U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

OAK RIDGE National Laboratory

Molten Salt Reactor PROGRAM

Graphite Salt Studies

Nidia C. Gallego
Oak Ridge National Laboratory

Annual MSR Campaign Review Meeting 2-4 May 2023

RD-23OR060304: Graphite Salt Studies

We acknowledge Financial Support from ART

- Regulatory (carryover)
- Graphite - GCR

Purpose:

- Assist in the near-term deployment of MSRs by help defining the safe working envelope for nuclear graphite

Objectives:

- To evaluate the performance of various graphite grades in molten salt environments by measuring salt intrusion into graphite porous structure and studying the graphite-salt chemical interactions that may affect structural or physical properties of graphite
- To study wear and erosion behavior of graphite in molten salt

Team Effort – Contributors

Nidia Gallego

Cristian Contescu

Jisue Moon

Yuxuan Zhang

Jim Keiser

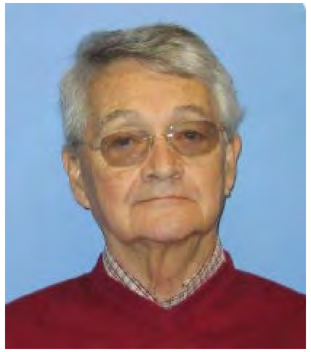
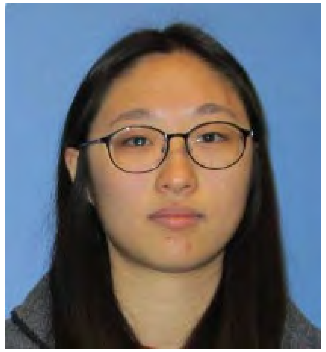
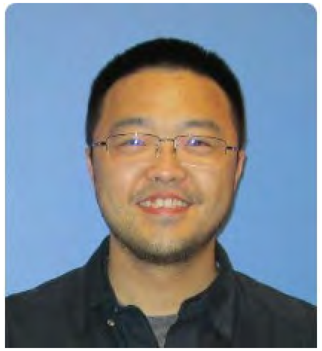
Adam Willoughby

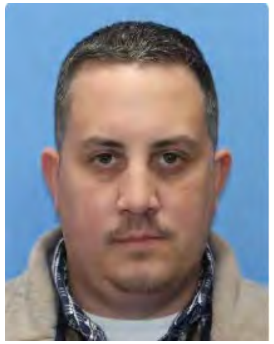
Dino Sulejmanovic

Jun Qu

Xin He

Many others around ORNL




Impact / Accomplishments

Intrusion

- 3 TMs, 1 publication under review, 1 publication under preparation

Wear

- 1 publication completed

ASME / ASTM

- 1 TM report to be issued
- 1 book chapter published in STP book

Intrusion Studies

- Implemented the use of neutron imaging study intrusion and determine salt penetration and distribution
- Commissioned contact angle measurement system and initiated data collection to support development of predicting models

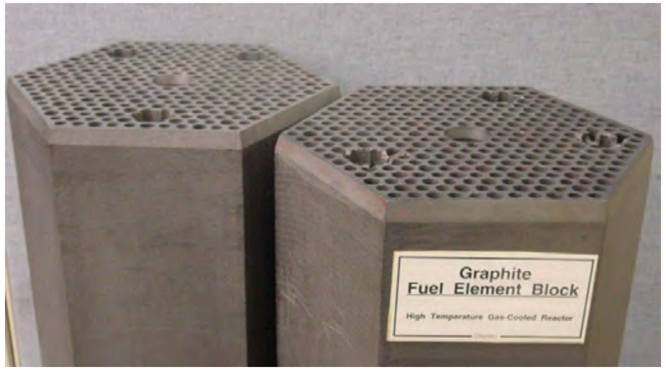
Wear Studies

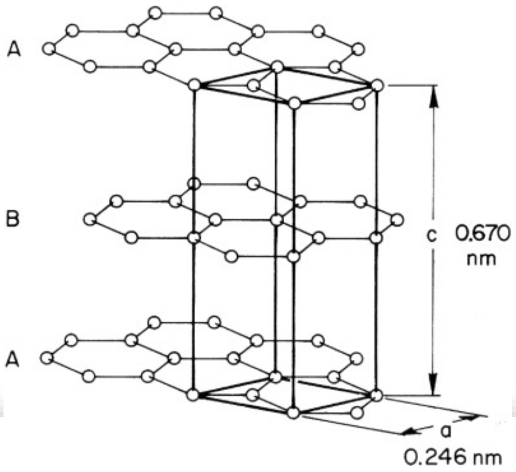
- Completed proof of principle studies of graphite pin on SS flat
- Procured and installed a new glovebox and tribometer that will allow experiments on a more controlled environment
- More controlled experiments to follow

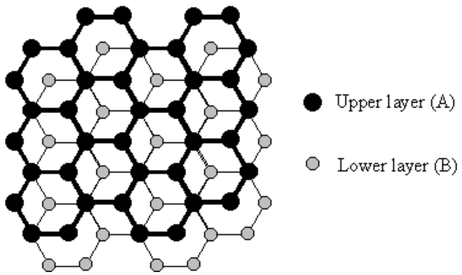
ASME / ASTM / GIF Activities

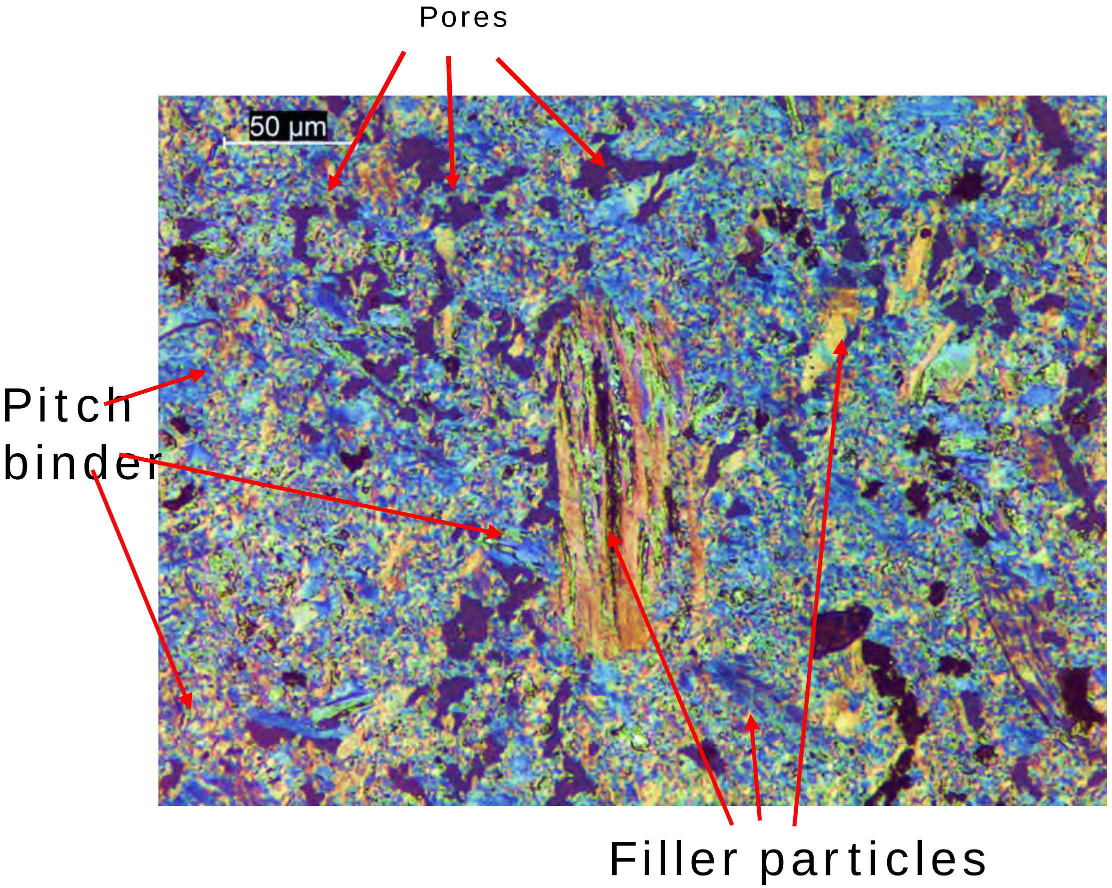
- Join ASME – formed task group
- Hosted a workshop
- Participating in ASTM
- GIF PMB – organized a graphite-MSR session
- GIF Education seminar

