July 26, 2023

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Graphite Activities Related to Molten Salt Reactors

ART Graphite R&D

Team Effort – ORNL Contributors

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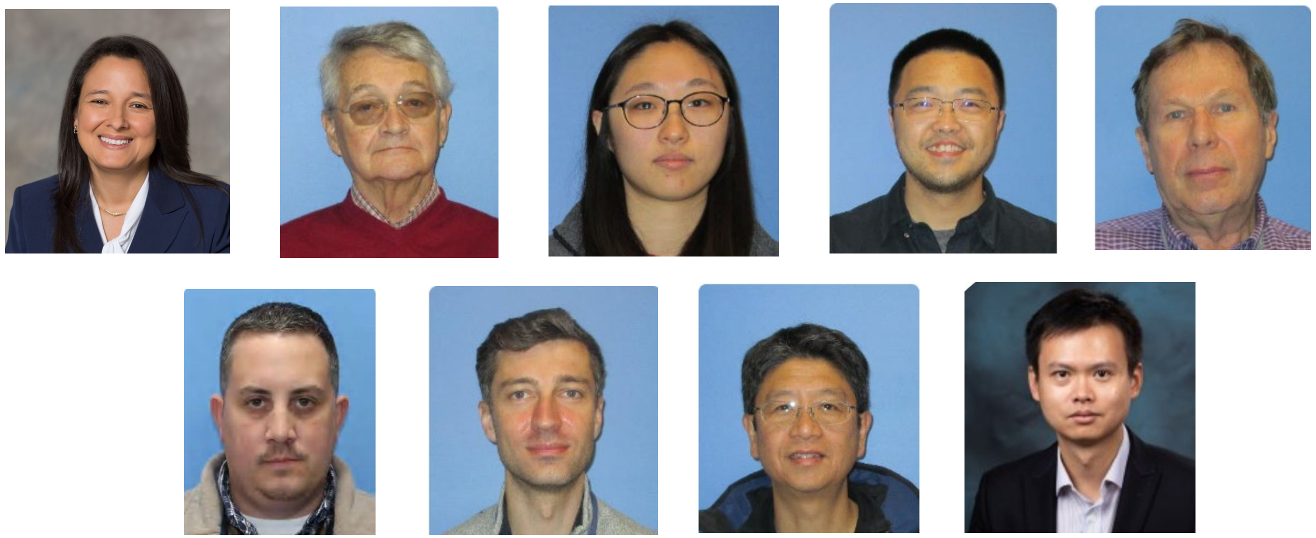
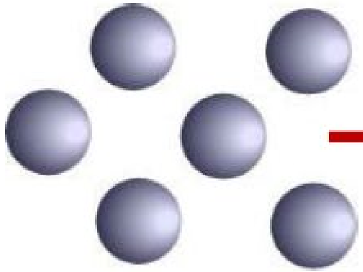


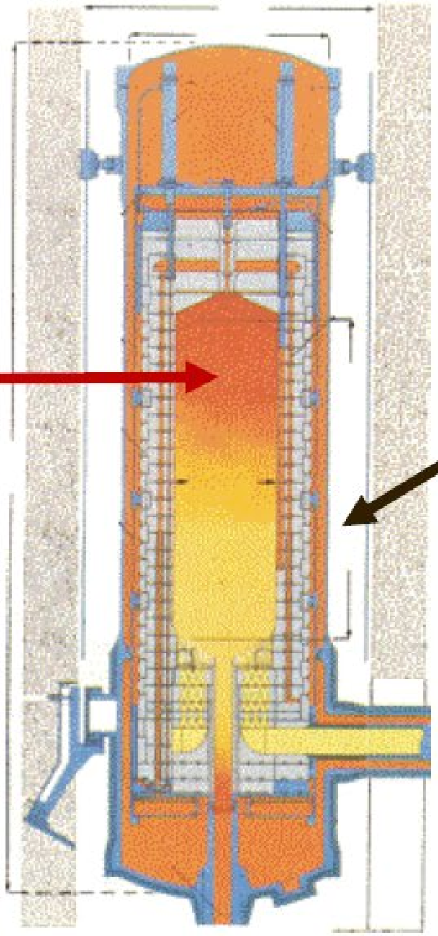
Financial Support from US DOE-NE Advanced Reactor Technology Program

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

High Temperature Reactors (HTR)

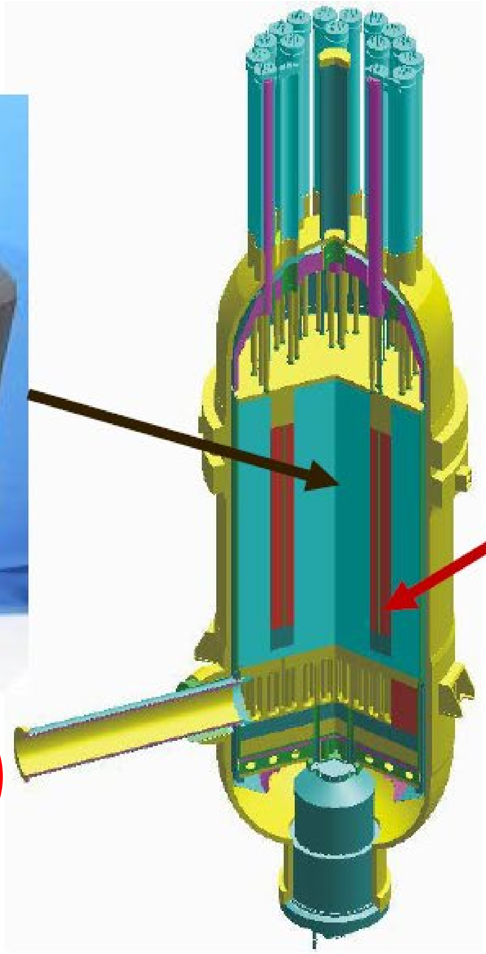
(Graphite) Fuel Pebbles





Graphite Core

Gas or molten salt coolant



Graphite Fuel Element

Pebble Bed

Prismatic

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/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
- ❖ Effect of potential heating/cooling cycles

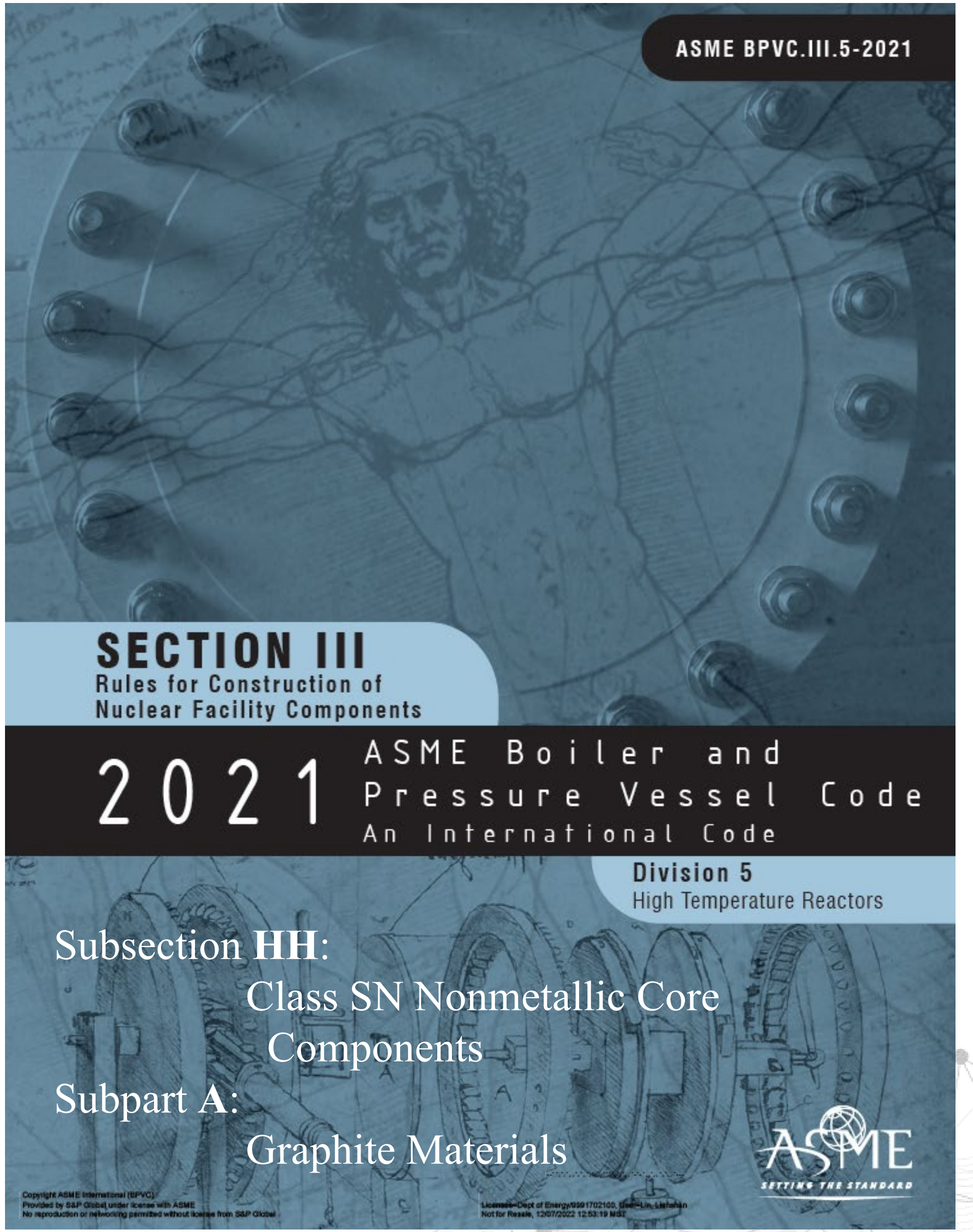
Chemical

- ❖ 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.

