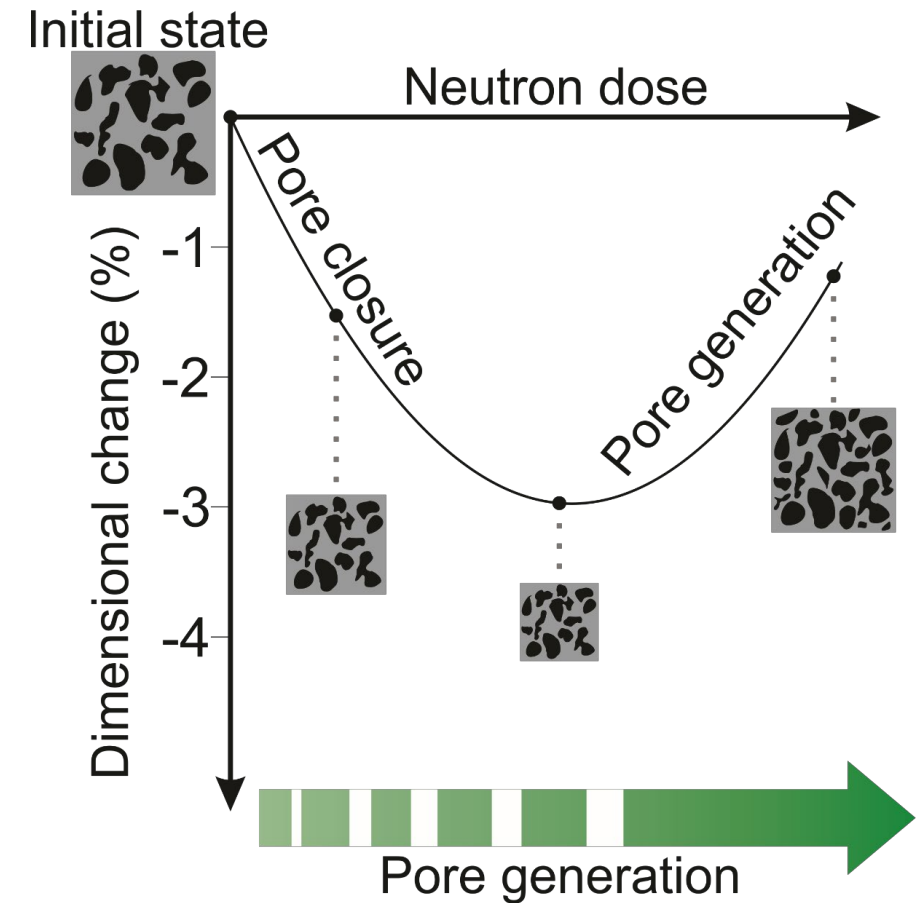
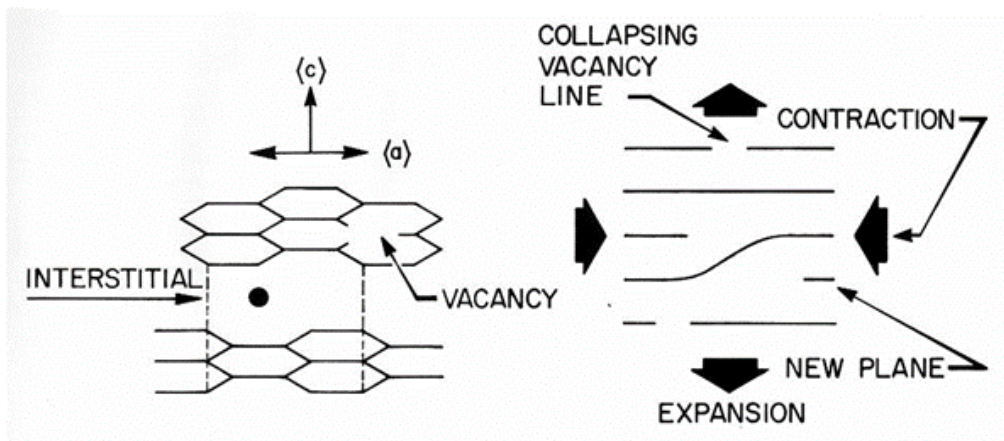


Manufactured Graphite has about **20 % porosity**

Why is porosity important in Graphite?

Microstructure and Porosity Defines the Properties and Irradiation Behavior of Graphite

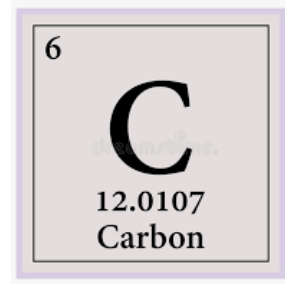
- Graphite contains pores at multiple length scales
- Neutron irradiation affects the size of the porosity in graphite
- The irradiation effects on graphite contribute to the generation of new porosity
- Porosity (edge / basal sites) determines **Reactivity**
- **Oxidation Rates** Correlates with Edge Sites (Porosity)



What does Porosity in Graphite Mean to MSR's?

- Salt intrusion into pores?
- Effect of that salt intrusion on graphite properties?
(mechanical, thermal)
- Chemical Interaction between salt and graphite?
 - Edge sites for tritium retention?

One carbon



... many graphites!

Porosity in graphite comes in different shapes, sizes and connectivity

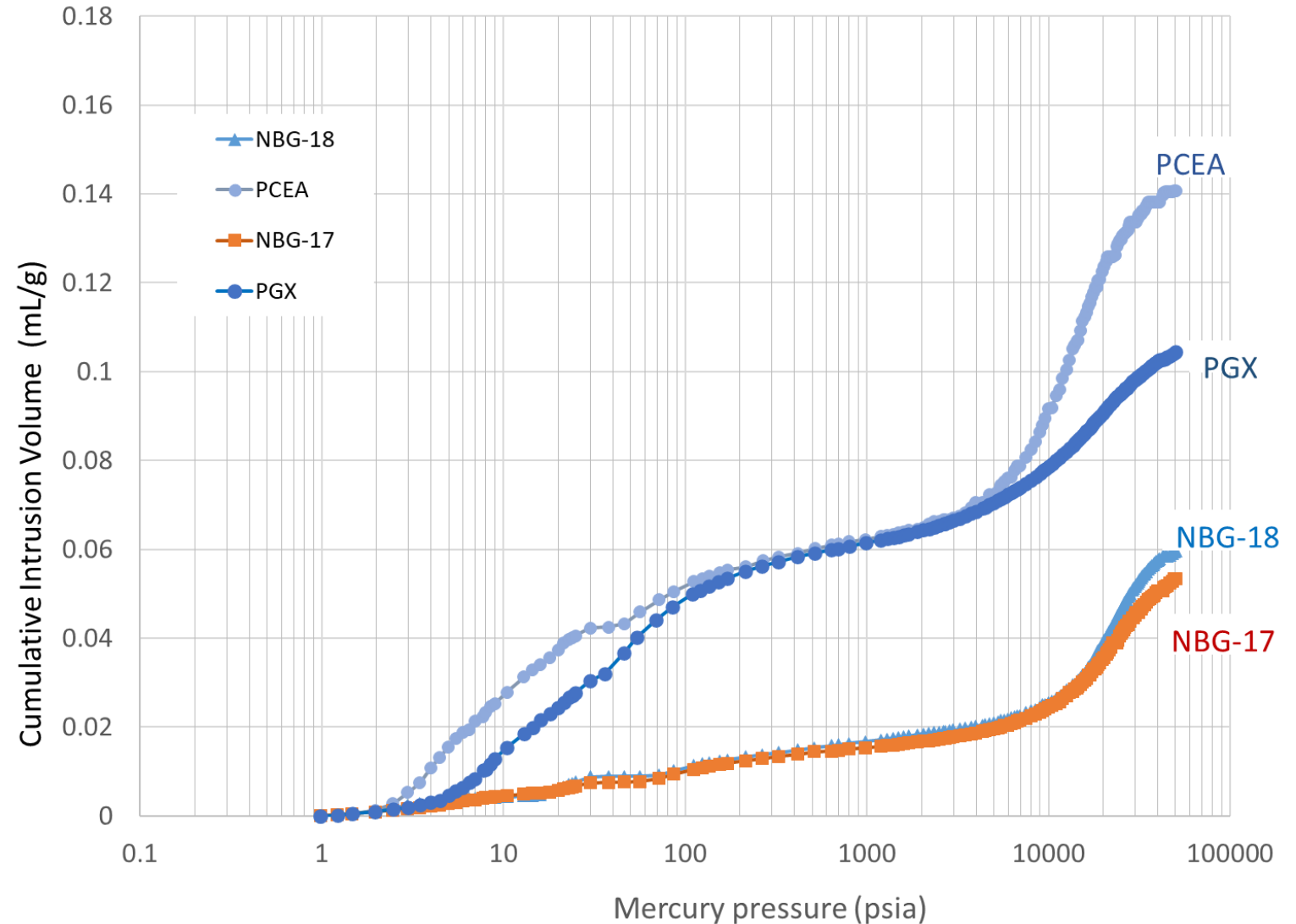
One carbon, many graphite grades

Graphite classification according to ASTM D8075

				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		
MSRE	CGB	Medium	1.86	Union Carbide (USA)		Extruded	
OTHER fine grain graphites	POCO-ZXF-5Q	Microfine < 2	1.78	USA	Low dose	Iso-pressing	
	POCO-AXF-50	Ultrafine < 10	1.78	USA	Low dose	Iso-pressing	
	POCO-TM	Ultrafine < 10	1.82	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)			

Mercury intrusion showed a wide range of porosity distributions in nuclear graphite