Understanding Manufactured Graphite







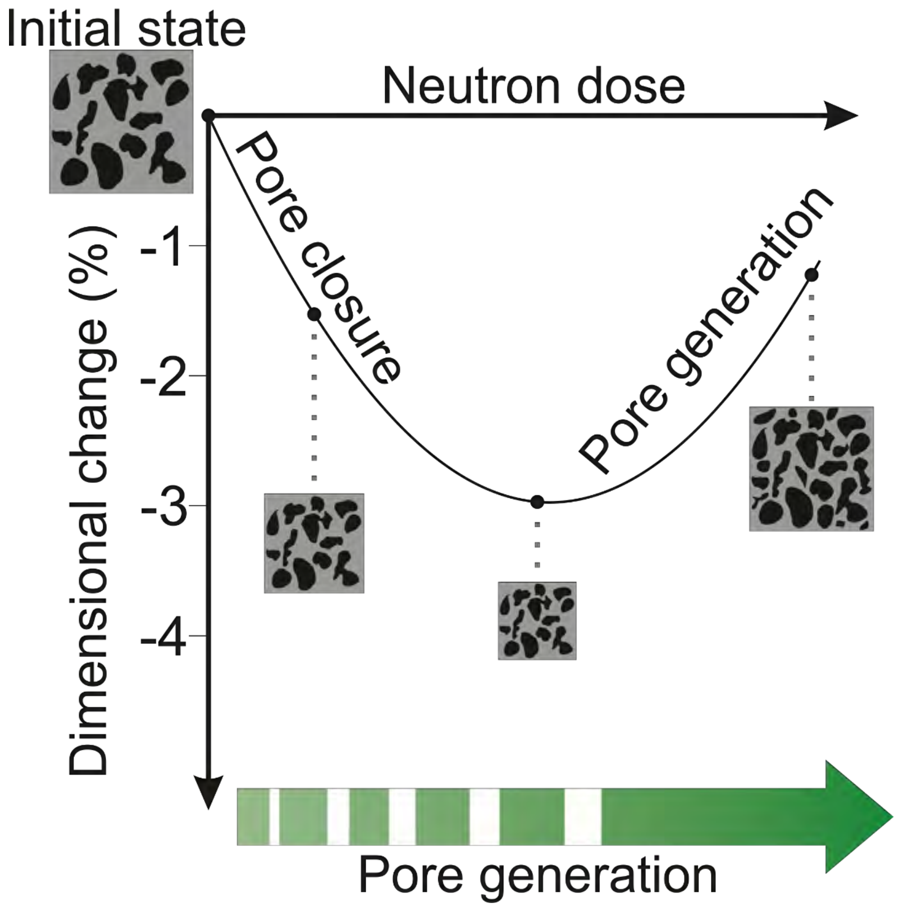


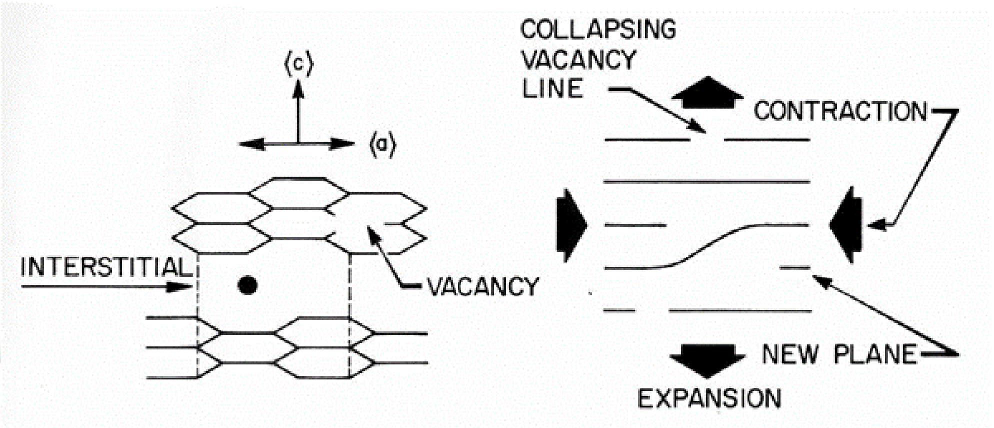
Manufactured Graphite has about **20 % porosity**

Why is porosity important in Graphite?

Microstructure and Porosity Defines the Properties and Irradiation Behavior of Graphite

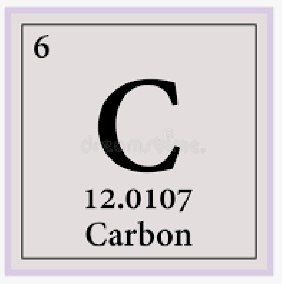
- **Graphite contains pores at multiple length scales**
- **Neutron irradiation affects the size of the porosity in graphite**
- **The irradiation effects on graphite contribute to the generation of new porosity**
- **Porosity (edge / basal sites) determines Reactivity**
- **Oxidation Rates Correlates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





What does Porosity in Graphite Mean to MSRs?

- **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?**

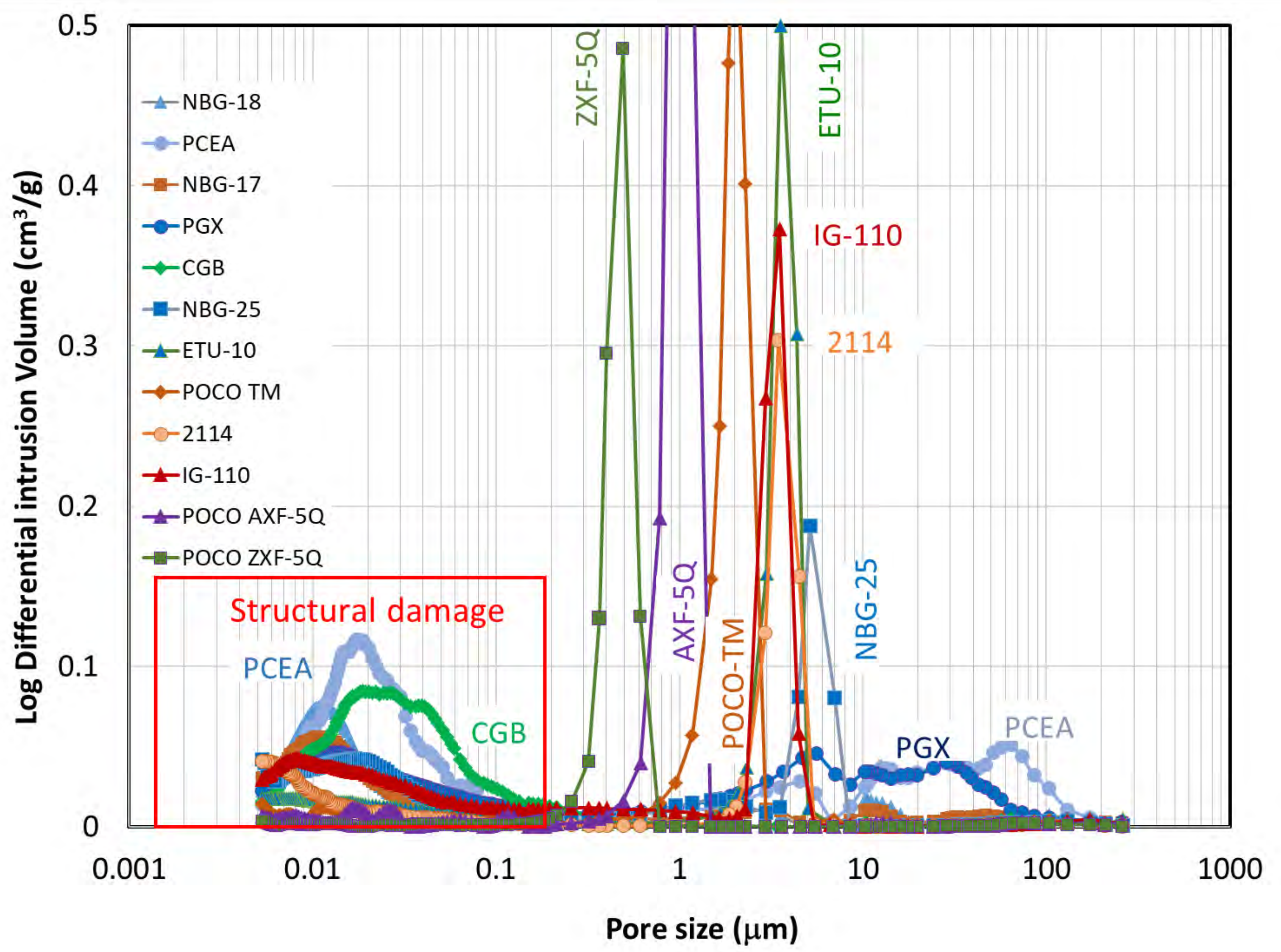
One carbon  … many graphites!