Chemical attack, salt infiltration and retention as well as wear and erosion aspects need to be incorporated in the design rules.



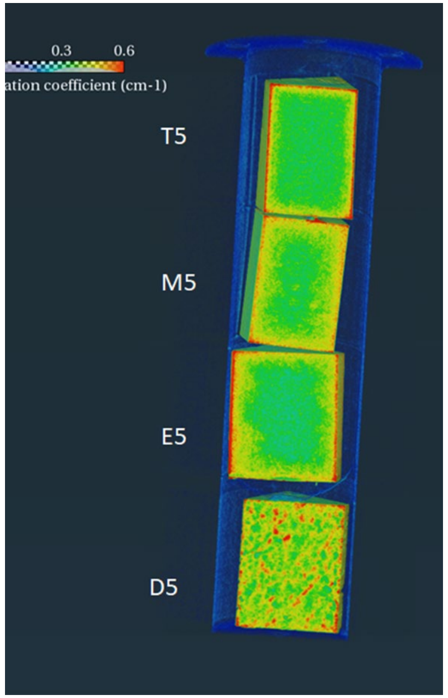
Graphite Salt Studies

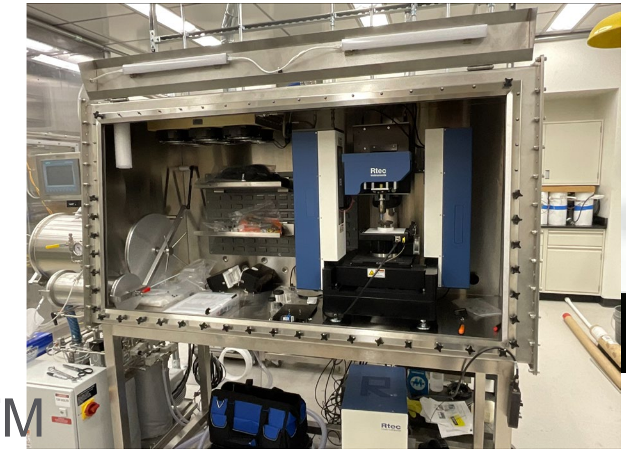
- Objectives:
  - To develop the needed knowledge and understanding of salt-graphite interactions in order to address the gaps in the ASME code, and therefore assist in the near-term deployment of MSRs

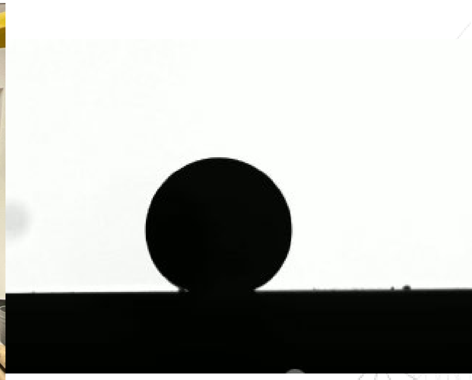
- Current Research Focus:
  - Understanding salt intrusion (penetration depth and salt distribution) in a wide range of graphite grades (various microstructures) as a function of temperature, pressure and time.
  - Studying wetting behavior of salt on graphite surfaces to develop predictive models for salt intrusion
  - Working with the ASTM community to develop ways to measure the effect of salt intrusion on graphite properties
  - Studying wear and erosion behavior of graphite in molten salt

Graphite - Salt studies: Highlights

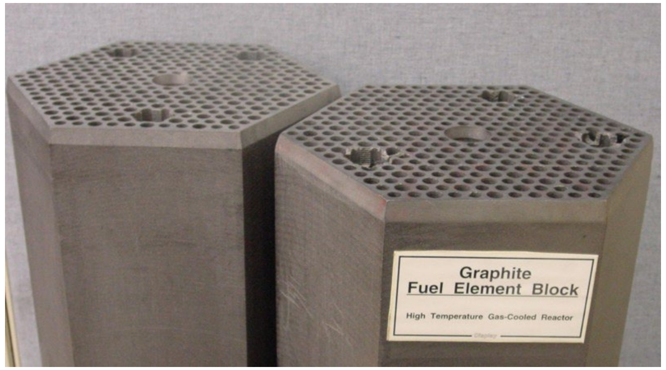
- Continued to utilize the intrusion system (FLiNaK, < 10 bar, < 750ºC) to conduct measurements on a wide range of graphite grades and intrusion conditions
- Demonstrated and implemented the use of neutron imaging to study intrusion and determine **salt penetration and distribution**: currently studying the effect of time and temperature
- Commissioned contact angle measurement system and initiated data collection to support development of predicting models.
- Completed initial scoping studies of the wear behavior of graphite in molten salts.
- Commissioned new wear facilities to have better environmental control.
- Participation in ASTM and ASME, GIF seminar and PMB.
- Publications: 3 TMs; 4 Journal Pub.; 1 book chapter (ASTM STP), and many presentations.