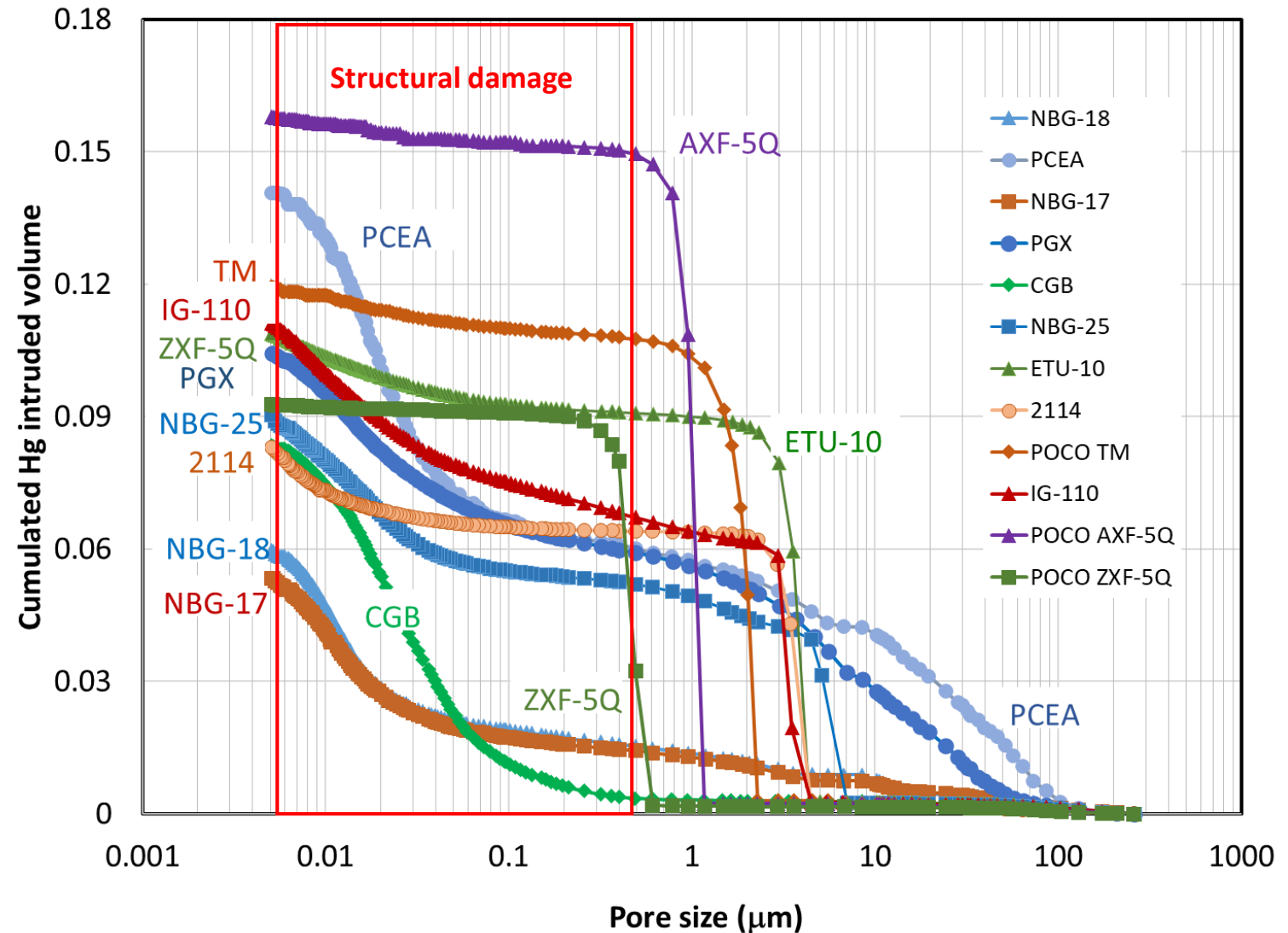
- Fine grade graphites showed a sharp uptake after a given threshold pressure
- Medium and large grain graphites showed a continuing uptake over the whole pressure range



Pore size distribution from mercury intrusion porosimetry

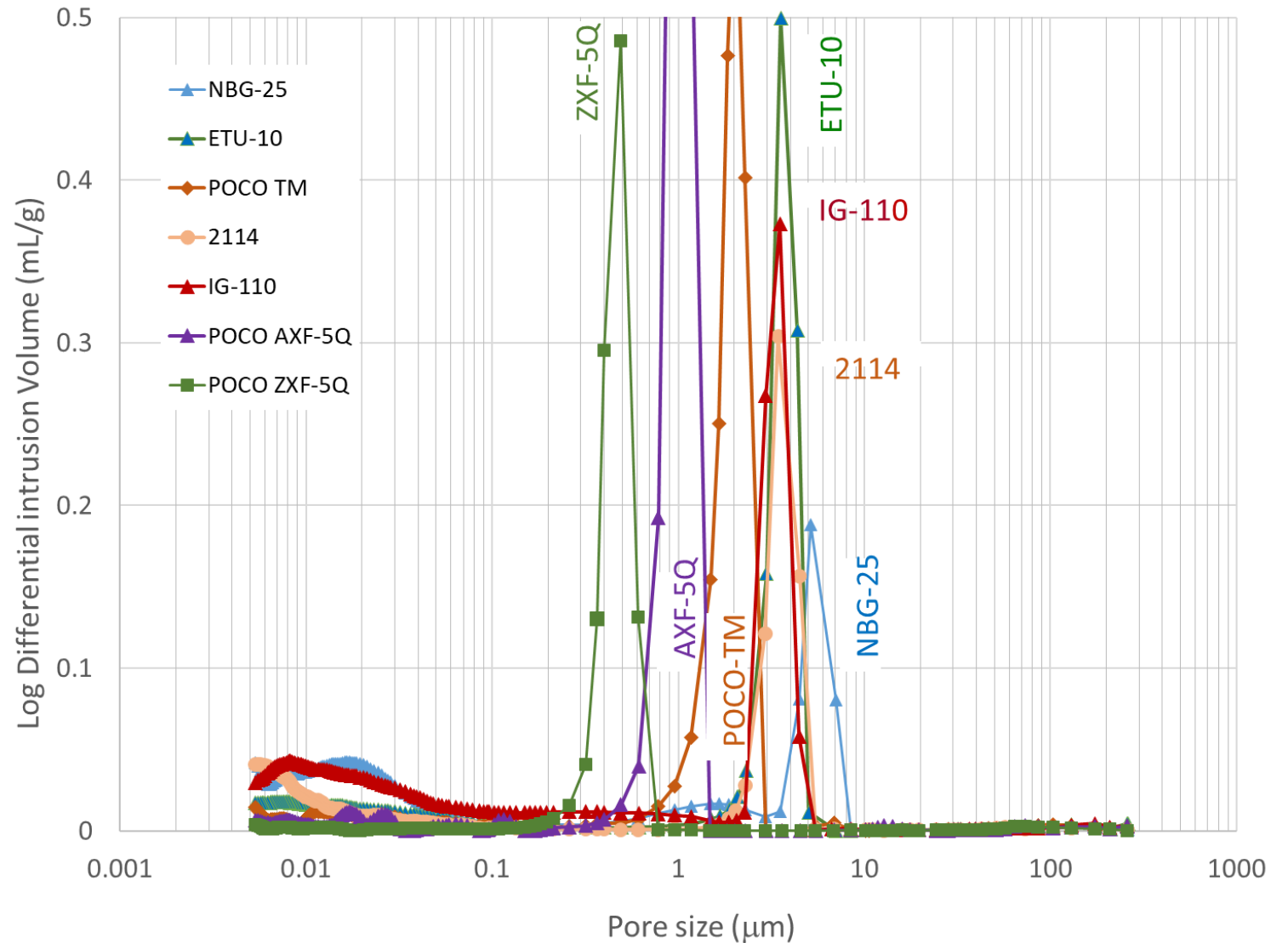
Washburn eq.

$$D_p = - \frac{4 \sigma \cos \theta}{P}$$



Pore size distribution from mercury intrusion porosimetry

Graphite grades	Grain size [μm]	Pore diameter [μm]
CGB	?	< 0.2
ZXF-5Q	1	0.5
AXF-5Q	5	0.9
TM	10	2
IG-110	10	3.9
2114	13	3.5
ETU-10	15	3.6
NBG-25	60	5.1
PGX	460	5.6 & 30
NBG-17	800	3 & 12 & 51
PCEA	800	64
NBG-18	1600	12



How to measure salt intrusion?

ASTM D8091-16 and revised in 2021

for
Graphite with Molten Salt¹

- Guideline for apparatus and procedure for producing graphite specimens impregnated with molten salts
- Introduces two quantification parameters for intrusion:
 - Fraction of open pore volume intruded
 - Fraction of total pore volume intruded
- Guide does not specify sample size or geometry
- Guide does not specify test conditions

How about salt distribution across the cross section of the sample?

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

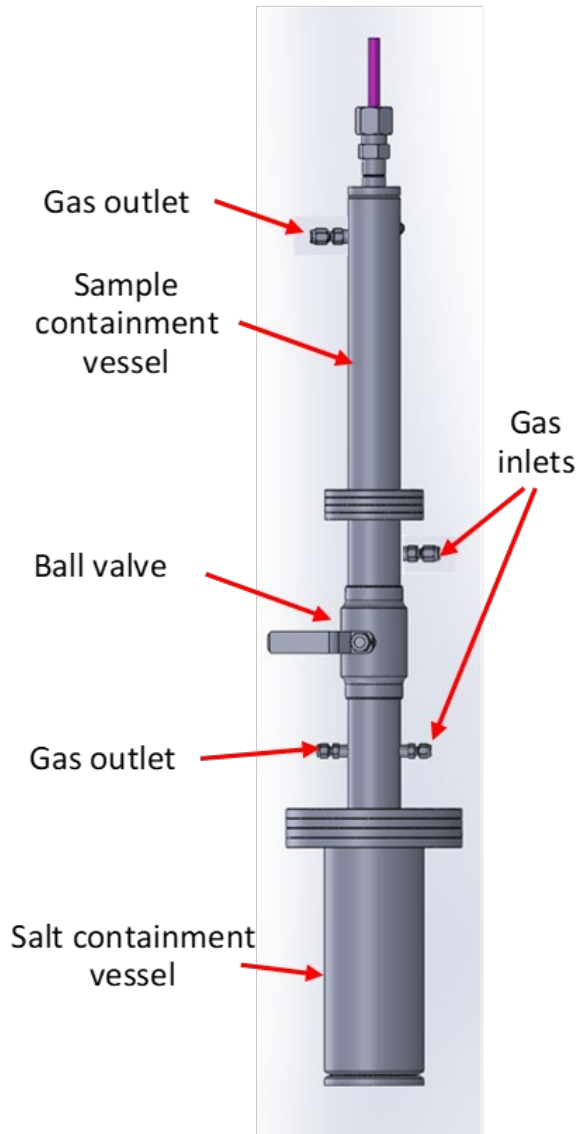
$$D_t = \frac{W_2 - W_1}{\rho V_t}$$

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.