Porosity in graphite comes in different shapes, sizes and connectivity

One carbon, many graphite grades

Graphite 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

		Class	Den [g/c
	H-451	Medium	1.7
OTH	IGS743NH	Superfine < 50	1.8
	ETU-10	Superfine < 50	1.7



How to measure salt intrusion?

ASTM D8091-16 and revised in 2021

- 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 (D_0)
  - Fraction of *total pore* volume intruded (D_t)
- Guide does not specify sample geometry or size
- Guide does not specify equilibrium conditions

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

Designation: D8091 – 21

Standard Guide for Impregnation of Graphite with Molten Salt[1]

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

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

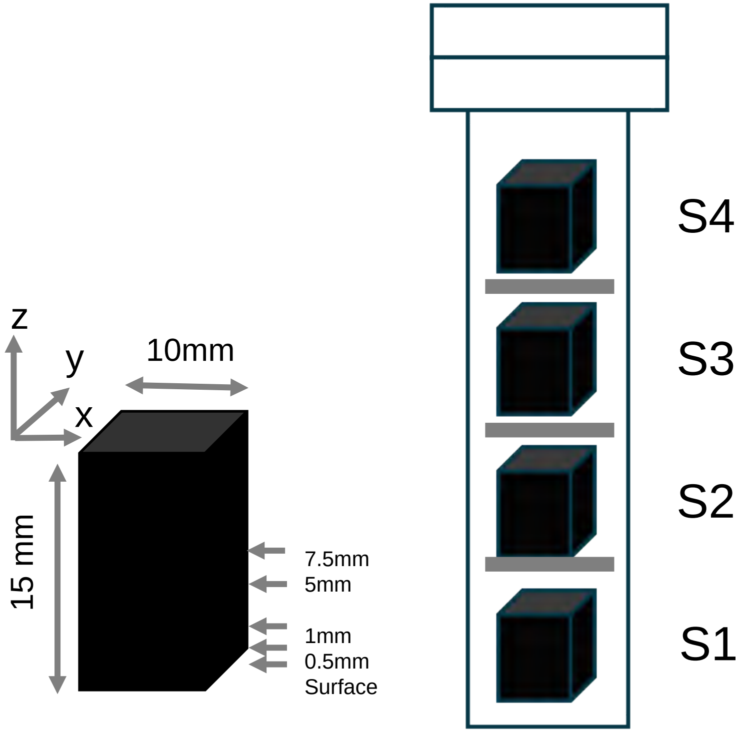
NOTE 3—If the user is using this guide to impregnate specimens for comparative purposes, it is recommended that a single specimen volume and geometry should be employed. If different specimen volumes and geometries are necessary to accommodate tests that follow, it is advisable that the user quantifies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

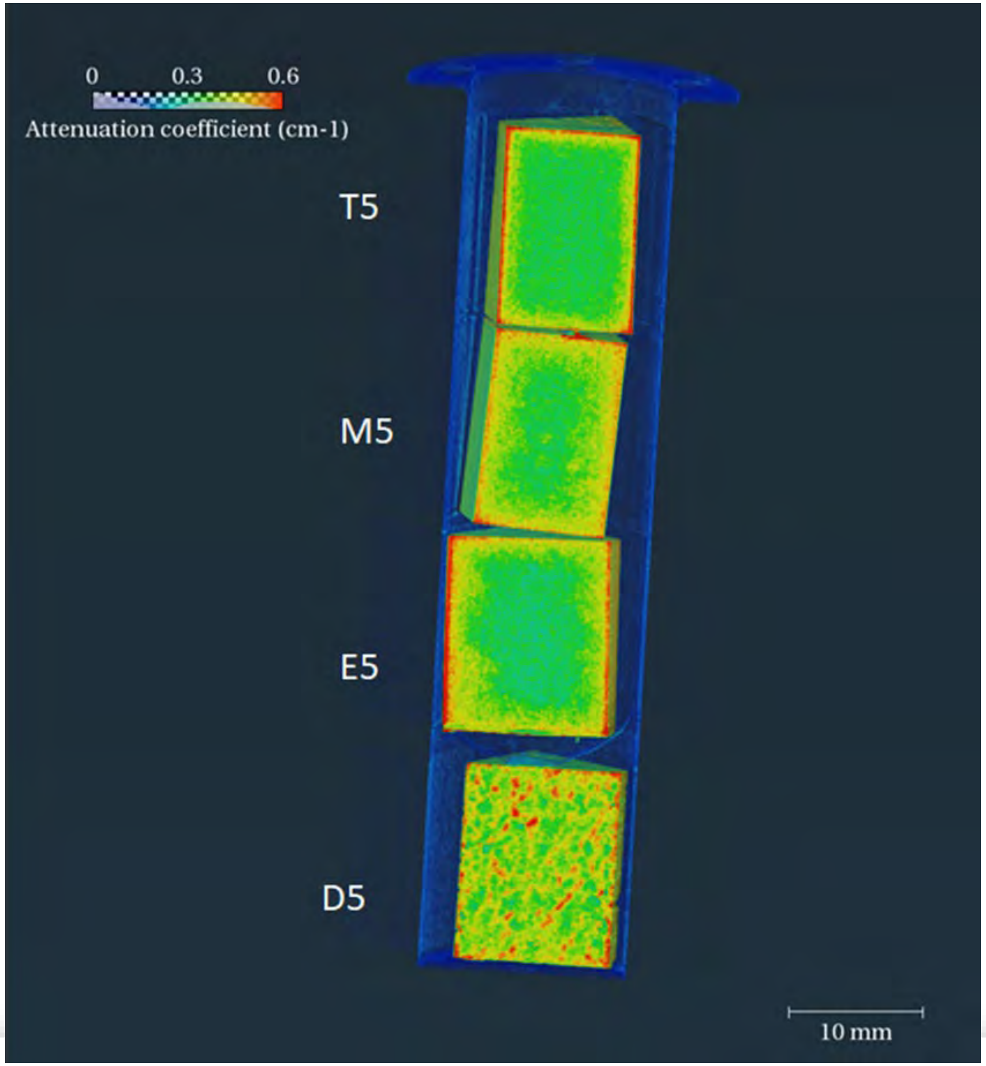
Neutron imaging enables the visualization of salt within the graphite

- Proof of principle experiment at Neutron Imaging Beamline CG-1D (ORNL's HFIR)
- Image resolution ~ 75 μm