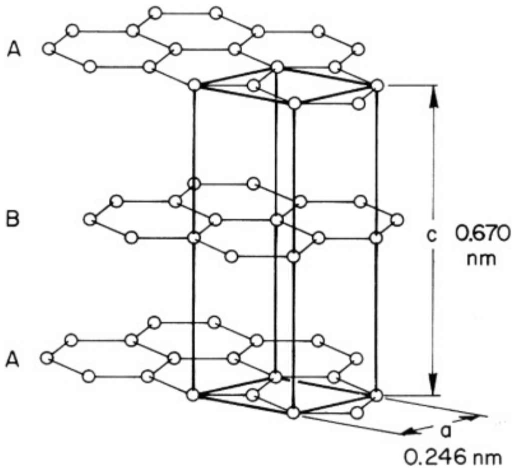


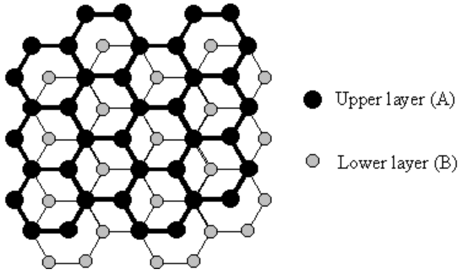


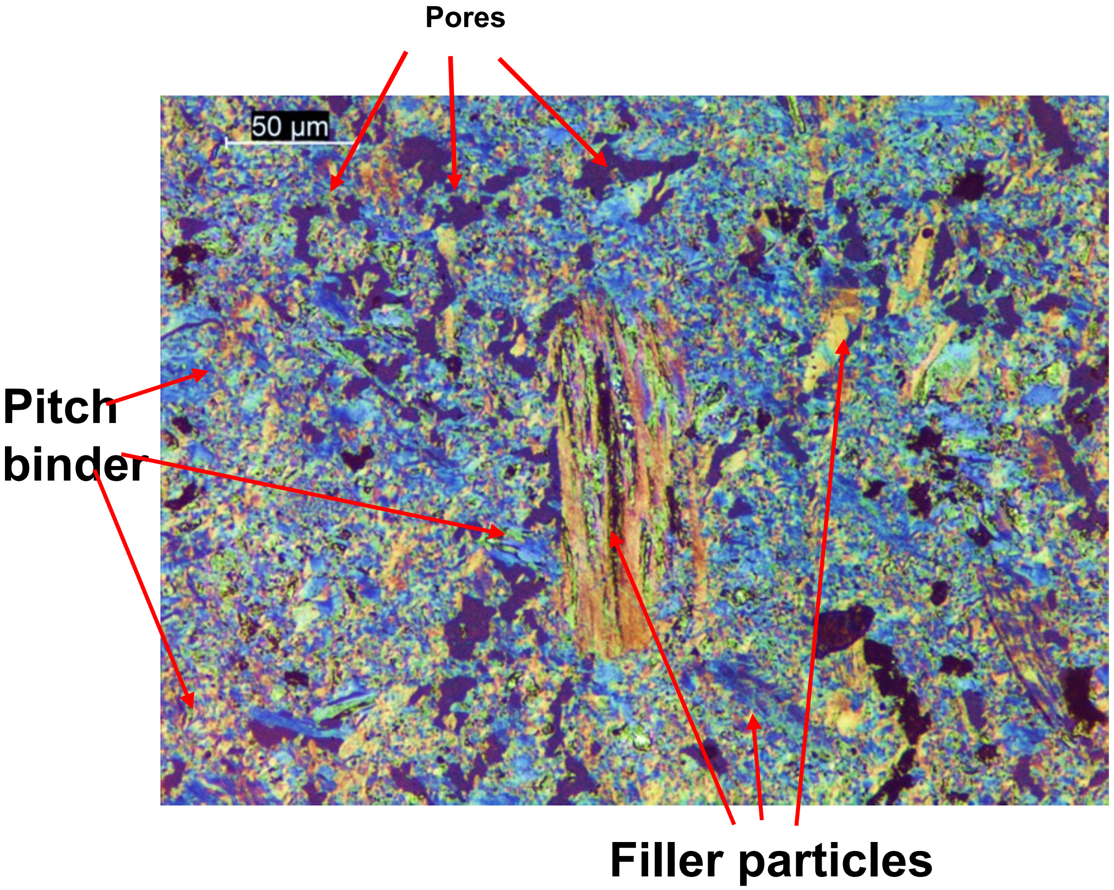


Understanding Manufactured Graphite





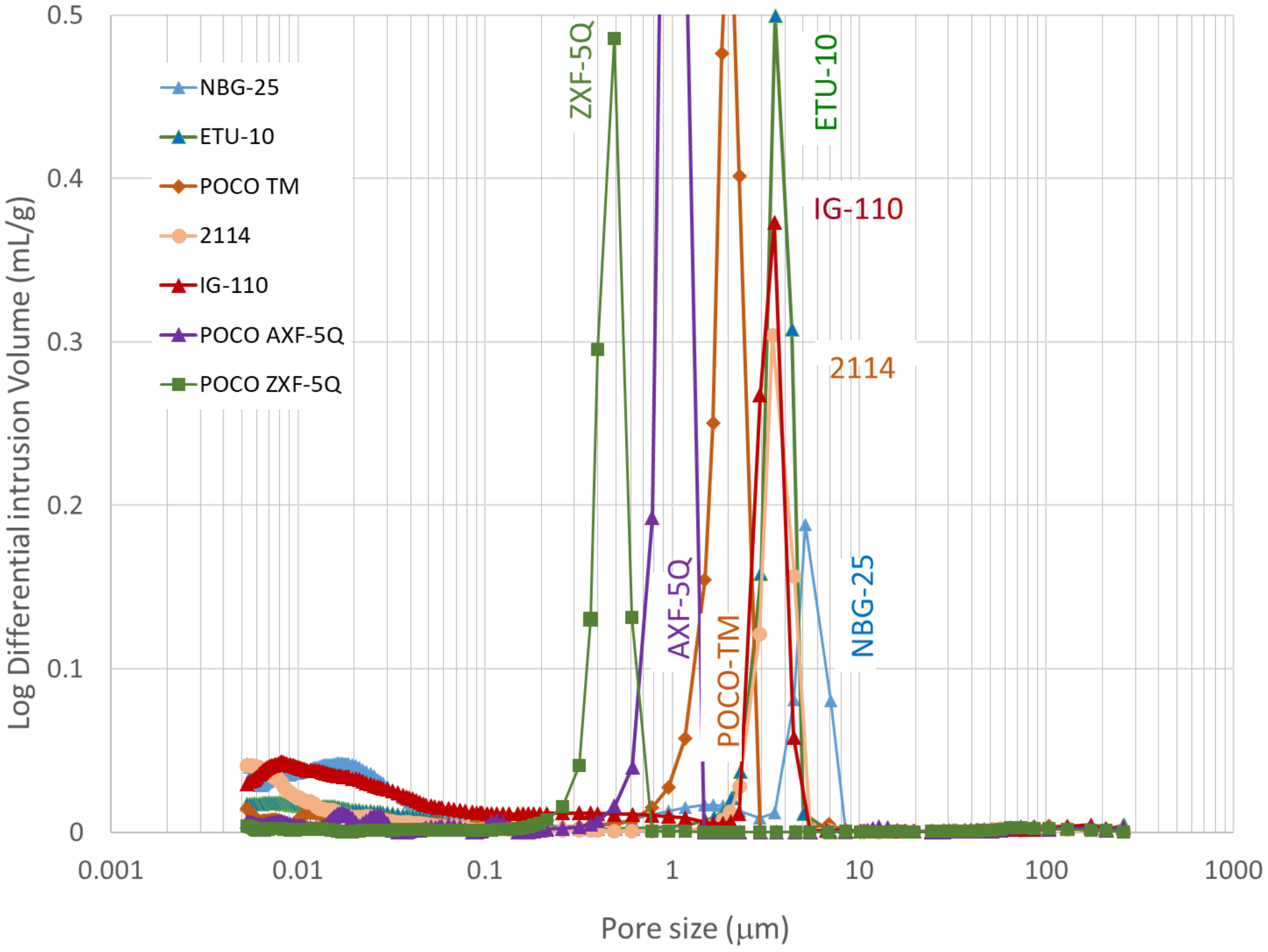




Manufactured Graphite has about **20 % porosity**

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

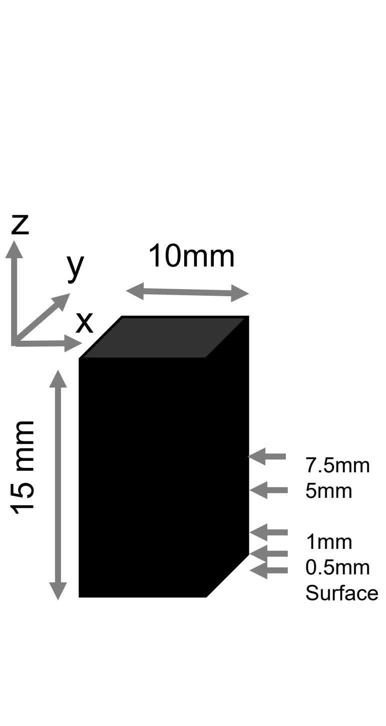


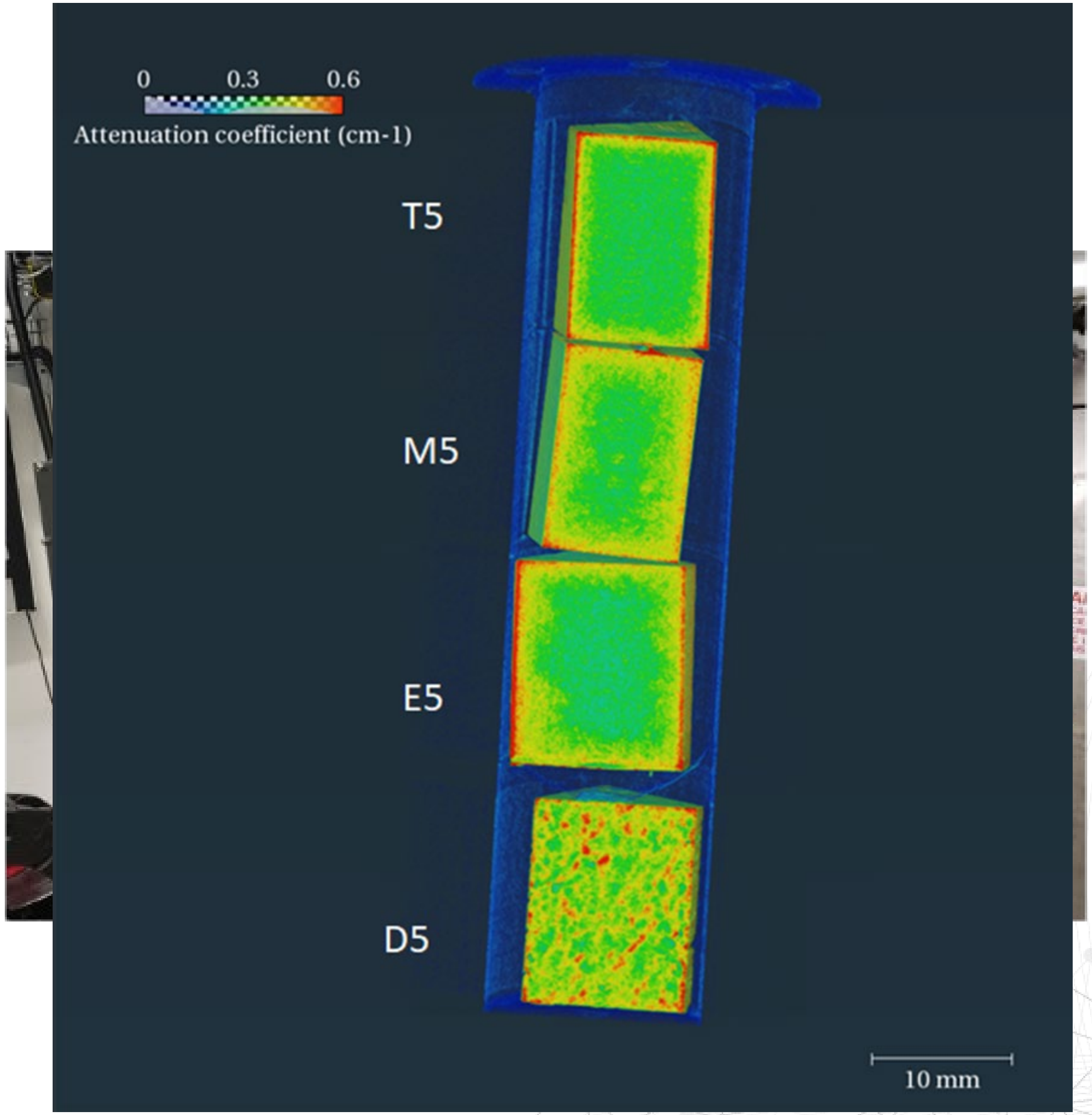
Neutron imaging enables the visualization of salt within the graphite