ORNL's Salt Intrusion System



Standard Guide for Impregnation of Graphite with Molten Salt¹



- Designed and built high pressure salt intrusion testing system (approved for FLiNaK)
- The system is designed for operation at temperatures up to 750°C and pressures up to 10 bar
- It includes an all-graphite holder that can accommodate up to six samples
- Includes in-situ vacuum of samples prior to salt intrusion, and cooling under gas pressure after removing from salt

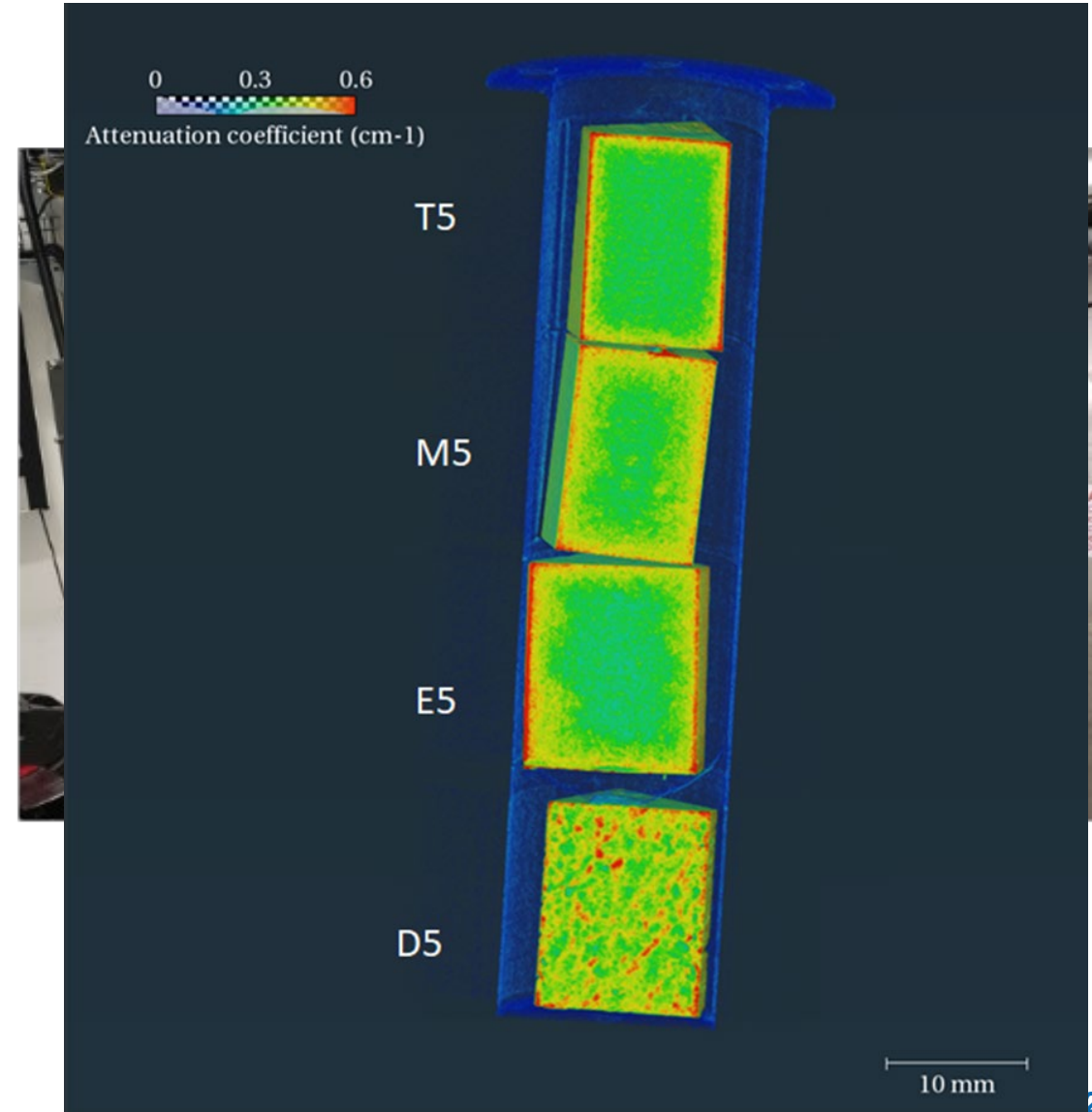
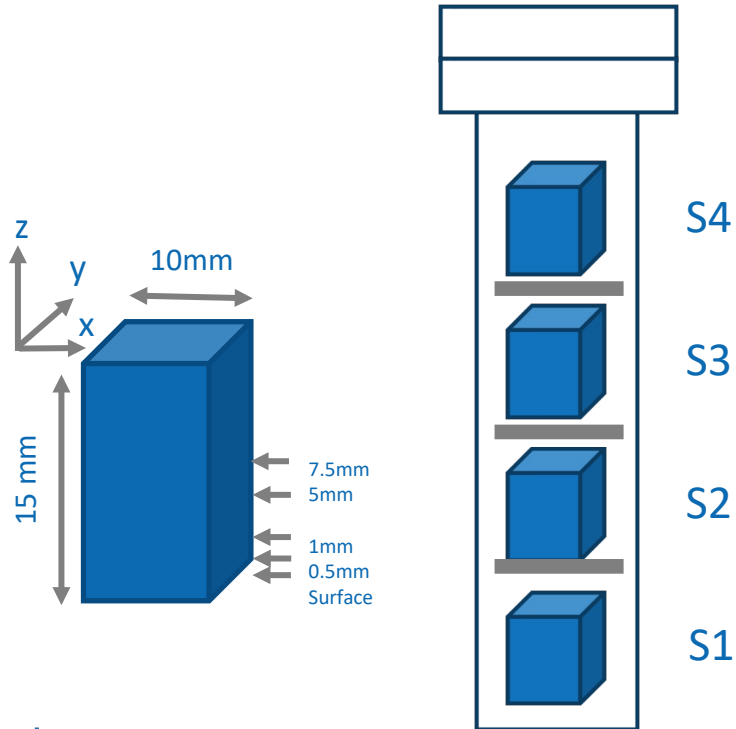


Neutron imaging enables the visualization of salt within the graphite

- Proof of principle experiment at Neutron Imaging Beamline CG-1D (ORNL's HFIR)
- Image resolution $\sim 75 \mu\text{m}$