FLiNaK impregnated graphite samples

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

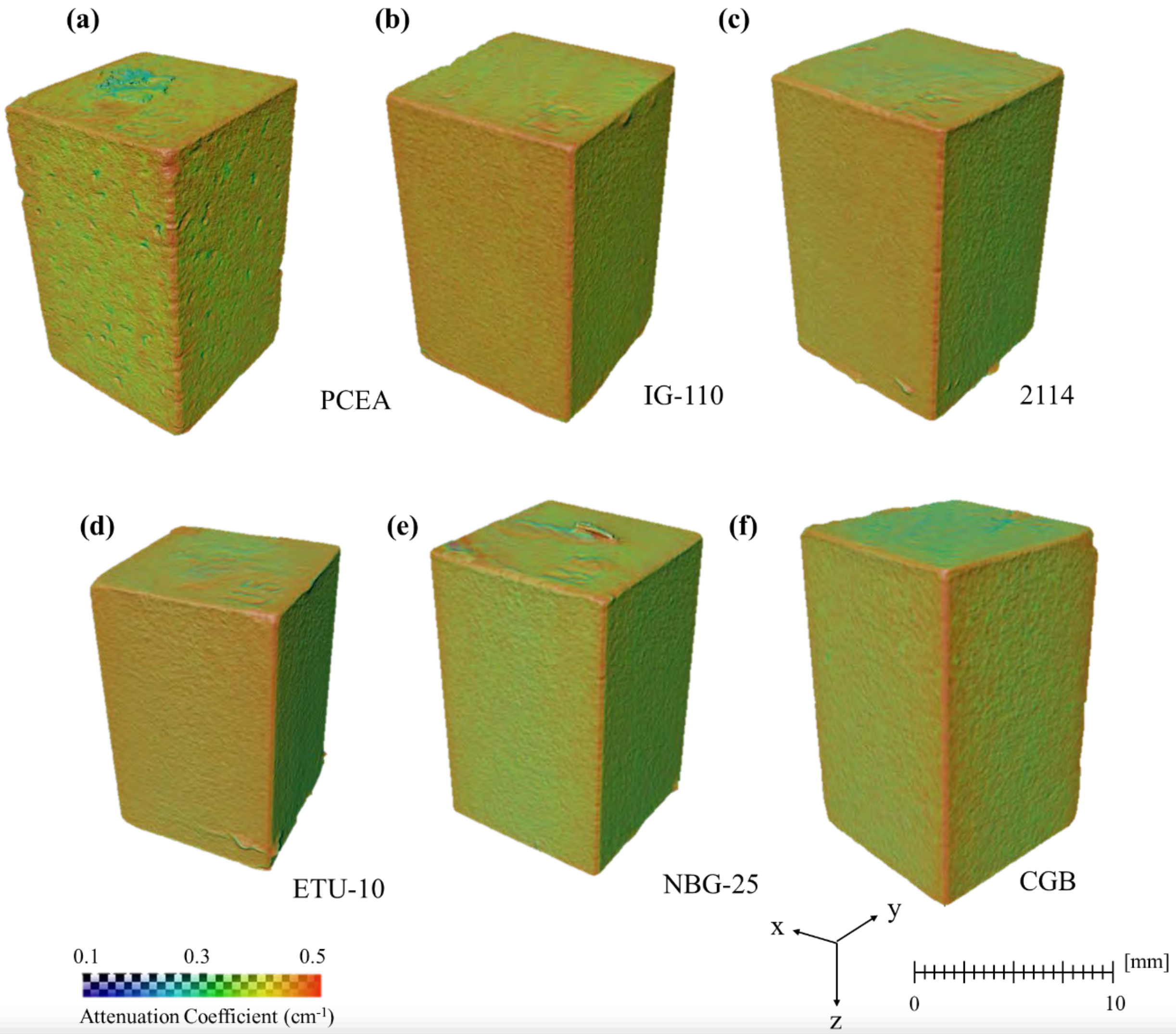




3D reconstructed images of the graphite samples after FLiNaK intrusion

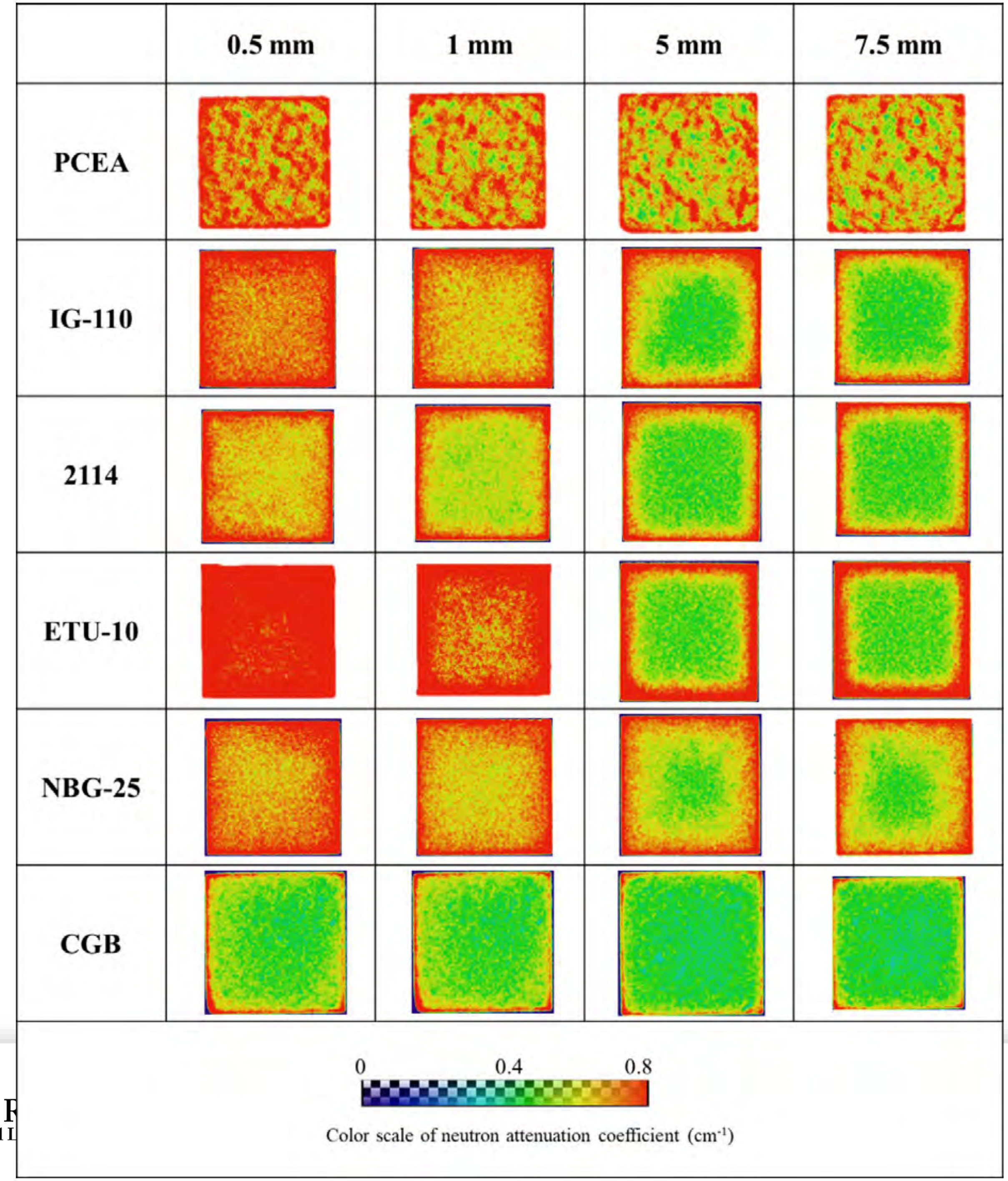
FLiNaK impregnated graphite samples

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



Moon, Gallego, et al. . Submitted for publication

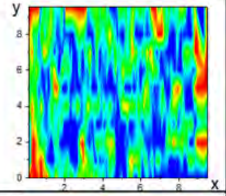
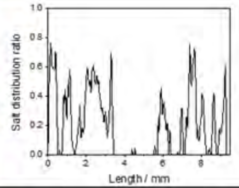
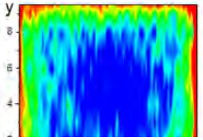
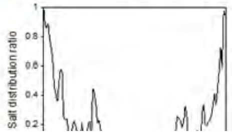
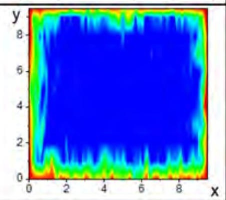
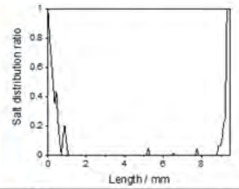
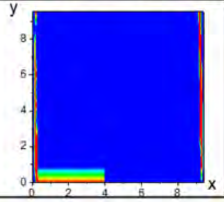
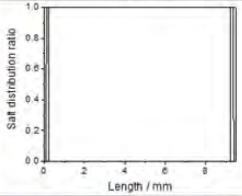
Neutron attenuation coefficient maps