- 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**



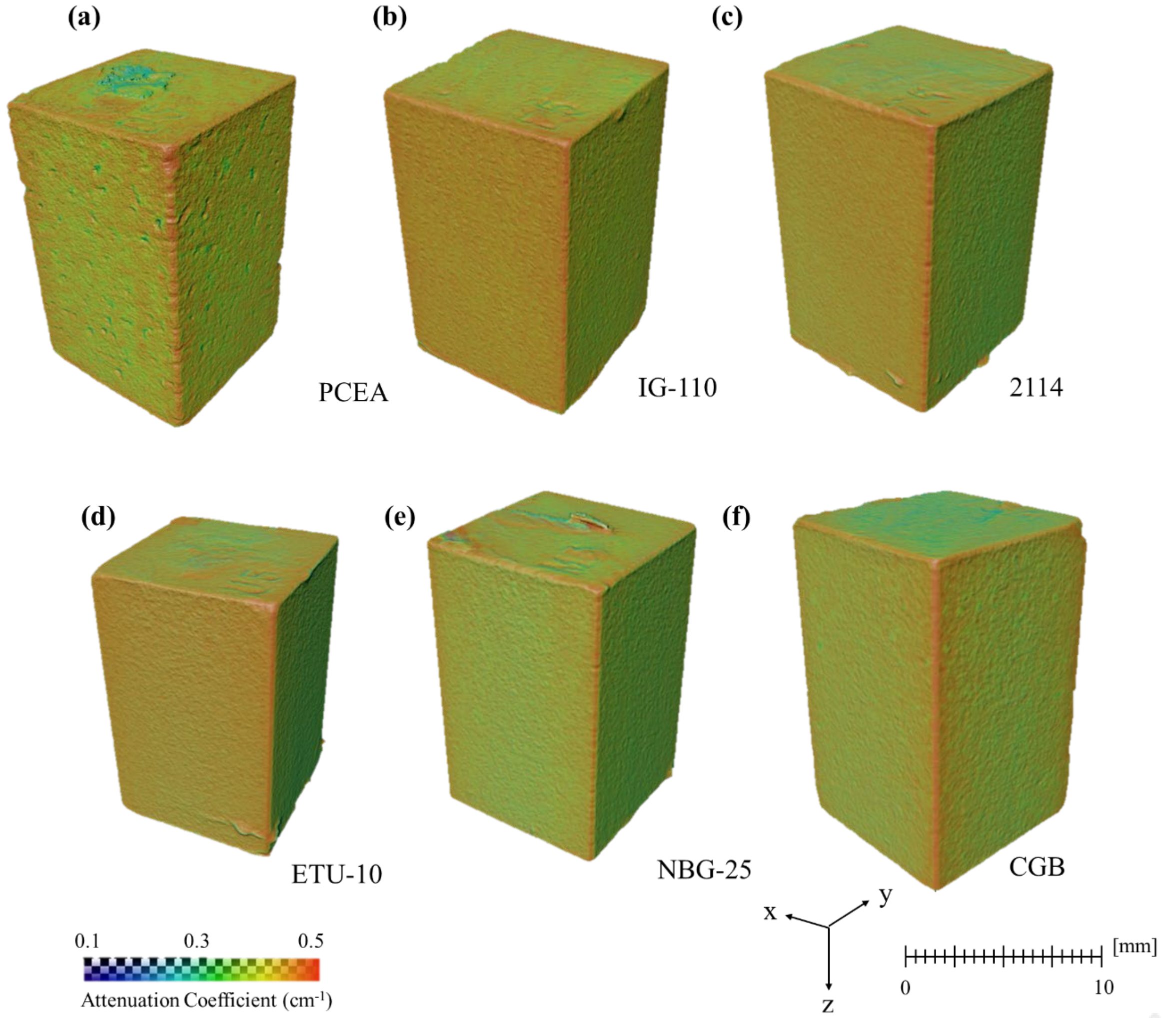


Moon, Gallego et al., Carbon 213 (2023)

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., Carbon 213 (2023)

Coverage maps

- Attenuation coefficient maps can be converted to coverage maps utilizing sample pr
intrusion.

Carbon 213 (2023) 118258

Contents lists available at ScienceDirect

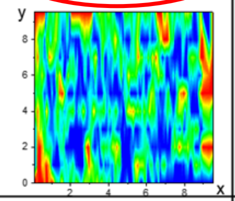
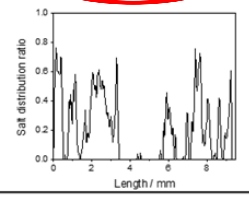
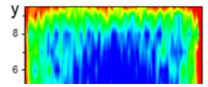
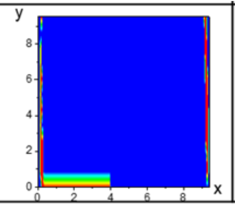
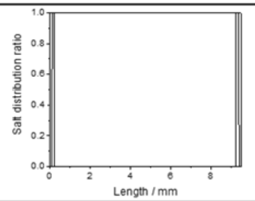
Carbon

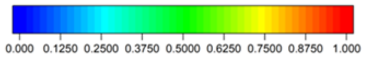
journal homepage: www.elsevier.com/locate/carbon

ELSEVIER

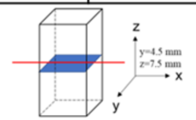
A neutron tomography study to visualize fluoride salt (FLiNaK) intrusion in nuclear-grade graphite

Jisue Moon [a,*], Nidia C. Gallego [b,**], Cristian I. Contescu [b], James R. Keiser [c], Dino Sulejmanovic [c], Yuxuan Zhang [d], Erik Stringfellow [d]

Sample	Surface image	Line profile at y=4.5	Salt coverage (%)	Curve area
PCEA			20.2	1.92
				1.85
				2.70
				1.19
				0.64
CGB			0.98	0.094



Color scale bar for surface images



Moon, Gallego et al., Carbon 213 (2023)