FLiNaK impregnated graphite samples

- **P: 5 bar**
- **T: 750C**
- **t: 12 hours**

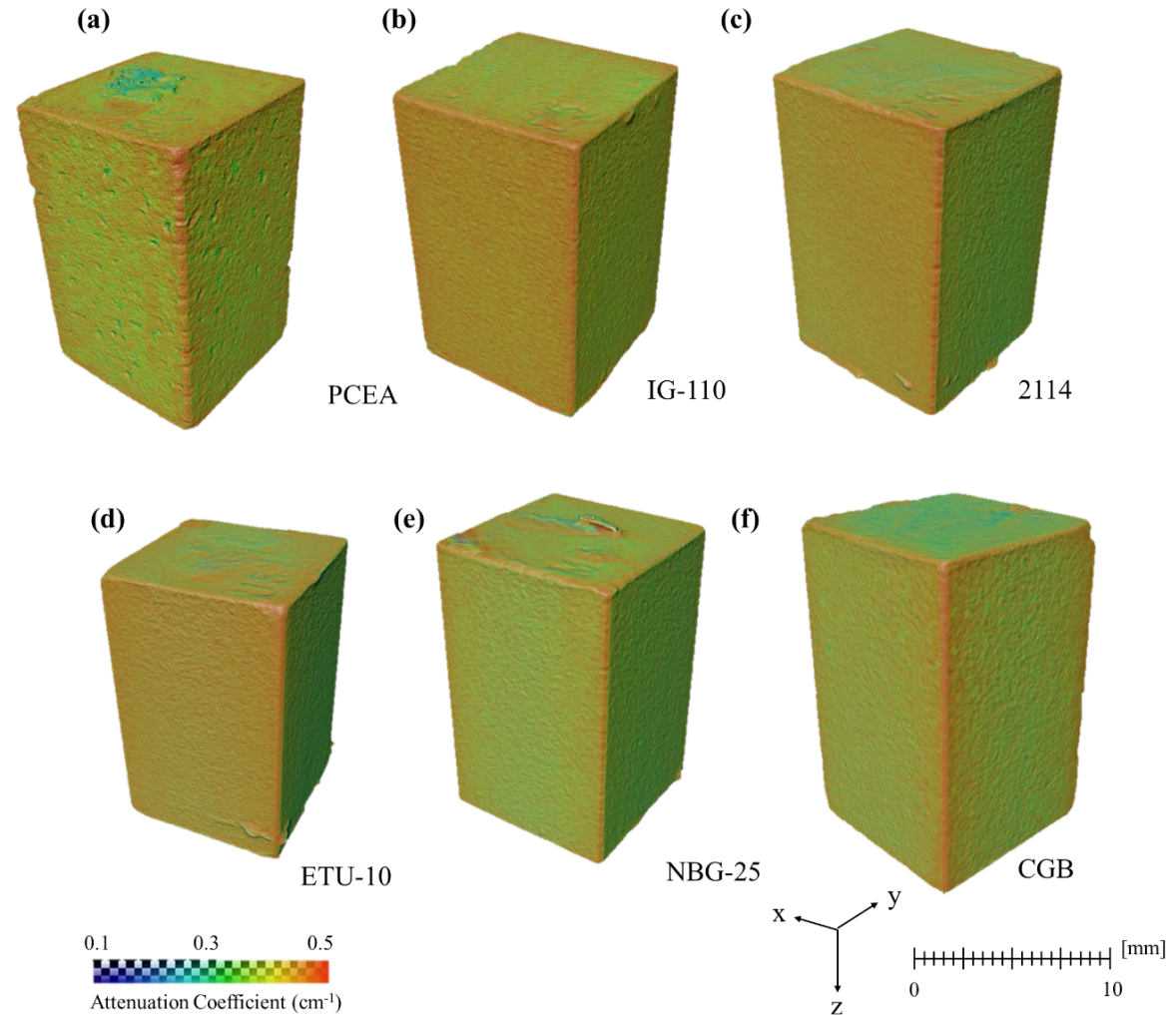


3D reconstructed images of the graphite samples after FLiNaK intrusion

FLiNaK impregnated graphite samples

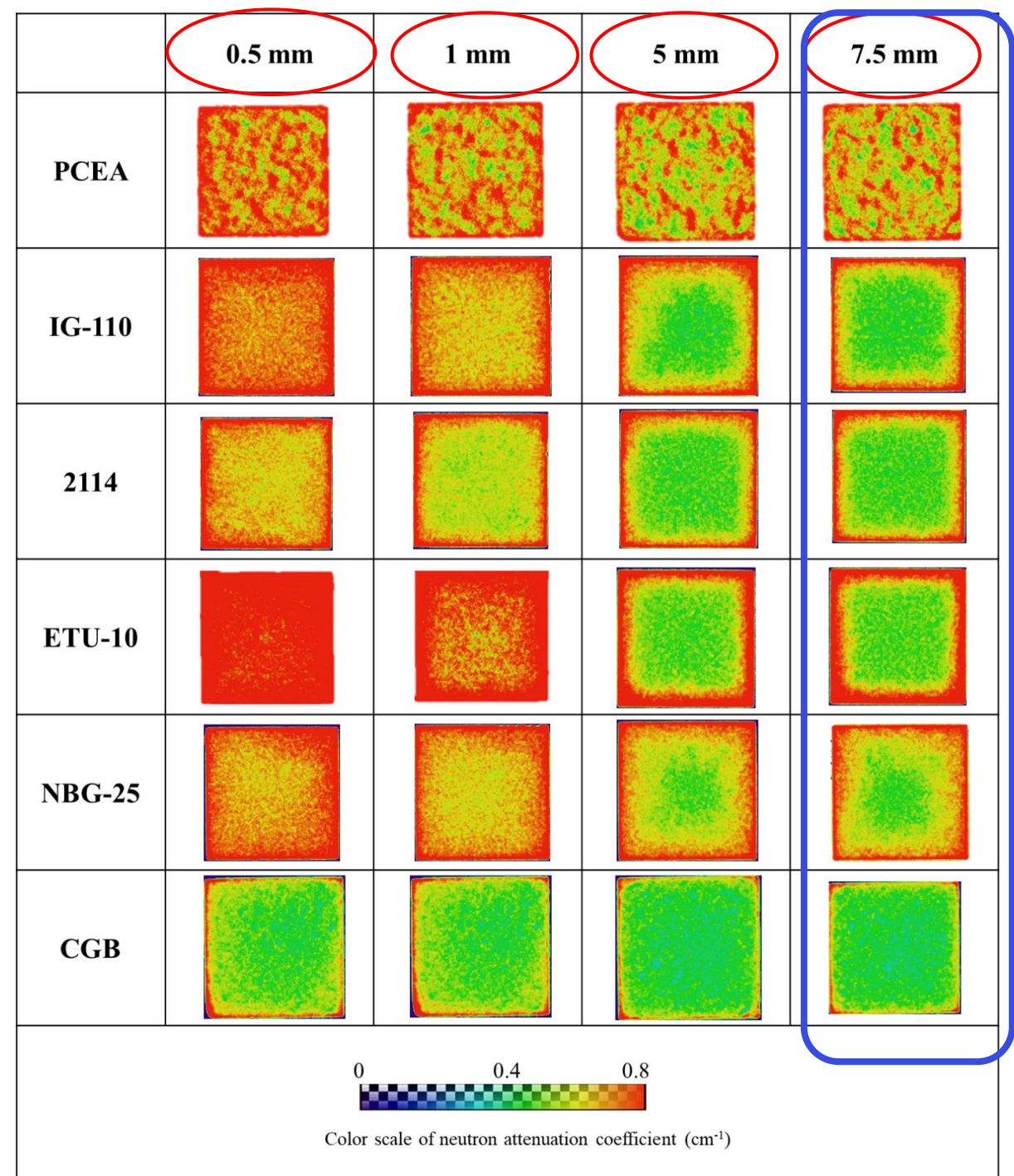
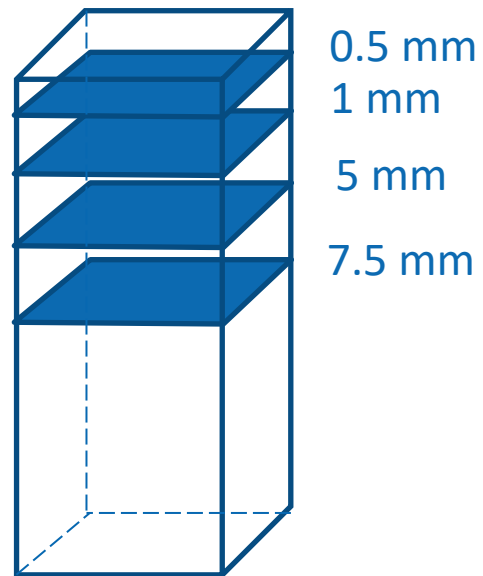
- **P: 5 bar**
- **T: 750C**
- **t: 12 hours**

Moon, Gallego, et al. . Submitted for publication



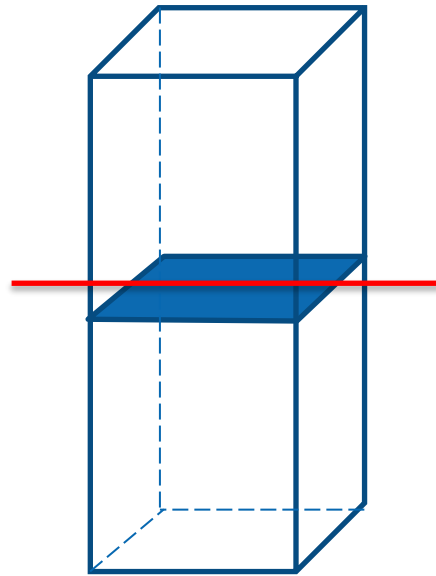
Neutron attenuation coefficient maps

- Neutron imaging planes at various locations allows the understanding of the salt distribution within the graphite sample.



Coverage maps

- Attenuation coefficient maps can be converted to coverage maps utilizing sample properties before and after intrusion.



Sample	Surface image	Line profile at y=4.5	Salt coverage (%)	Curve area
PCEA			20.2	1.92
NBG-25			19.4	1.85
ETU-10			28.4	2.70
IG-110			12.5	1.19
2114			6.7	0.64
CGB			0.98	0.094

Color scale bar for surface images

z
y=4.5 mm
z=7.5 mm
y
x

**A neutron tomography study to visualize fluoride salt (FLiNaK) intrusion in nuclear-grade
graphite**

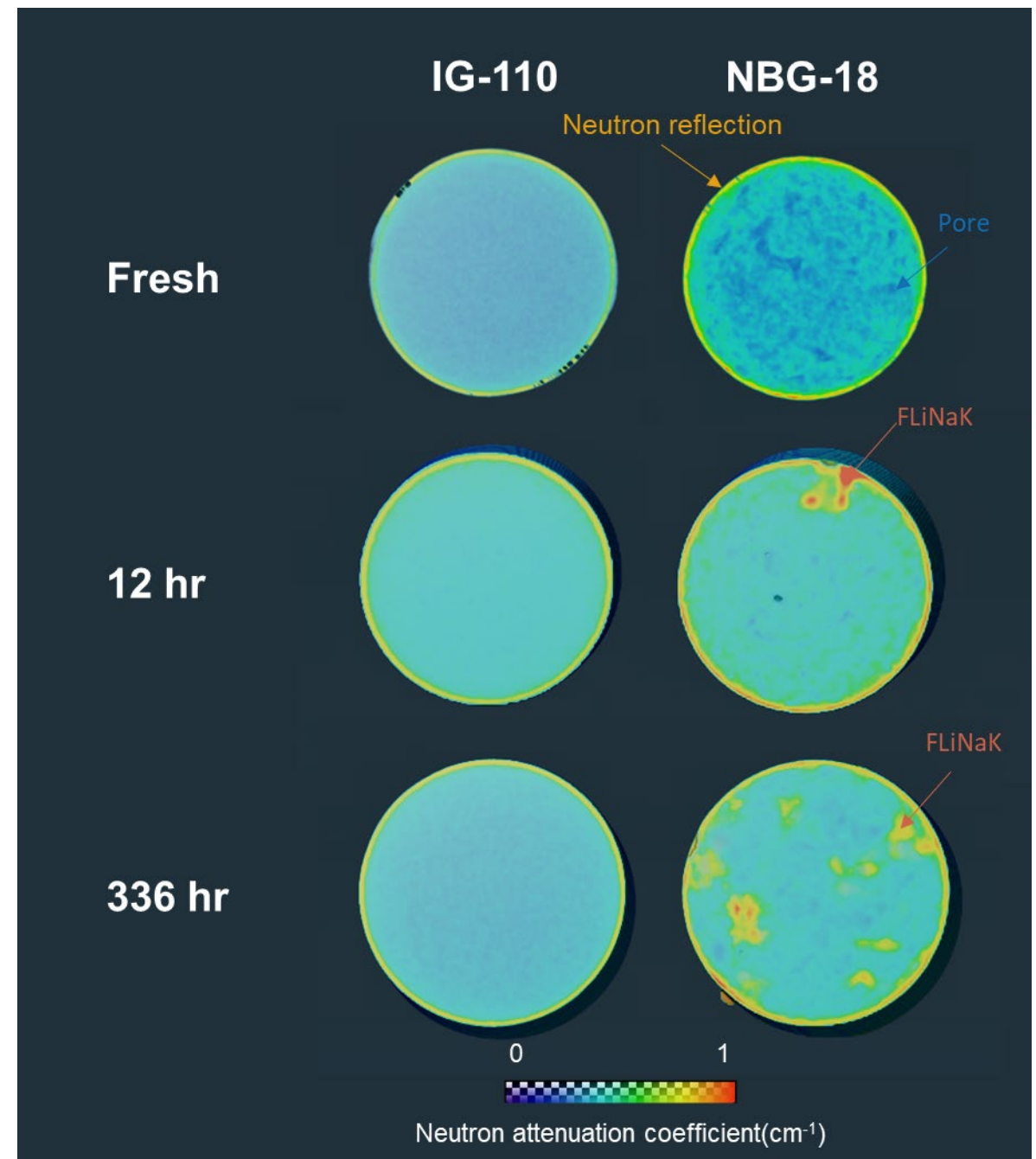
Under review

Jisue Moon^{1*}, Nidia C. Gallego^{2*}, Cristian I. Contescu², James R. Keiser³, Dino Sulejmanovic³, Yuxuan Zhang⁴ and Erik Stringfellow⁴

How about time?

Neutron tomography analysis with different infiltration time

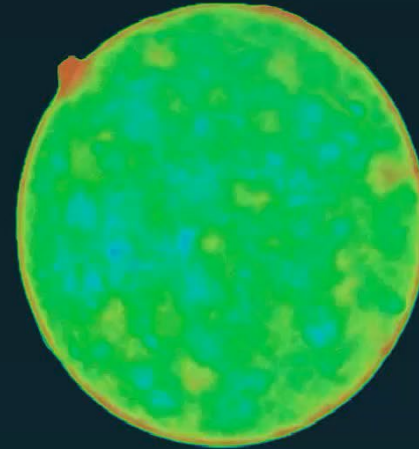
- Graphite sample: cylinders of 10 mm (diameter) X 20 mm (height)
- Infiltration time: 12 hr vs. 336 hr (2 week)
- For fine graphite, there is no evidence of infiltration (both imaging and weight change)
- For coarse graphite, pores near the surface were filled with FLiNaK and the degree of the infiltration increased with time.
- FLiNaK impregnation conditions
 - **P: 3 bar**
 - **T: 750C**
 - **t: 12 hours or 336 hours (2 weeks)**