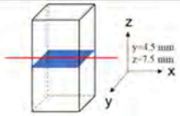
- **Neutron imaging planes at various locations allows the understanding of the salt distribution within the graphite sample.**

Coverage maps

- **Attenuation coefficient maps**

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				
IG-110				
2114			6.7	0.64
CGB			0.98	0.094

Color scale bar for surface images



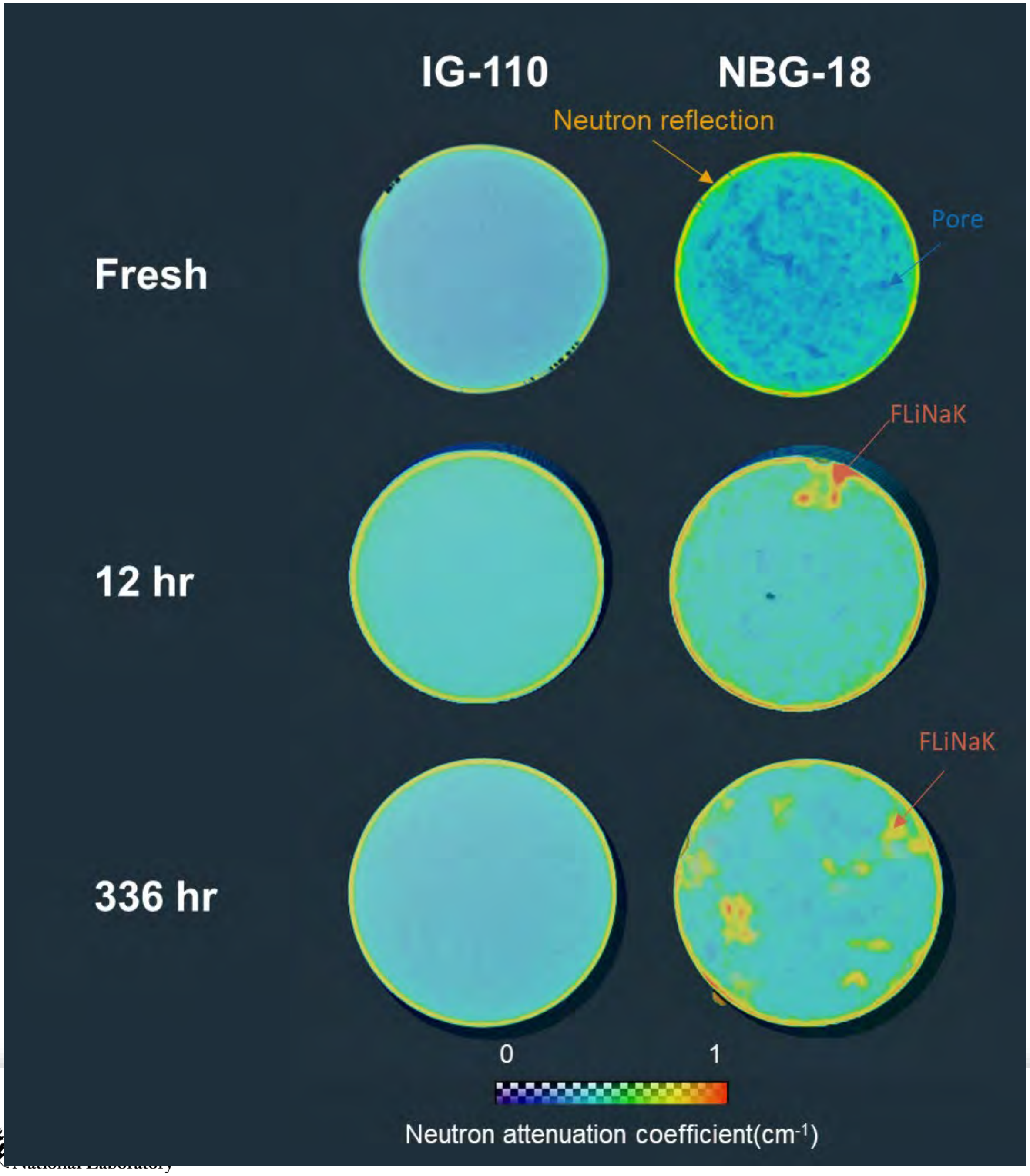
A neutron tomography study to visualize fluoride salt (FLiNaK) intrusion in nuclear-grade graphite

Jisue Moon[1*], Nidia C. Gallego[2*], Cristian I. Contescu[2], James R. Keiser[3], Dino Sulejmanovic[3], Yuxuan Zhang[4] and Erik Stringfellow[4]

Under review

How about time?

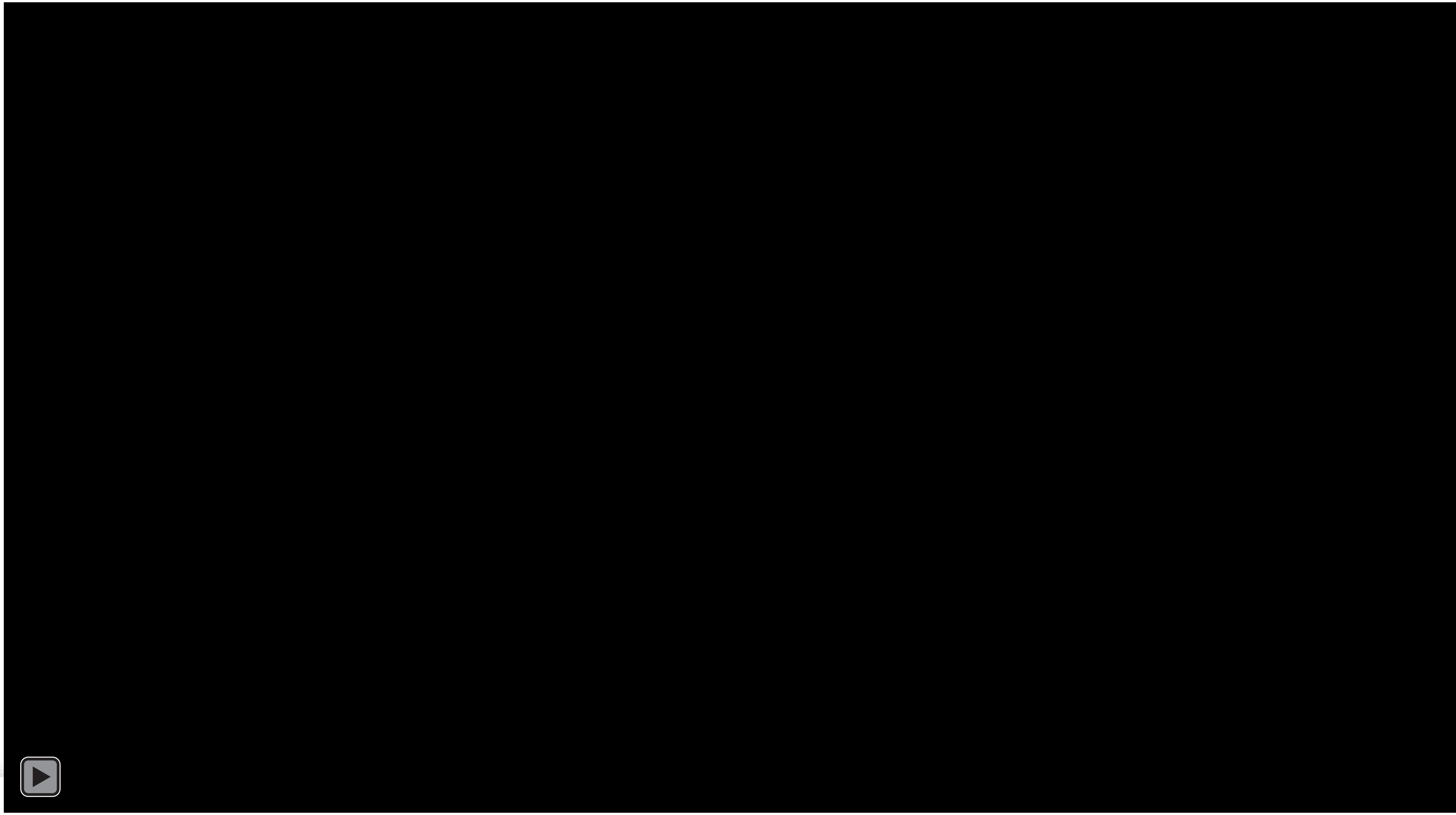
Neutron tomography analysis with different infiltration time