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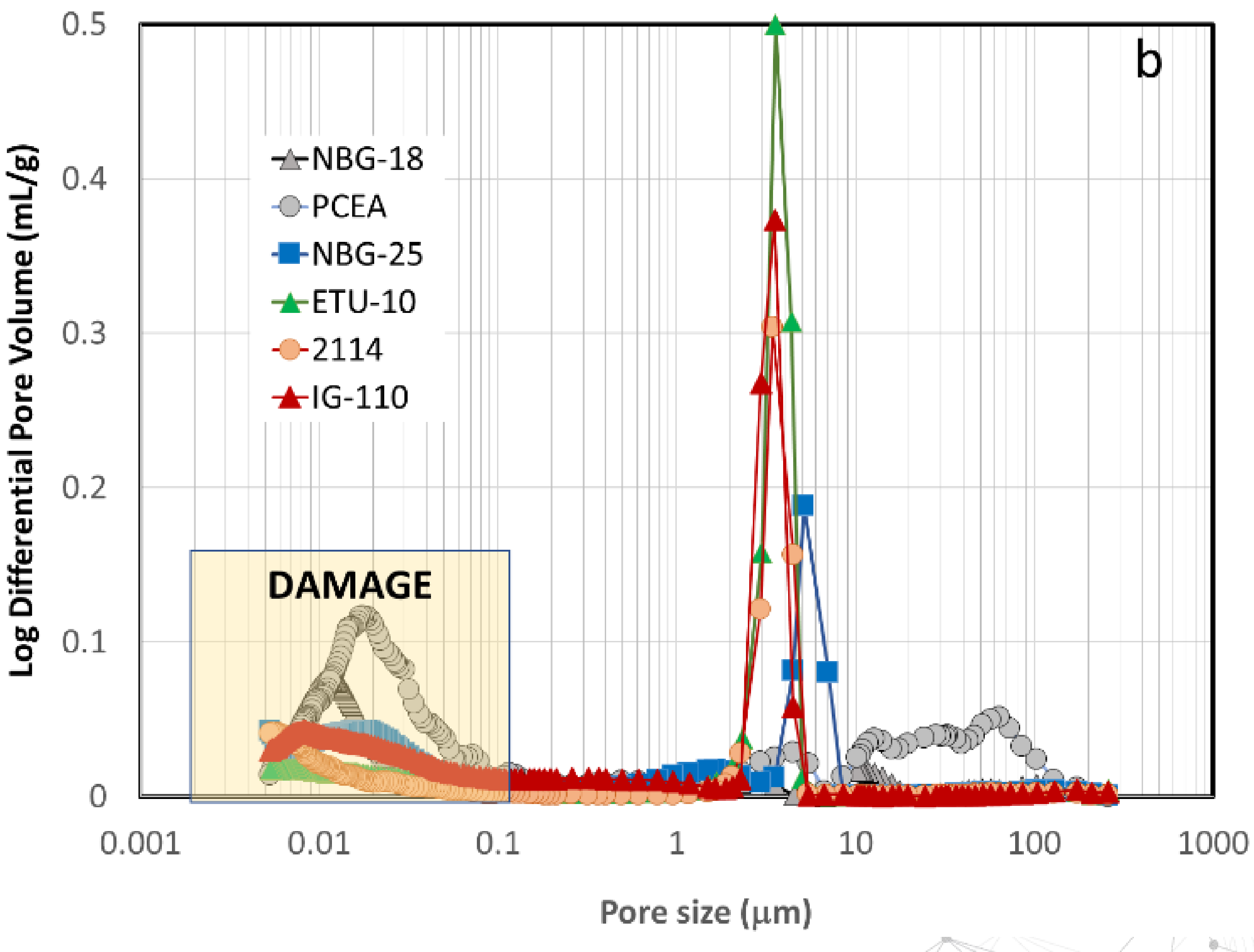
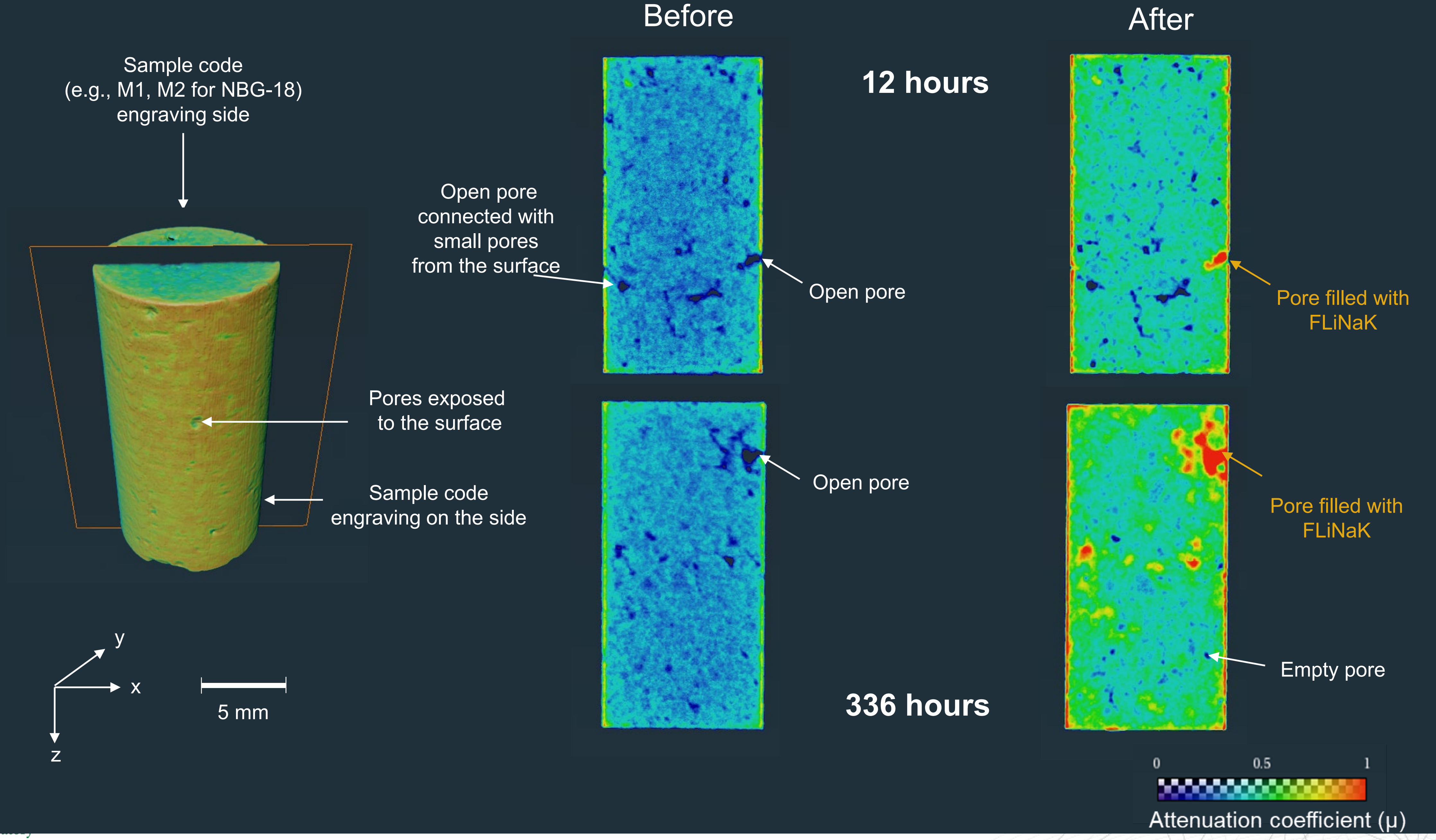
How about time? (12 hrs vs 336 hrs)