Preliminary Results

- Intrusion Conditions:
- P: 3 bar ;
- T: 750°C;
- 336 hrs

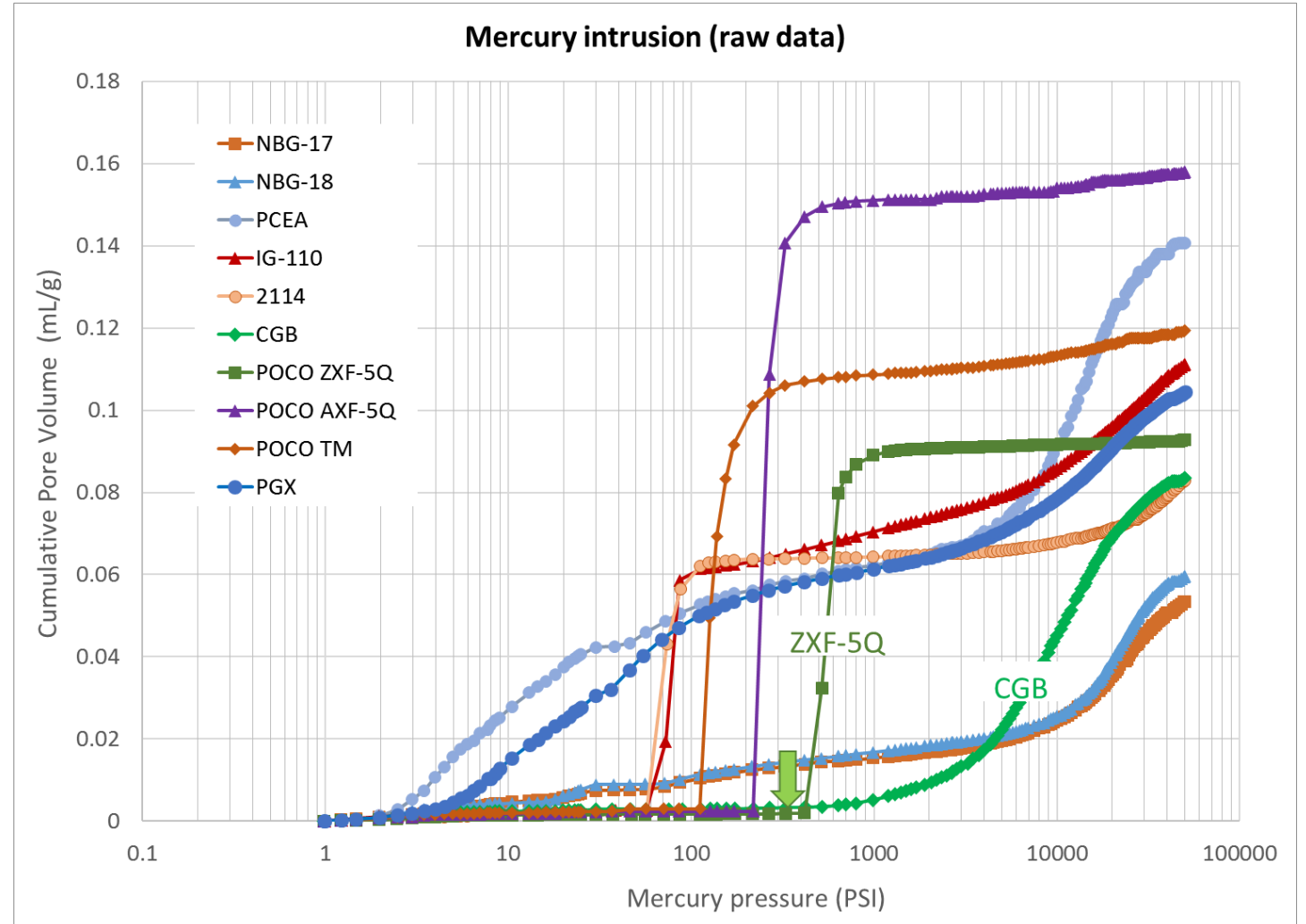
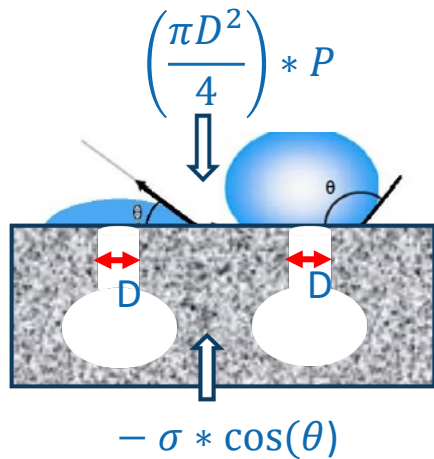
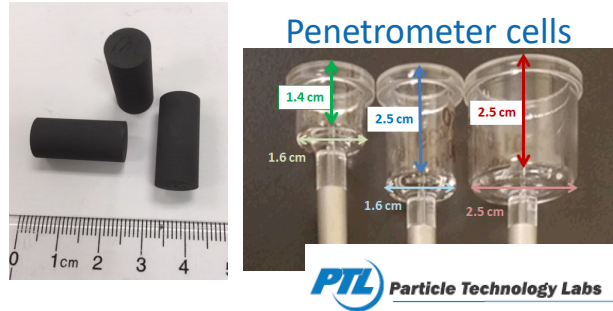
NBG-18 , 1023K, 3bar, 336 hr



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

Can we predict salt intrusion?

The Washburn equation may be used to study how salt might penetrate into graphite



The Washburn equation

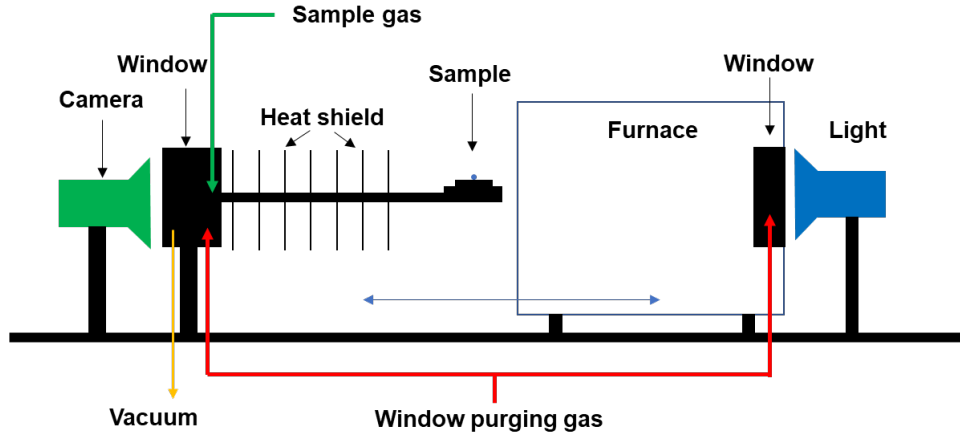
$$P = \frac{4\gamma}{d} \cos \theta .$$

- Pressure differential (P) required to push a fluid into a capillary tube (assumed right cylinders) of diameter (d)

Fluid properties:

- Surface tension (γ) and
- Wetting angle (θ) at the solid-liquid interface

High temperature contact angle measurement

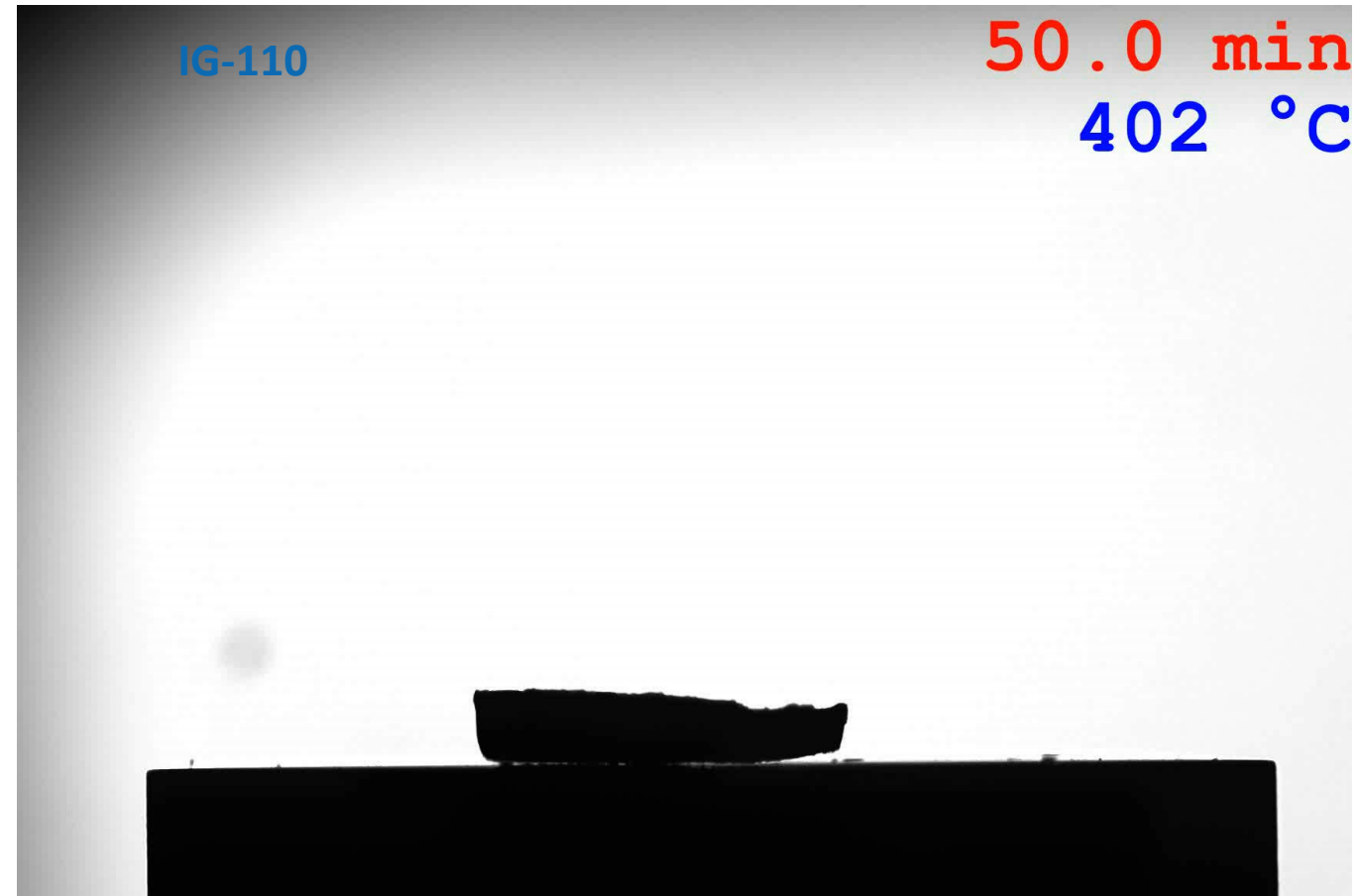


Contact angle measurement condition

- Salt : 3mm diameter salt(~8 mg)
- Graphite dimension: 10mm diameter with 2mm thickness