- Graphite sample: cylinders of 10 mm (diameter) X 20 mm (height)
- Infiltration time: 12 hr vs. 336 hr (2 week)
- Bright edge of the surface from all sample is due to neutron reflection
- 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

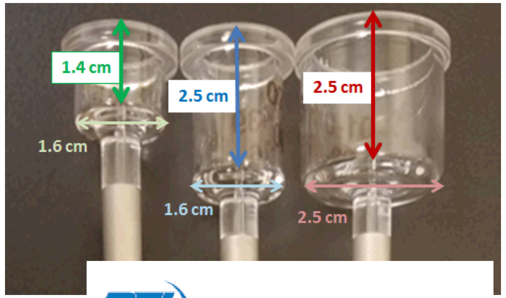
- Intrusion Conditions:
- P: 3 bar ;
- T: 750ºC;
- 336 hrs



Can we predict salt intrusion?

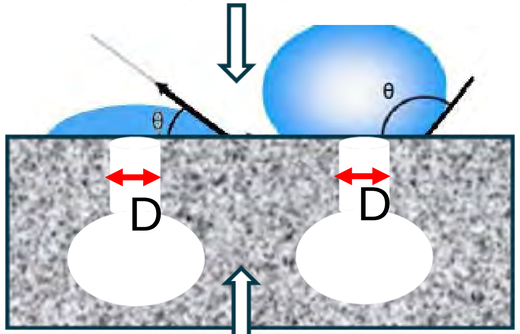
The Washburn equation may be used to study how salt might penetrate into graphite