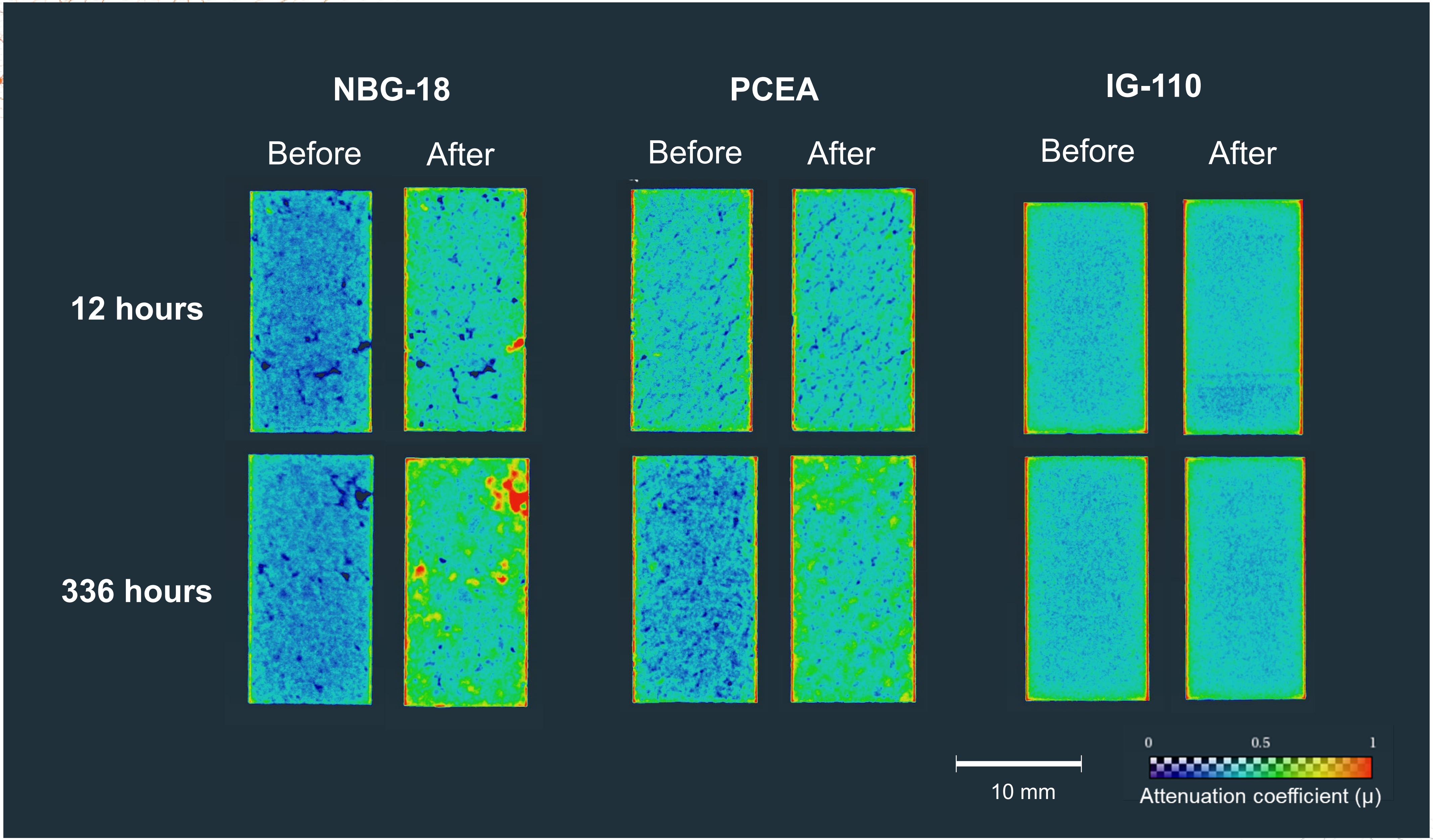
- Graphite sample geometry:
  - Cylinders
  - 10 mm (diameter) X 20 mm (height)
- Graphite grades studied:
  - NBG-18, PCEA, IG-110, 2114, ETU-10, NBG-25
- FLiNaK Intrusion conditions:
  - **Temperature: 750ºC**
  - **Pressure: 3 bar**
  - **Time: 12 hr vs. 336 hr (2 week)**
- Imaging completed **before and after** salt intrusion



NBG-18

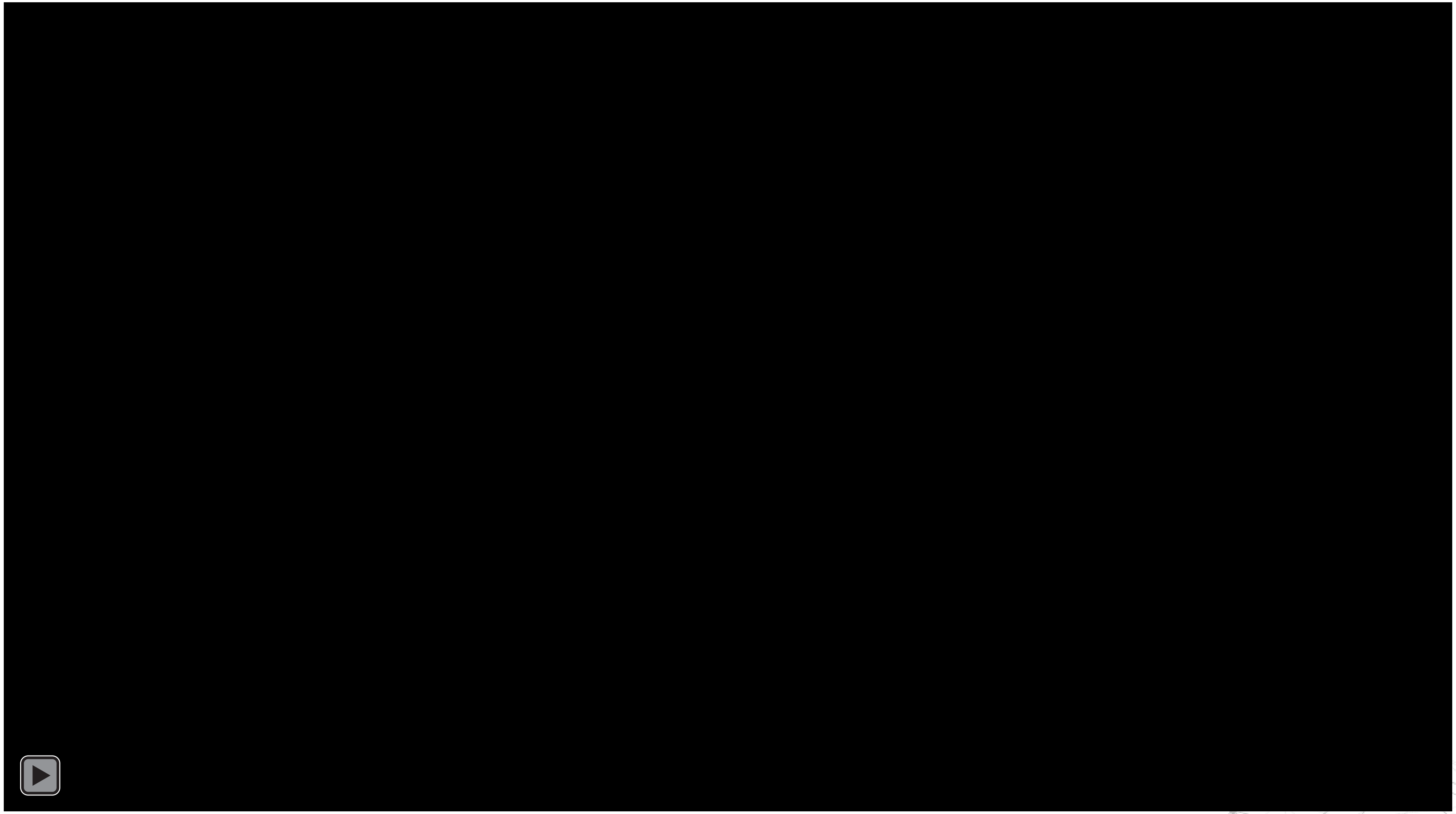


Before
After
Sample code
(e.g., M1, M2 for NBG-18)
engraving side
Open pore
connected with
small pores
from the surface
12 hours
Open pore
Pore filled with
FLiNaK
Pores exposed
to the surface
Sample code
engraving on the side
Open pore
Pore filled with
FLiNaK
Empty pore
y
x
z
5 mm
336 hours
0
0.5
1
Attenuation coefficient (μ)


NBG-18
PCEA
IG-110
Before
After
Before
After
Before
After
12 hours
336 hours
10 mm
0
0.5
1
Attenuation coefficient (μ)