Salt properties

- FLiNaK Melting point 454 °C



Understanding wear properties of graphite in a molten salt

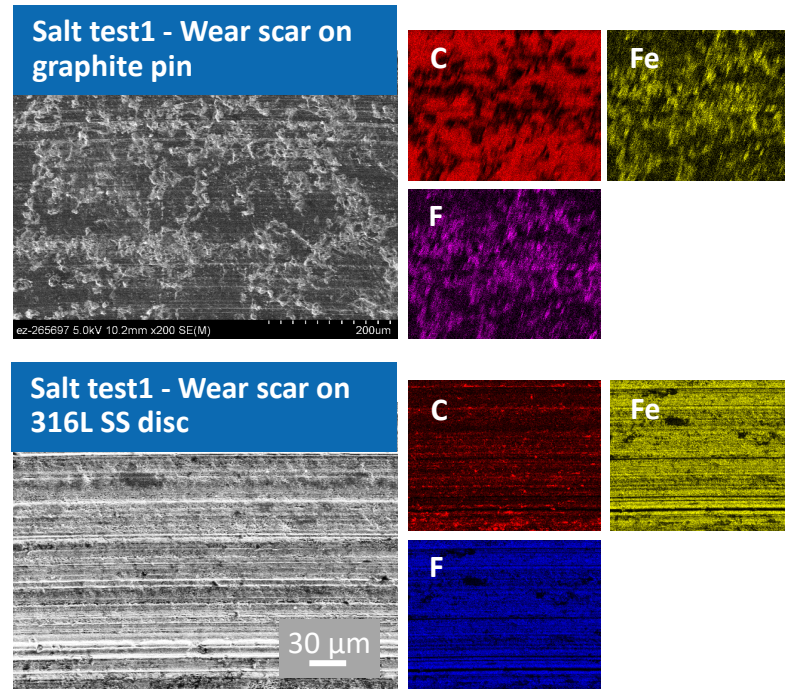
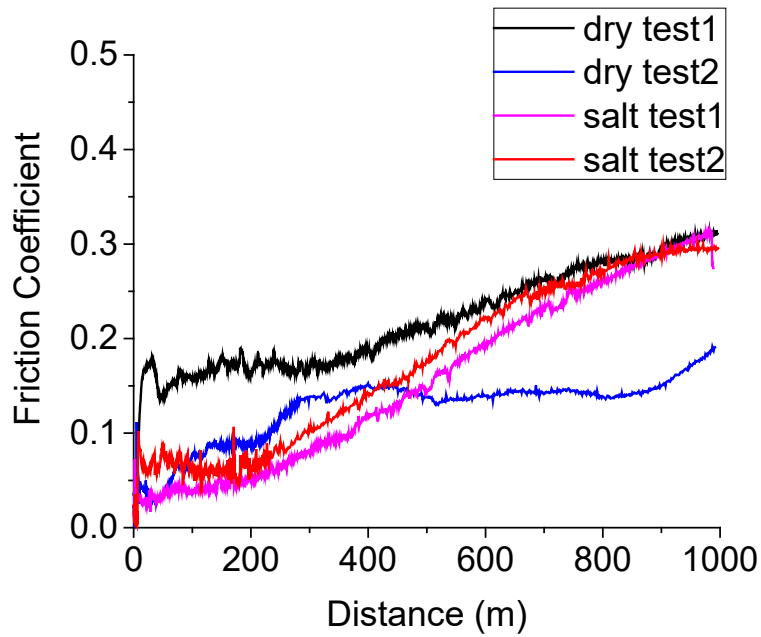
Feasibility Study of Graphite Wear Testing in Molten FLiNaK Salt

Experimental:

- Graphite pin sliding against 316L SS surface
- Salt: FLiNaK
- **Temperature: 550 & 650 °C** (up to 1000 °C)
- Gas environment: Ar
- Normal load: 20 N (up to 100 N)
- Rotating speed: 120 rpm (up to 1000 rpm)
- **Sliding speed: 1, 10 & 100 mm/s**
- Sliding distance: 1000 m (~2 hrs 30 mins)



Initial friction and wear results of graphite pin sliding against 316L SS (Argon vs. molten FLiNaK salt)



Observations:

- Molten FLiNaK appears to significantly increased wear losses of both the graphite pin and stainless steel disc.
- Mutual material transfer occurred between the graphite pin and 316L SS disc.
- Salt-reacted compounds were found on the graphite wear scar, possibly as a result of salt intrusion into graphite pores.
- Salt-reacted compounds were also found on the 316L SS worn surface, possibly as a result of tribocorrosion.

Wear Volume (mm ³)	Dry testing (Argon)		Testing in FLiNaK Salt	
	Test1*	Test2	test1	Test2
Graphite pin	0.32	0.14	0.29	0.53
316L SS disc	(0.02)	(0.01)	0.11	0.07

“() ” represents volume increase or deposit (instead of wear loss)

*Dry test1 might have something wrong based on the surface morphology post test...

Test Matrix for graphite pebble pin sliding against 316H stainless steel (SS) disc in molten FLiNaK salt

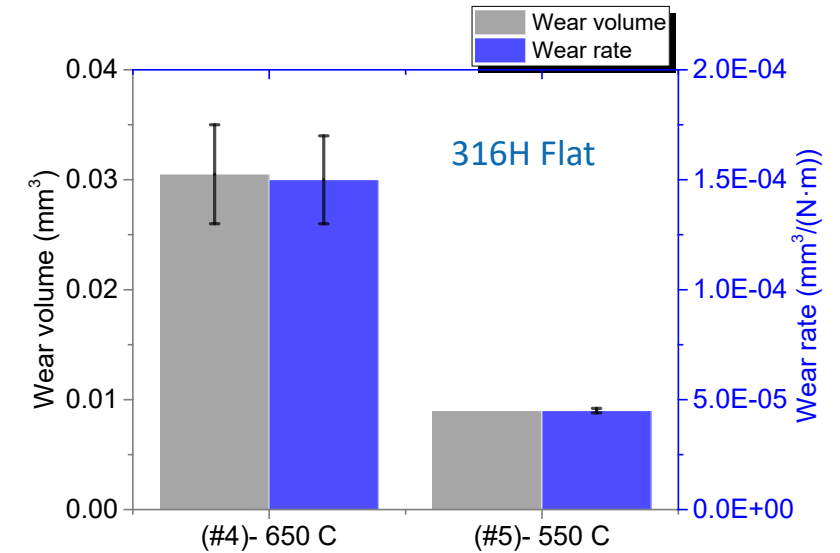
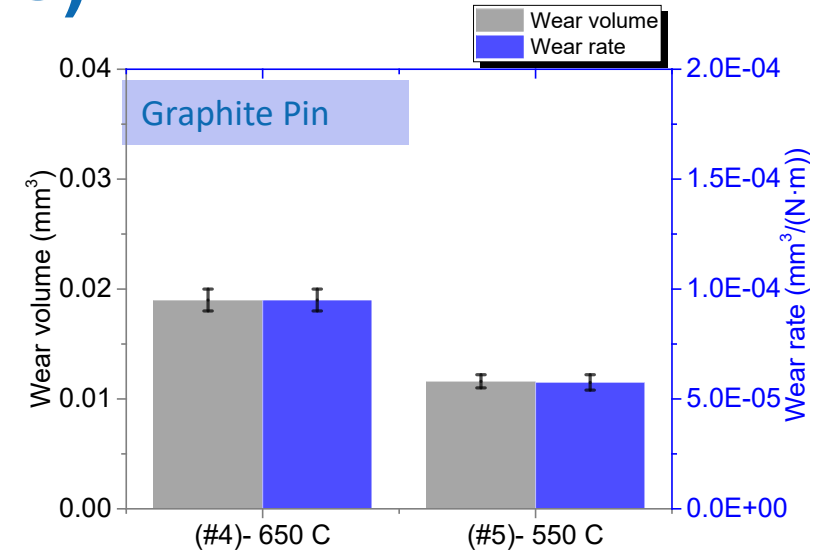
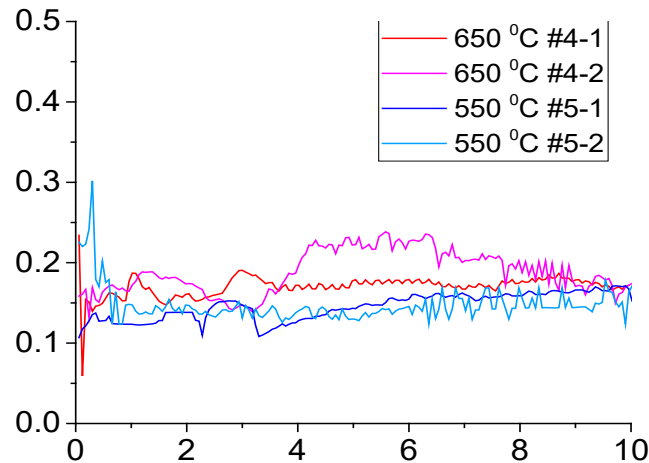
Ar gas, 20 N	Sliding speed (mm/s) – constant test duration (10,000 sec)		
Temperature (°C)	1	10	100
650	(#3) No salt (Dry)		
	(#4) Molten salt flooded	(#6) Molten salt flooded	(#8) Molten salt flooded
	(#9) Molten salt starved		(#7) Molten salt starved
550	(#5) Molten salt flooded		



Effect of Temperature (@Speed = 1 mm/s)

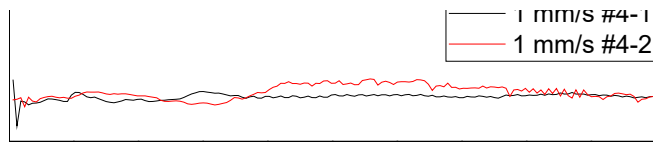
Increased wear losses for both the graphite and 316H SS at a higher temperature with more pronounced change for SS:

- **Viscosity** of the molten salt is lower at a higher temperature, leading to poorer lubrication and thus more solid-solid contact;
- The salt **corrosion rate** on the 316H SS would increase at a higher temperature. On the other hand, the graphite pin is expected to have little corrosion because graphite is chemically inert in the molten salt;
- **316H SS is softened** (more prone to wear) but **graphite becomes stronger** (less prone to wear) at a higher temperature.