Penetrometer cells

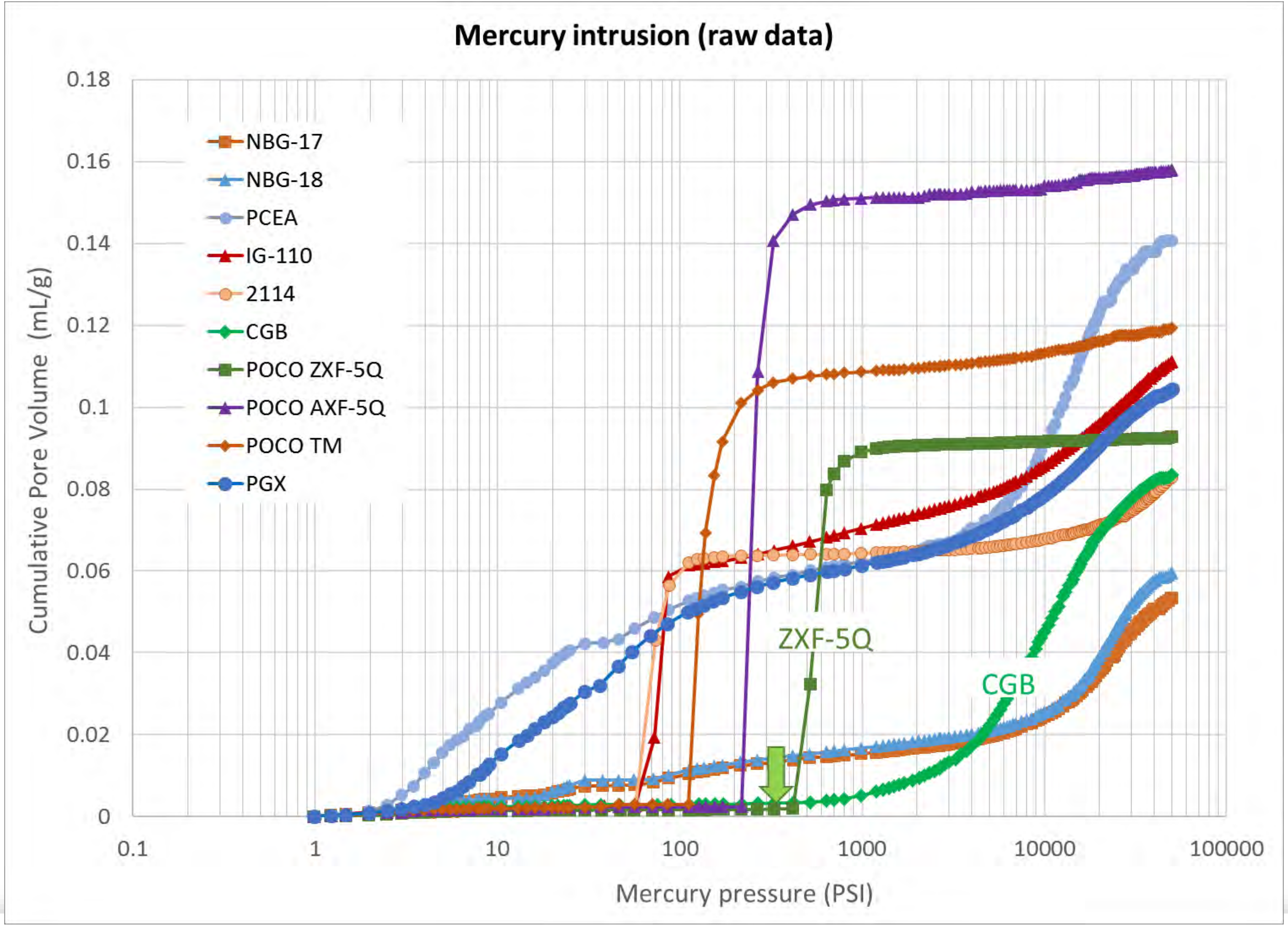


Particle Technology Labs

$$\left(\frac{\pi D^2}{4}\right) * P$$



$$-\sigma * \cos(\theta)$$



The Washburn equation

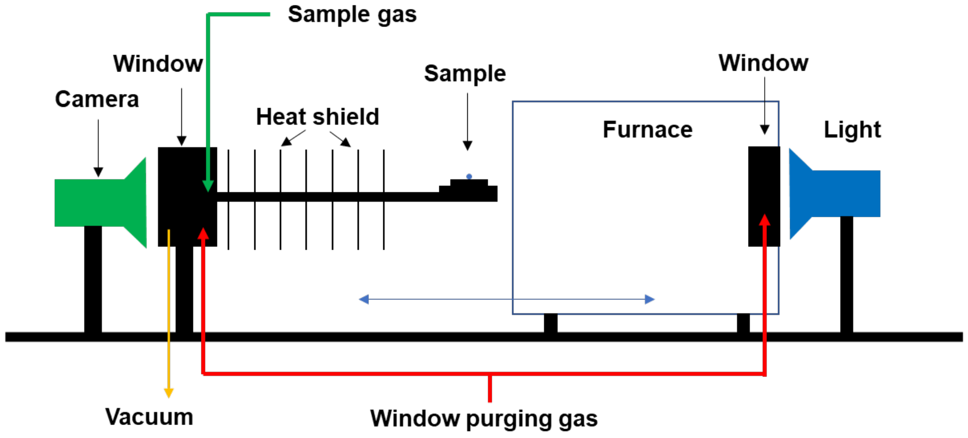
$$P = \frac{4\gamma}{d}\cos\theta\ .$$

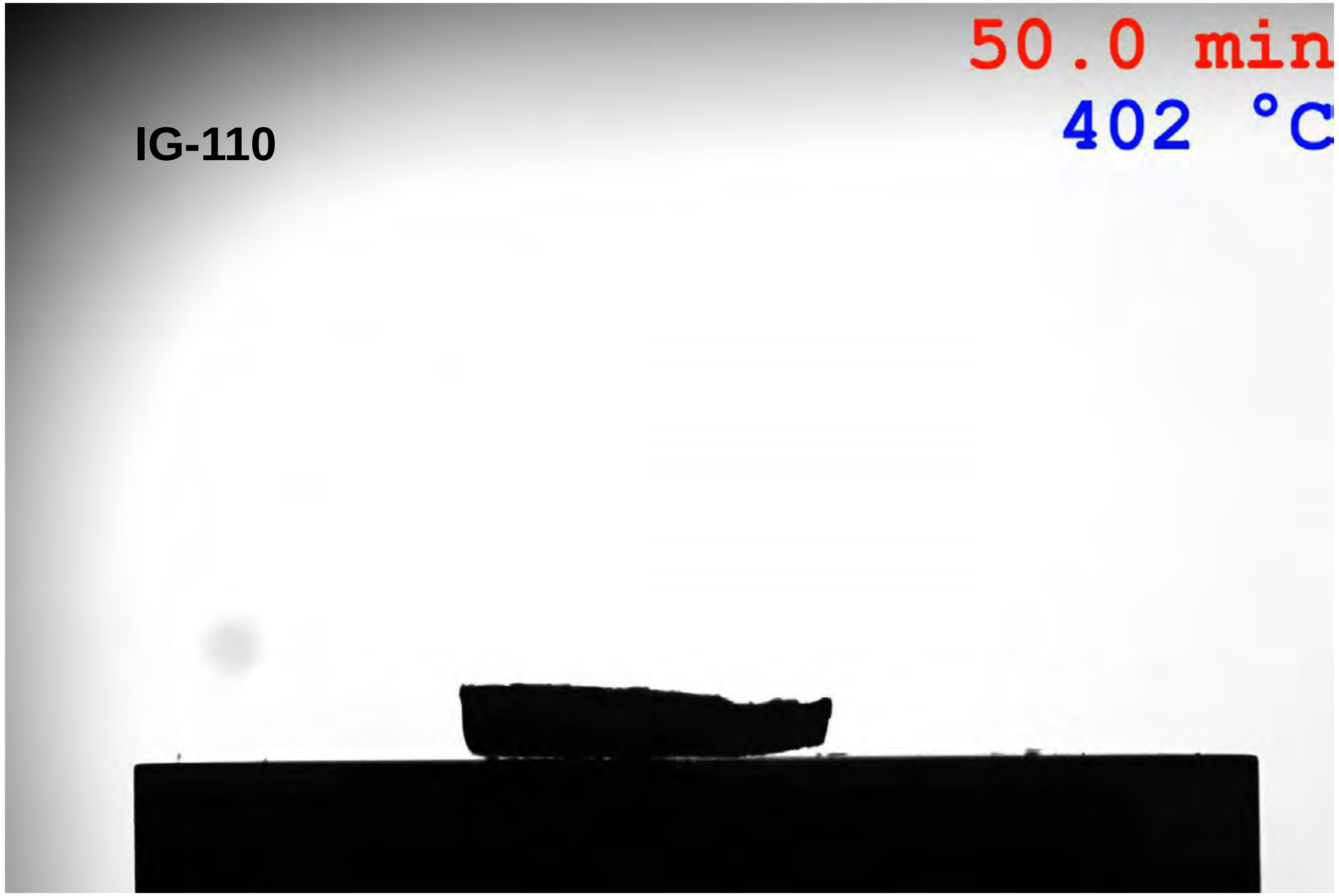
- Pressure differential (*P*) required to push a fluid into a capillary tube (assumed right cylinders) of diameter (*d*)

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

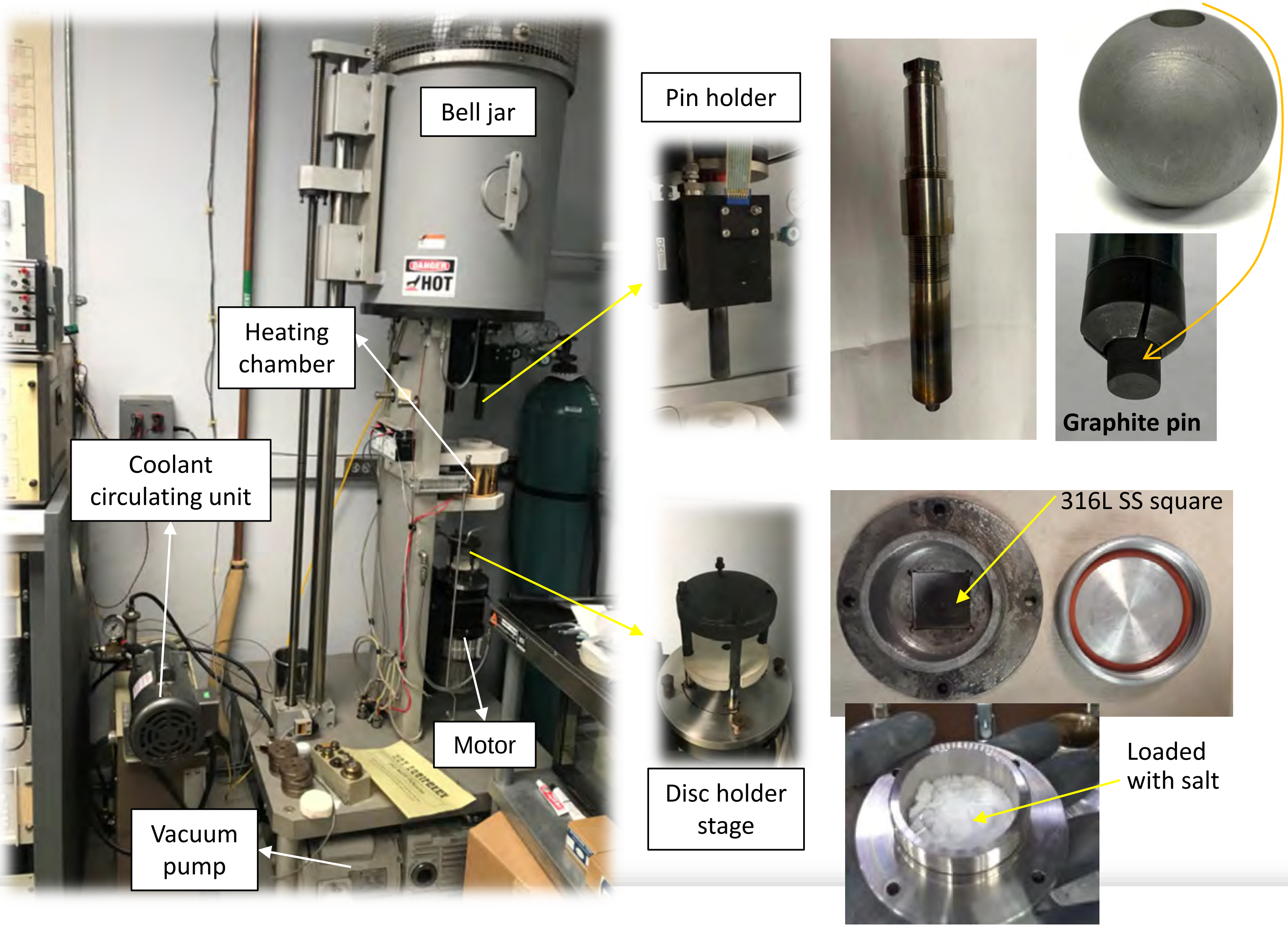
- FLiNaK Melting point 454 ^{o}C

Summary – Intrusion / contact angle

- 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…)

Understanding wear properties of graphite in a molten salt

Feasibility Study of Graphite Wear Testing in Molten FLiNaK Salt



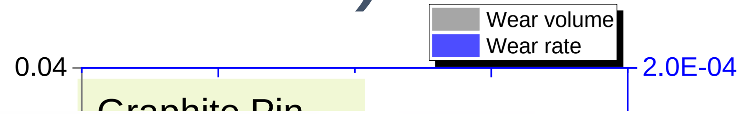
Experimental:

- Graphite pin sliding against 316L SS surface
- Salt: FLiNaK
- **Temperature: 550 & 650 ºC** (up to 1000 ºC)
- 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)

In-situ friction measurement combined with post-test wear quantification and surface characterization to investigate:

- Tribocorrosion behavior of graphite pebble rubbing against the container alloy in molten FLiNaK salt with understanding of the impact of temperature, sliding speed, and salt quantity (completed)
- Wear behavior of graphite pebbles upon collision and rubbing between each other in molten FLiNaK salt (future work)

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



Increased wear losses for both the graphite and 316H SS at a higher

- **Visc** to p
- The temp little
- **316** **stro**

Wear 522 (2023) 204706

Contents lists available at ScienceDirect

Wear

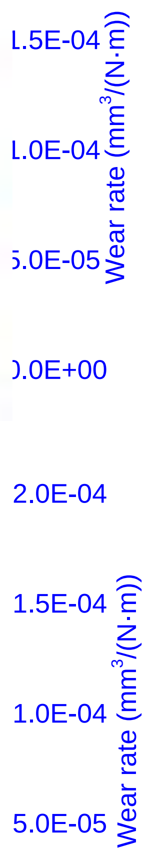
journal homepage: www.elsevier.com/locate/wear

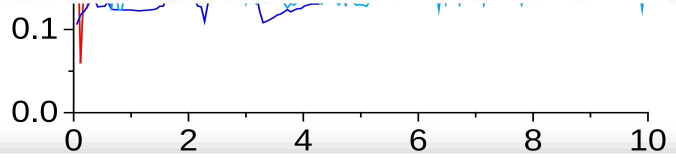
ELSEVIER

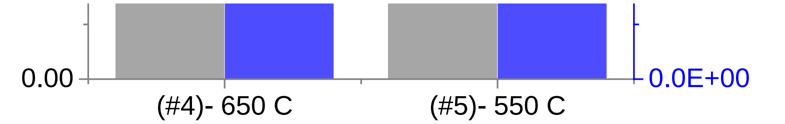
Tribocorrosion of stainless steel sliding against graphite in FLiNaK molten salt☆

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

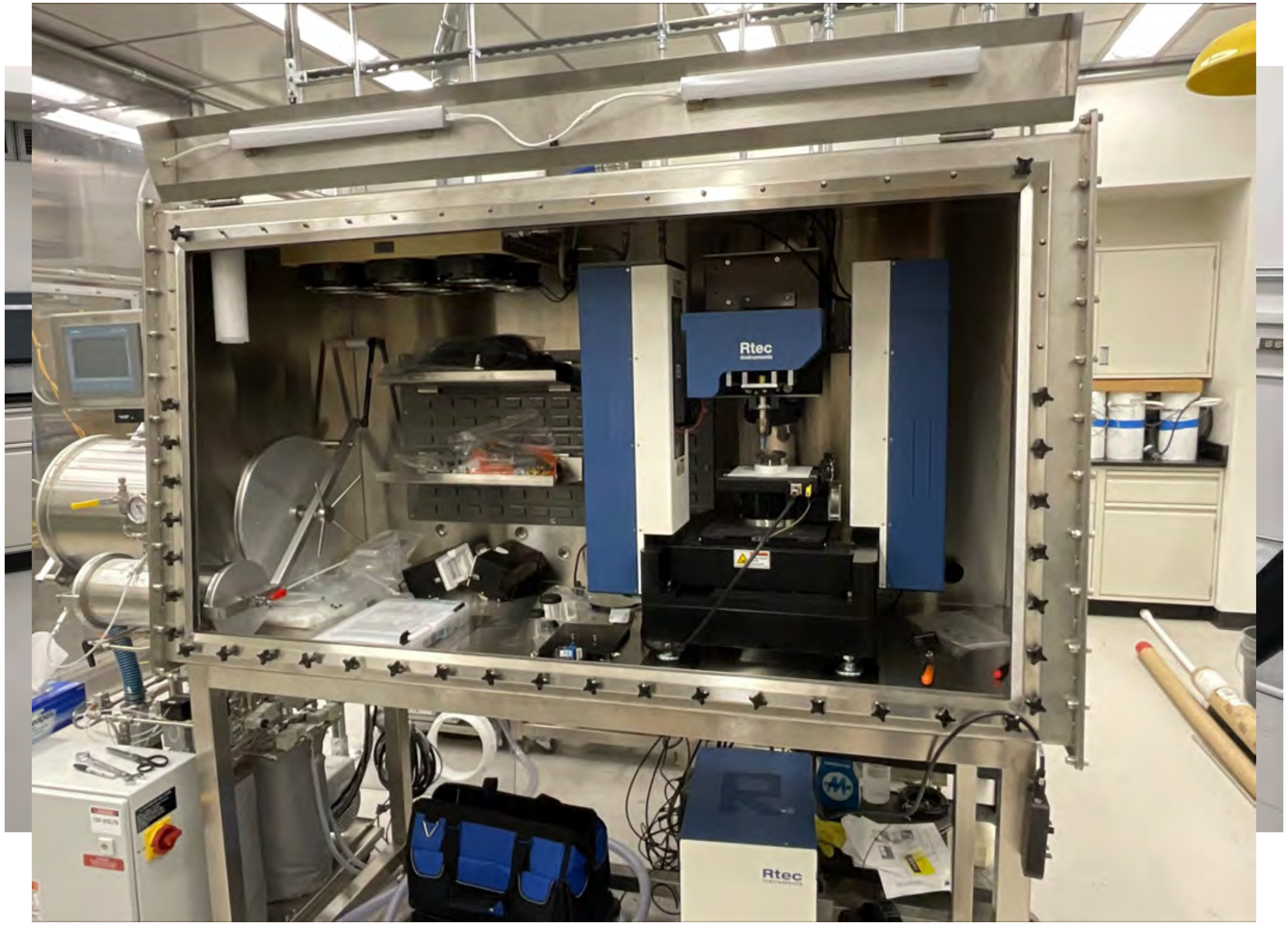
[a] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA
[b] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA







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 - Wear

- 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)
- 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).

* All available at OSTI

GEN IV International Forum

Education and Training Working Group

Webinar Invite

Join us on April 5, 2023 8:30 a.m. EDT (UTC-4)

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).

Free webcast!

April 5, 2023
8:30 am EDT (UTC-4)

Register NOW at:
https://attendee.gotowebinar.com/register/7270939981646037336

Who should attend:
policymakers, managers, regulators, students, general public

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.

Upcoming Webinars

24 May 2023, Graphite-Molten Salt Interactions, Dr. Nidia Gallego, ORNL, USA

21 June 2023, International Knowledge Management and Preservation of SFR Panel Session Cal Doucette, ARC Energy, Canada; Joel Guidez, retired CEA, France; Hiroki Hayafune, JAEA, Japan; Patrick Alexander, Terrapower, USA; Ron Omberg, PNNL, USA

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

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

www.gen-4.org

GEN IV International Forum

Education and Training Working Group

Webinar Invite

Join us on May 24, 2023 8:30 a.m. EDT (UTC-4)

Graphite-Molten Salt Interactions

The new High Temperature Reactor (HTR) designs being considered for future Gen IV nuclear reactor deployment include designs utilizing 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. In MSRs, graphite is not only exposed to fast neutron irradiation but also in continuous contact with the coolant molten salt, the fuel salt, or both, depending on the design. The continuous operation in contact with the molten salts is expected to affect graphite's local composition and microstructure, which in turn impacts the mechanical, thermal, and irradiation-resistance properties of the graphite. These issues are currently under investigation within the DOE Advanced Reactor Technologies (ART) graphite program and will be presented at this seminar.

Free webcast!

May 24, 2023
8:30 am EDT (UTC-4)

Register NOW at:
https://attendee.gotowebinar.com/register/7530835943262809689

Who should attend:
policymakers, managers, regulators, students, general public

Dr. Nidia C Gallego is a 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.

Upcoming Webinars

21 June 2023, Panel Session International Knowledge Management and Preservation of SFR
Cal Doucette, ARC Energy, Canada; Joel Guidez, retired CEA, France; Hiroki Hayafune, JAEA, Japan; Patrick Alexander, Terrapower, USA; Ron Omberg, PNNL, USA

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

31 August 2023, Corrosion and Cracking of SCWR Materials, Prof. Lefu Zhang, Shanghai Jiao Tong University, China

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

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Thank you

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