Preliminary Results

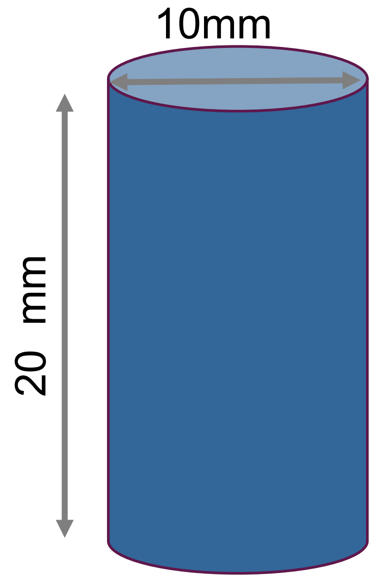
NBG-18: 3 bar; 750ºC;336 hrs



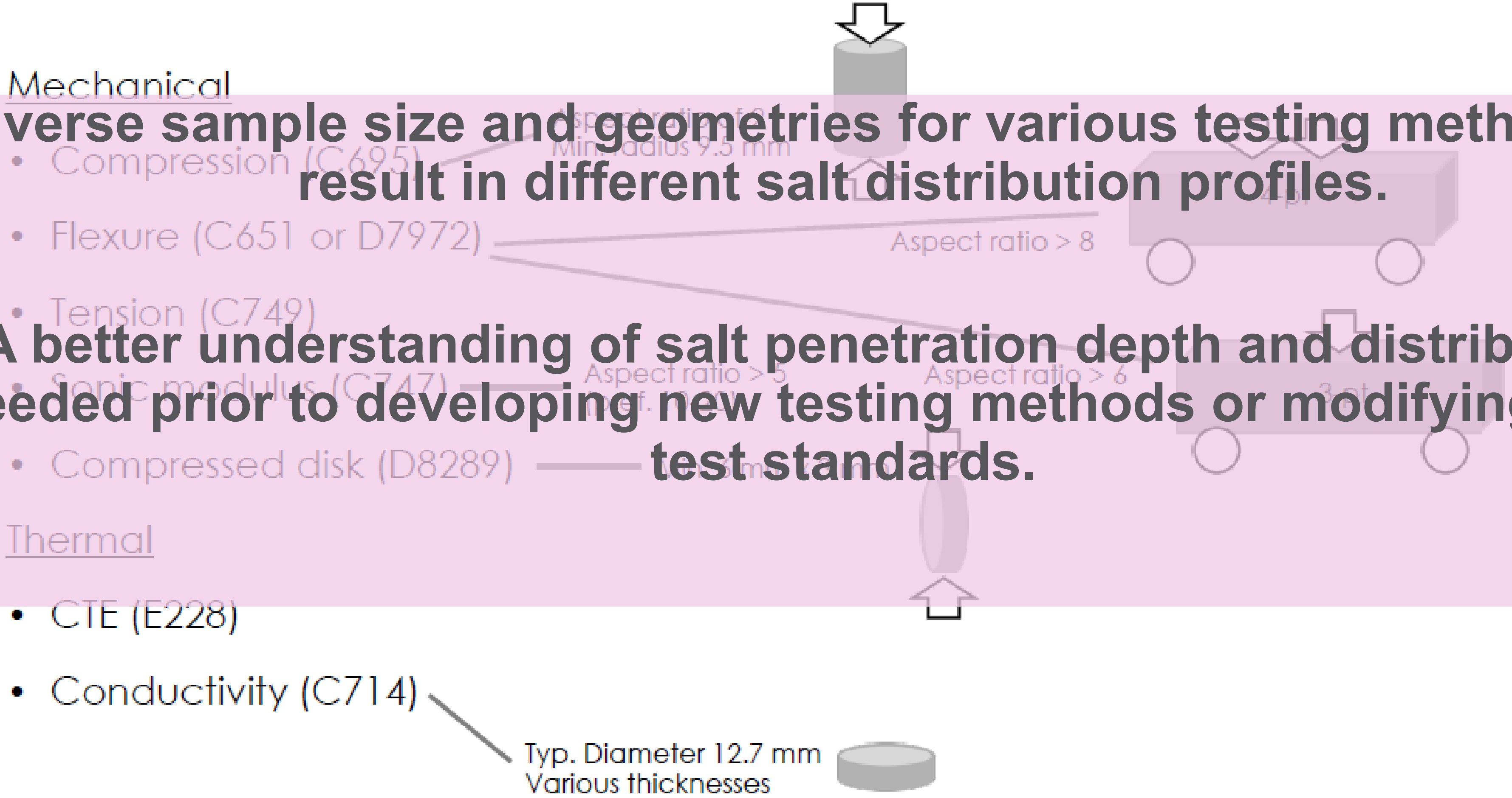
How about temperature? (650ºC vs 750ºC)

- Graphite sample geometry:
  - Cylinders
  - 10 mm (diameter) X 20 mm (height)
- Graphite grades studied:
  - NBG-18, PCEA, IG-110, 2114, ETU-10, NBG-25
- FLiNaK Intrusion conditions:
  - **Pressure: 3 bar**
  - **Time: 336 hr (2 week)**
  - **Temperature: 650 and 750ºC**
- Imaging completed <u>**before and after**</u> salt intrusion

On-going



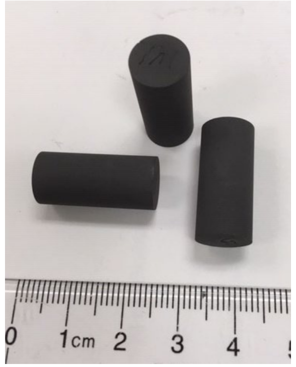
How about the effect of salt intrusion on graphite properties?

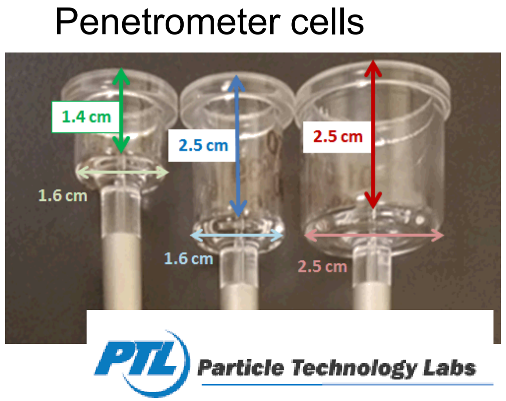


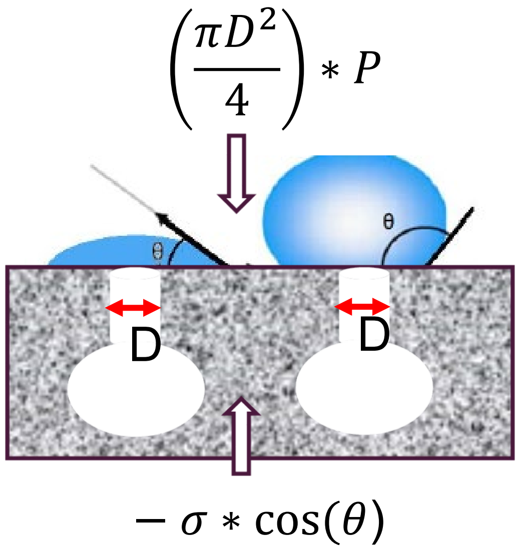
- **Diverse sample size and geometries for various testing methods may result in different salt distribution profiles.**
- **A better understanding of salt penetration depth and distribution is needed prior to developing new testing methods or modifying current test standards.**

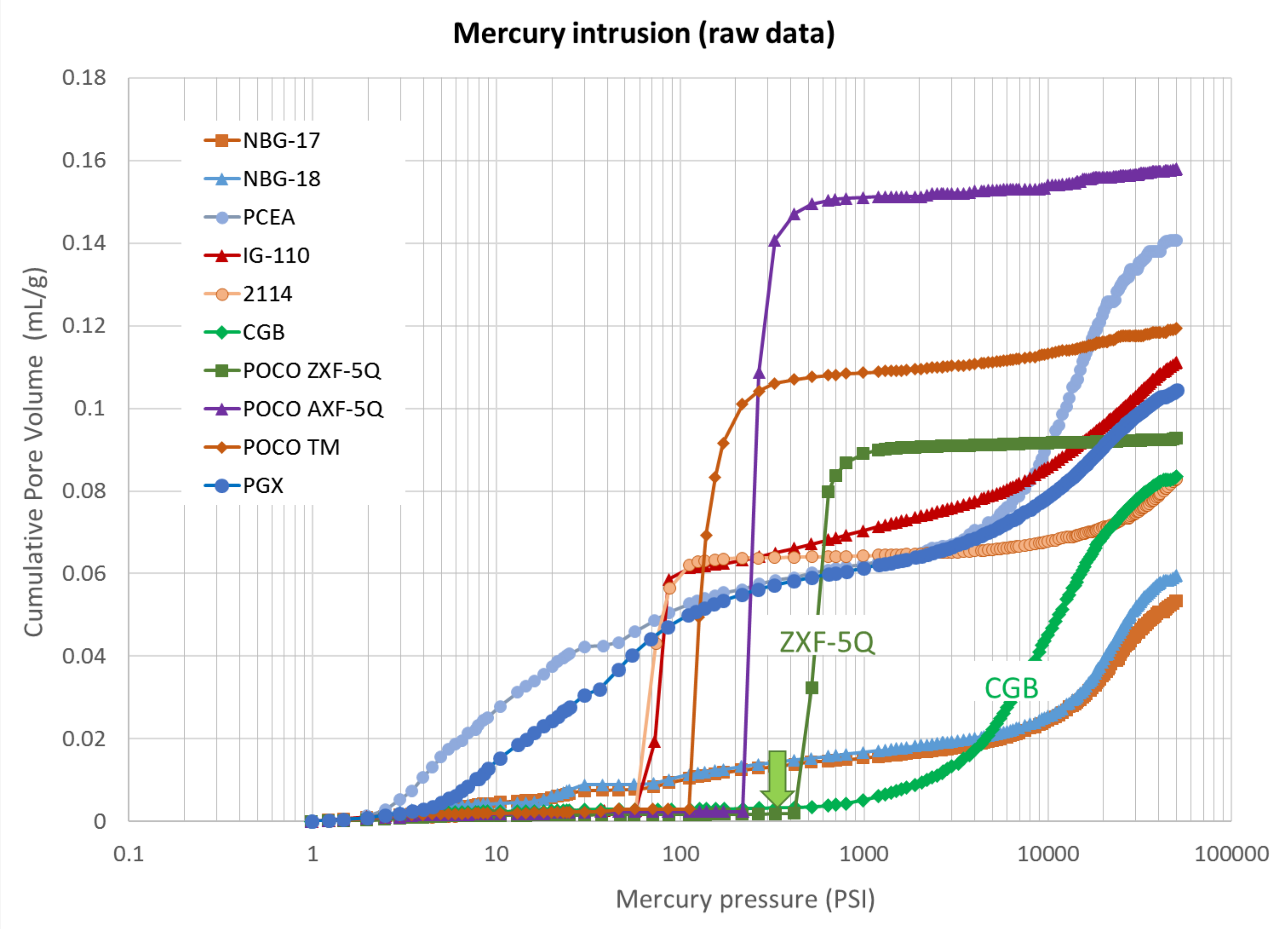
Can we predict salt intrusion?