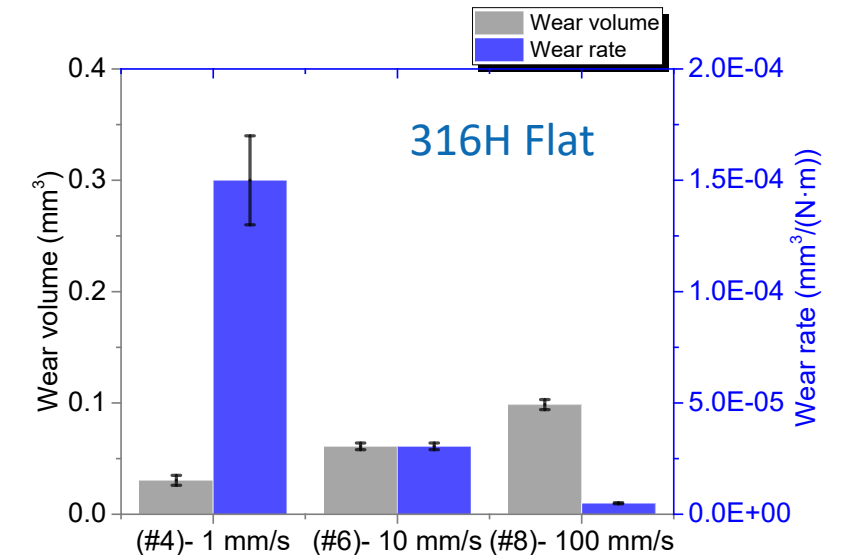
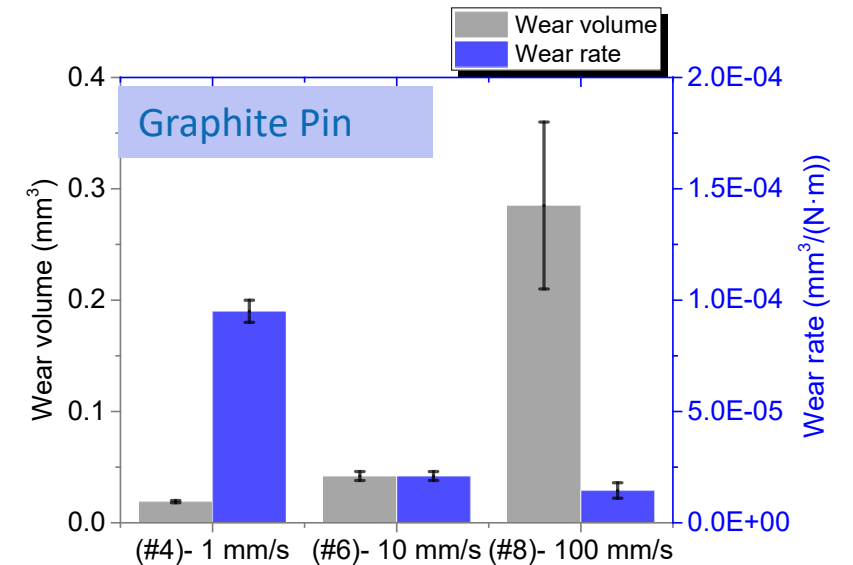


Effect of Sliding Speed

- **A higher speed generated a higher wear volume but a lower wear rate.**
 - A higher speed experienced a longer sliding distance but had a thicker lubricant film at the interface;
 - Running-in generally has a higher wear rate than steady-state because of reducing contact pressure as a result of enlarging contact area (wear scar).
- **Graphite pin wear was smaller at 1 mm/s, became similar at 10 mm/s, and larger at 100 mm/s in comparison with the SS flat wear.**
 - While both the graphite and SS experienced the vibration-induced impact, the brittle graphite is more prone to microfracture and consequently more wear loss when vibration becomes more intense at a higher sliding speed.

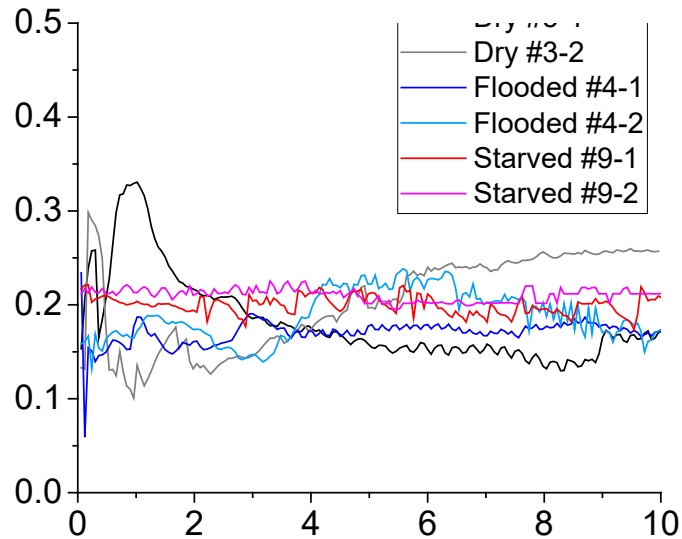


(@T = 650 °C)

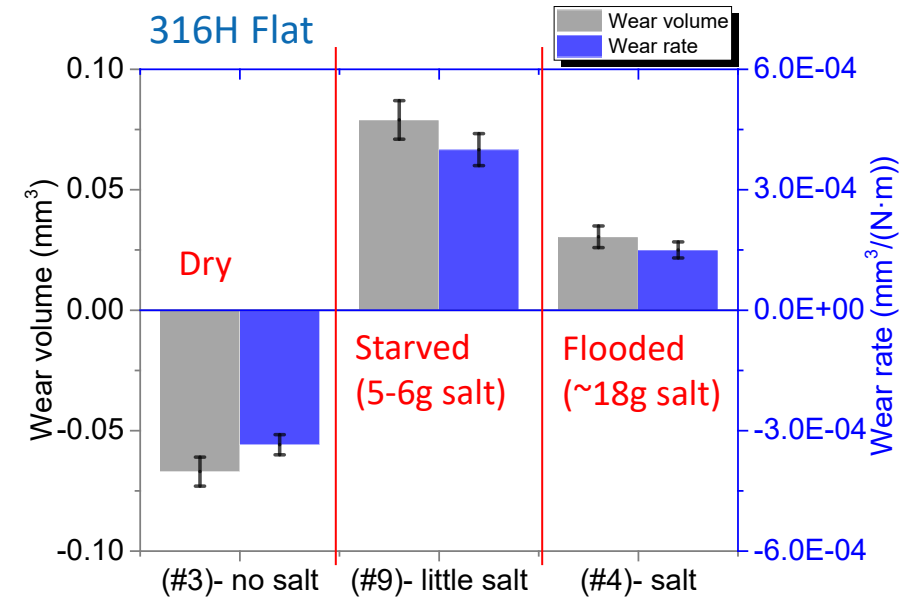
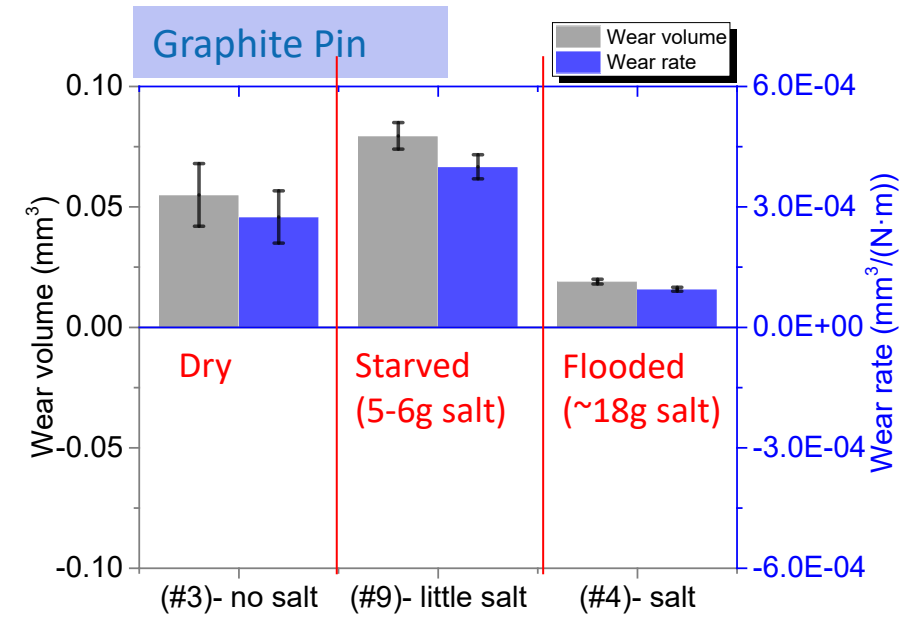


Effect of Salt Presence and Quantity

- **In dry sliding, graphite pin had wear loss but SS flat had deposition.**
 - Volume loss on the graphite pin was similar to volume gain on the SS flat.
- **Molten salt flooded lubrication reduced the graphite wear while made the SS have material removal rather than deposition.**
 - Flooded molten salt lubricated the contact interface to reduce material transfer or adhesive wear.
- **Molten salt starved lubrication generated much more wear on both graphite and SS than either dry or flooded lubrication.**
 - Limited molten salt prevented formation of a self-lubricating graphite transfer film but was unable to provide a stable protective lubricant film at the contact interface.



(@Speed = 1 mm/s & T = 650 °C)

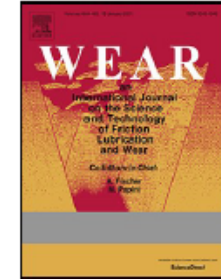




Contents lists available at [ScienceDirect](#)

Wear

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



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

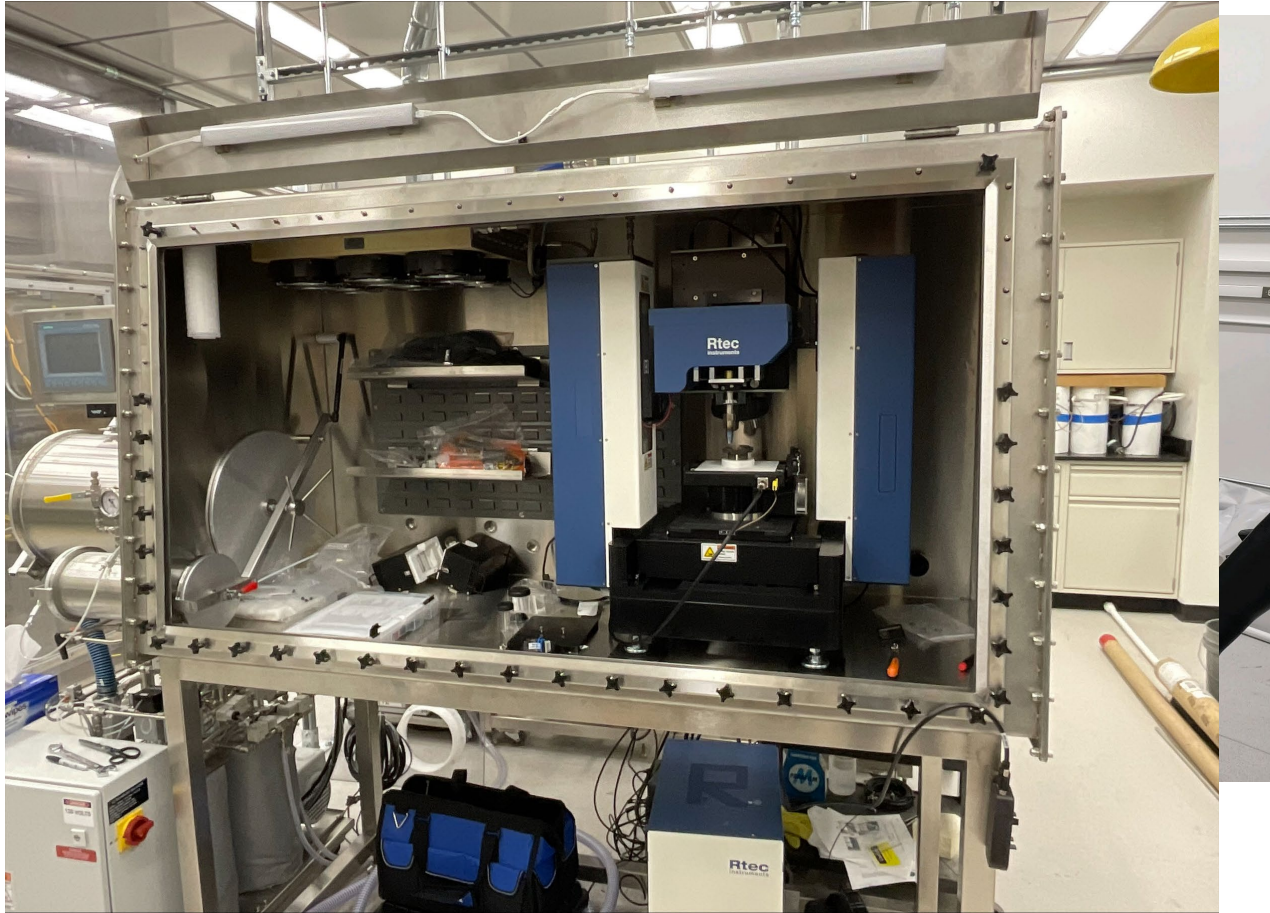
Xin He^a, Chanaka Kumara^a, Dino Sulejmanovic^a, James R. Keiser^a, Nidia Gallego^b, Jun Qu^{a,*}

^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*



New glovebox and tribometer will enable measurements under more controlled environment



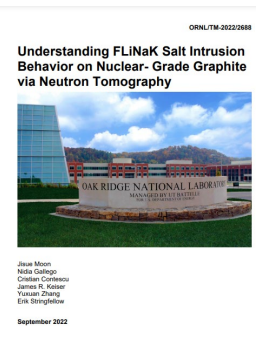
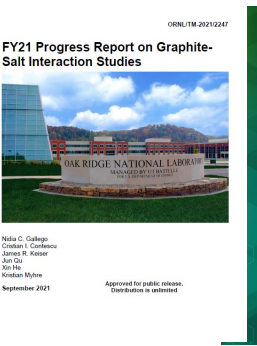
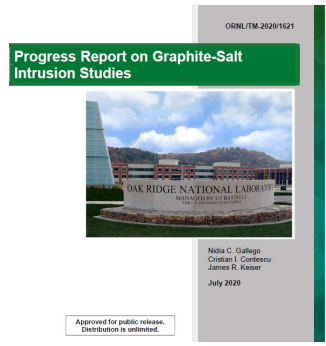
- A customized four-glove glovebox (LC Technology Solutions Inc., of Salisbury, MA) was procured and installed (05/31/2022) by the Graphite –GCR campaign
- New tribometer (RTEC Instruments Inc., from San Jose, CA)(Graphite –GCR campaign): Installed in glovebox; tests are being conducted to exercise capabilities and understand system prior to closing the glovebox
- Tests will be conducted in inert environments and with molten salts.

Summary

- Salt intrusion happens but it is highly dependent on temperature, pressure, time and graphite grade
- Salt distribution and penetration depth is highly dependent on pore structure
- On-going work to further analyze the data collected on effect of intrusion time, and additional neutron imaging time has been approved
- Continue the evaluation of contact angle measurements and the effect of other variables (graphite grade, surface finish, pre-treatment, moisture content, salt impurities...)
- Initial scoping studies of the wear behavior of graphite in molten salts were completed and published.
- New facilities have been installed and will allow us to continue our studies under more control environments.

Publications

- Gallego NC, Contescu CI, Keiser JR, “Progress Report on Graphite-Salt Intrusion Studies” ORNL/TM-2020/1621 (August 2020)
- Gallego NC, Contescu C, Keiser J, Qu J, He X, Myhre K., “FY21 Progress Report on Graphite-Salt Interaction Studies” ORNL/TM-2021/2247 (October 2021)
- Moon J, Gallego NC, Contescu C, Keiser JR, Zhang Y, Stringfellow E, “Understanding FLiNaK salt intrusion behavior on nuclear grade graphite via neutron tomography” ORNL/TM-2022-2688 (September 2022)
- Vergari L, Gallego N, Scarlat S, et al., Infiltration of molten fluoride salts in graphite: phenomenology and engineering considerations for reactor operations and waste disposal. J Nuclear Materials, 154058. (2022)
- Myhre K, Andrews H, Gallego NC, et al., Approach to using Three-Dimensional Laser Induced Breakdown Spectroscopy Data to Explore the Interaction of Molten FLiNaK with Nuclear Grade Graphite (JAAS 37 (8), 2022, 1629-1641)
- Gallego NC, Contescu CI, Paul R, “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, ASTM 2023
- He X., Qu J, et al., Tribocorrosion of stainless steel sliding against graphite in FLiNaK molten salt (Wear 522 (1) 2023, 204706)
- Workshop Report – being finalized
- Moon J, Gallego NC et al., A neutron tomography study to visualize fluoride salt (FLiNaK) intrusion in nuclear-grade graphite (submitted for publication, under review).



Infiltration of molten fluoride salts in graphite: Phenomenology and engineering considerations for reactor operations and waste disposal
 Lorenzo Vergari^a, Malachi Nelson^a, Alex Droster^a, Cristian Contescu^a, Nidia Gallego^a, Balazs O. Scarlat^{a,*}
^aDepartment of Nuclear Engineering, University of California, Berkeley, CA 94720, USA
^{*}Physical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

GRAPHITE TESTING FOR NUCLEAR APPLICATIONS: THE VALIDITY AND EXTENSION OF TEST METHODS FOR MATERIAL EXPOSED TO OPERATING REACTOR ENVIRONMENTS
 STP 1639, 2022 / available online at www.astm.org / doi: 10.1520/STP163900201010

Nidia C. Gallego,¹ Cristian I. Contescu,¹ and Ryan M. Paul²
 Evaluating the Effects of Molten Salt on Graphite Properties: Gaps, Challenges, and Opportunities

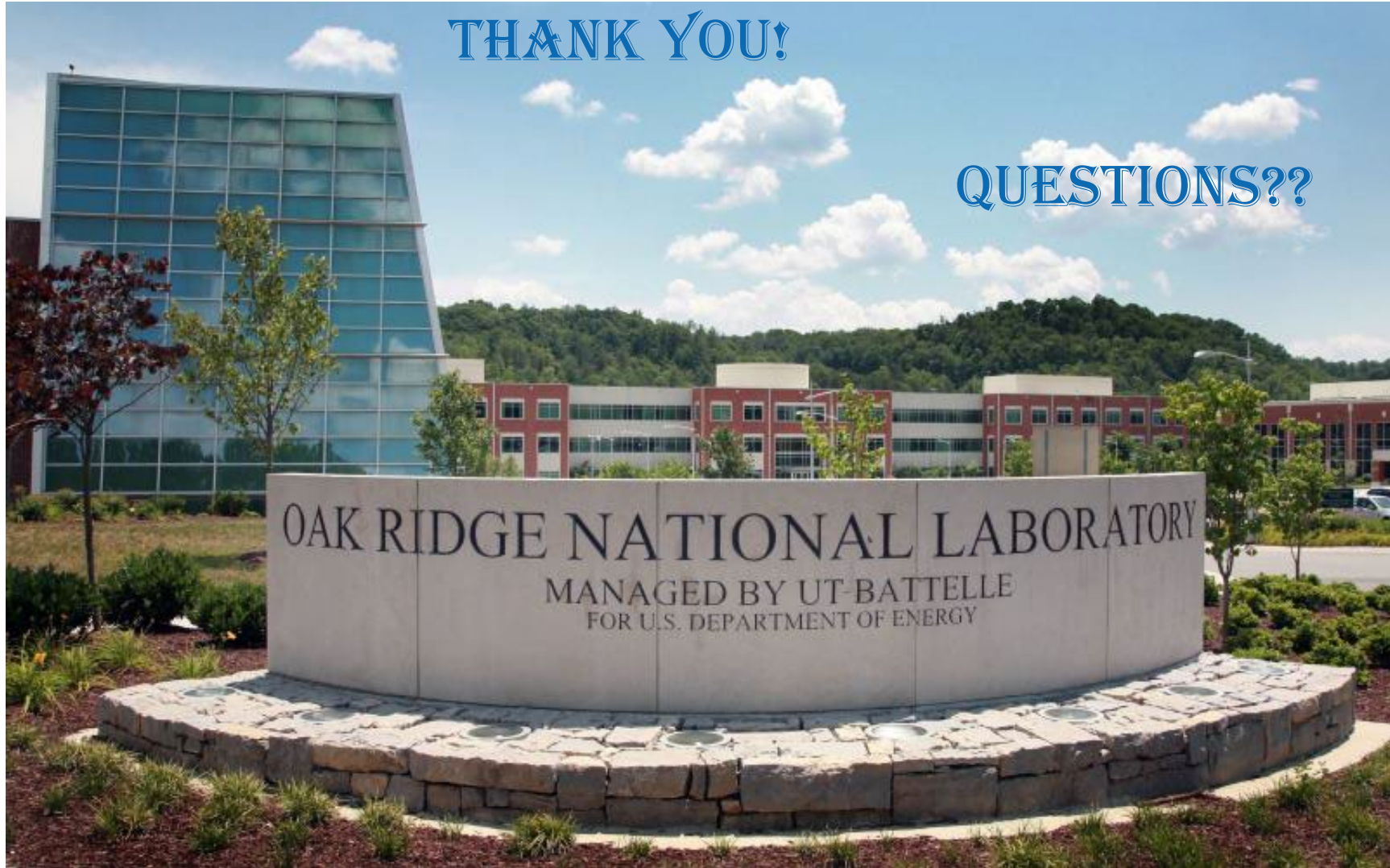


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Upcoming Webinars

Date	Title	Presenter
21 June 2023	Panel Session: International Knowledge Management and Preservation of SFR	Joel Guidez, CEA (retired), France; Hiroki Hayafune, JAEA, Japan; Ron Omberg, PNNL, USA; Cal Doucette, ARC Energy, Canada; and Patrick Alexander, Terra Power, USA
26 July 2023	Off-Gas Xenon Detection and Management in Support of MSR	Dr. Hunter Andrews, ORNL Dr. Praveen Thallapally, PNNL, USA
31 August 2023	Corrosion and Cracking of SCWR Materials	Prof. Lefu Zhang, Shanghai Jiao Tong University, China