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

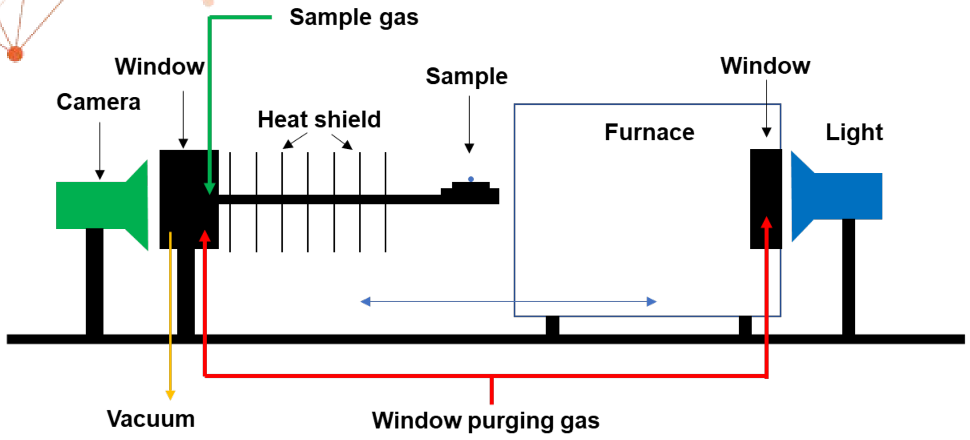


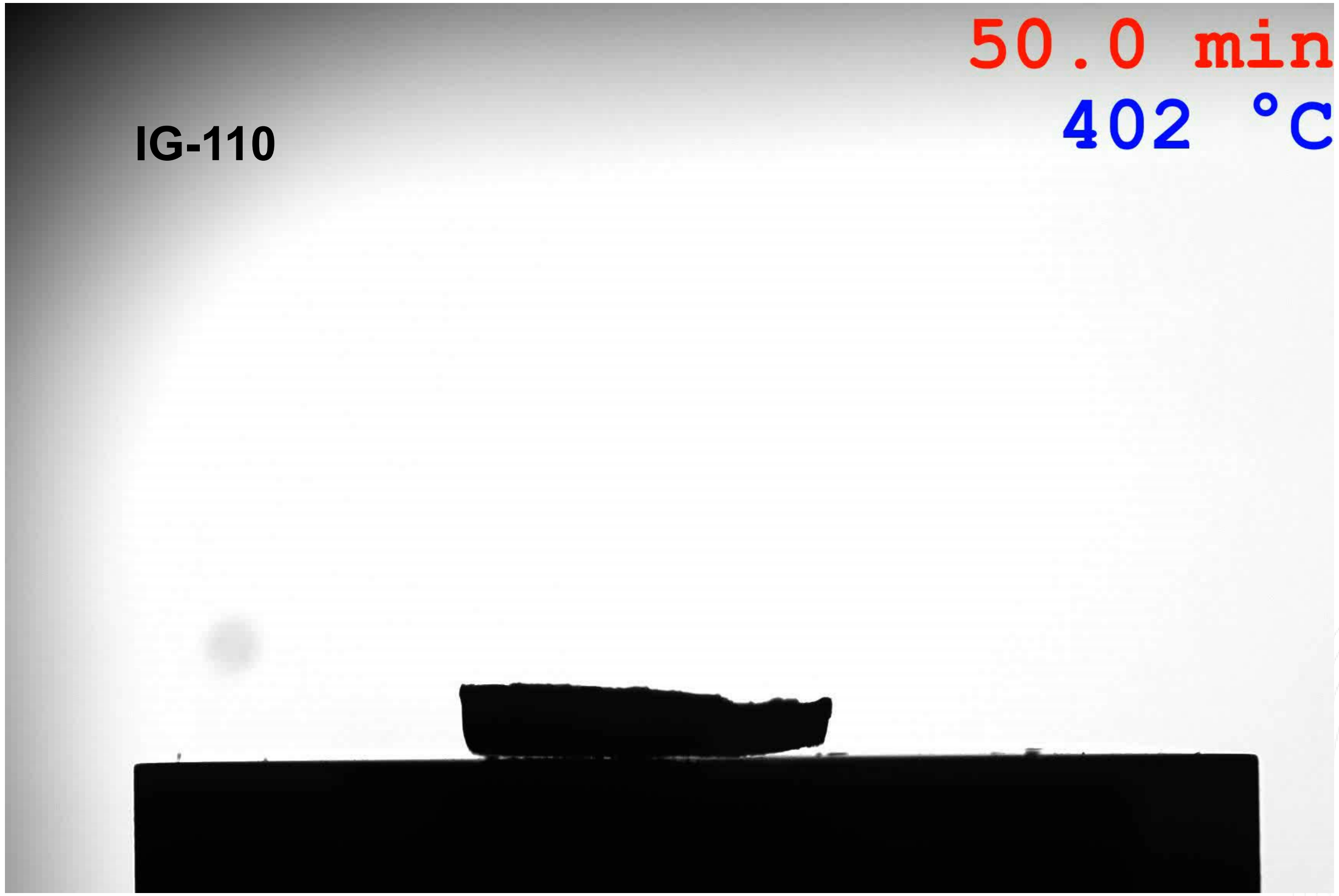






High temperature contact angle measurement

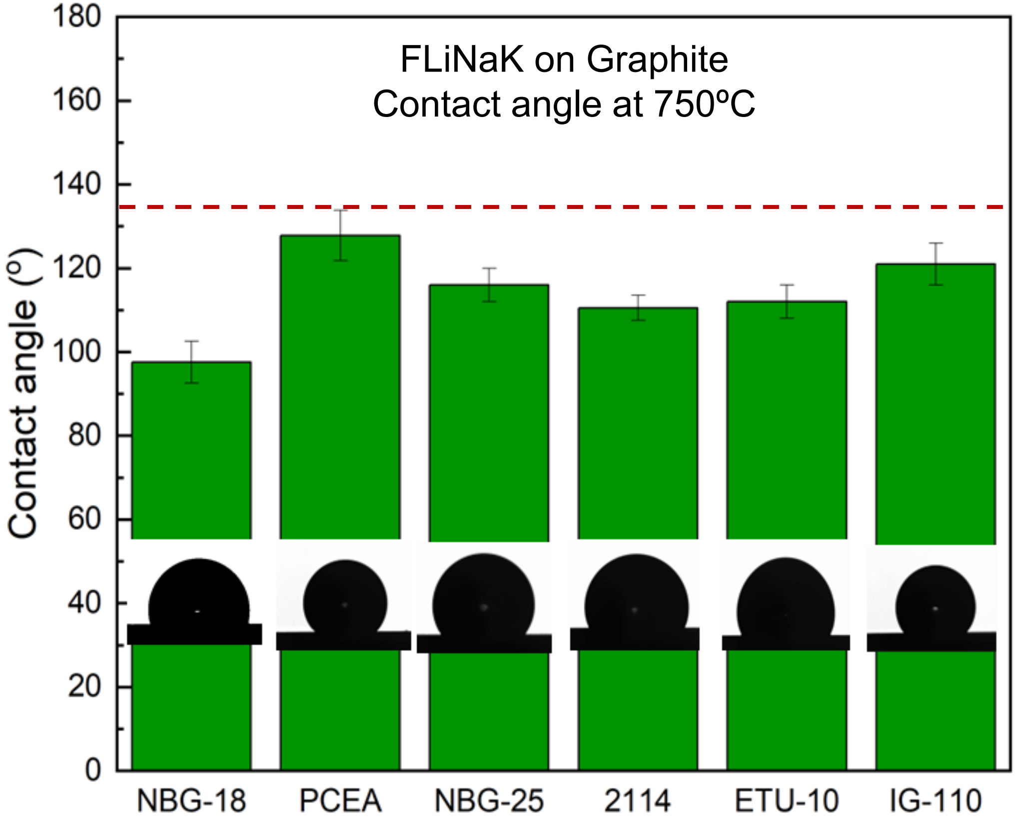


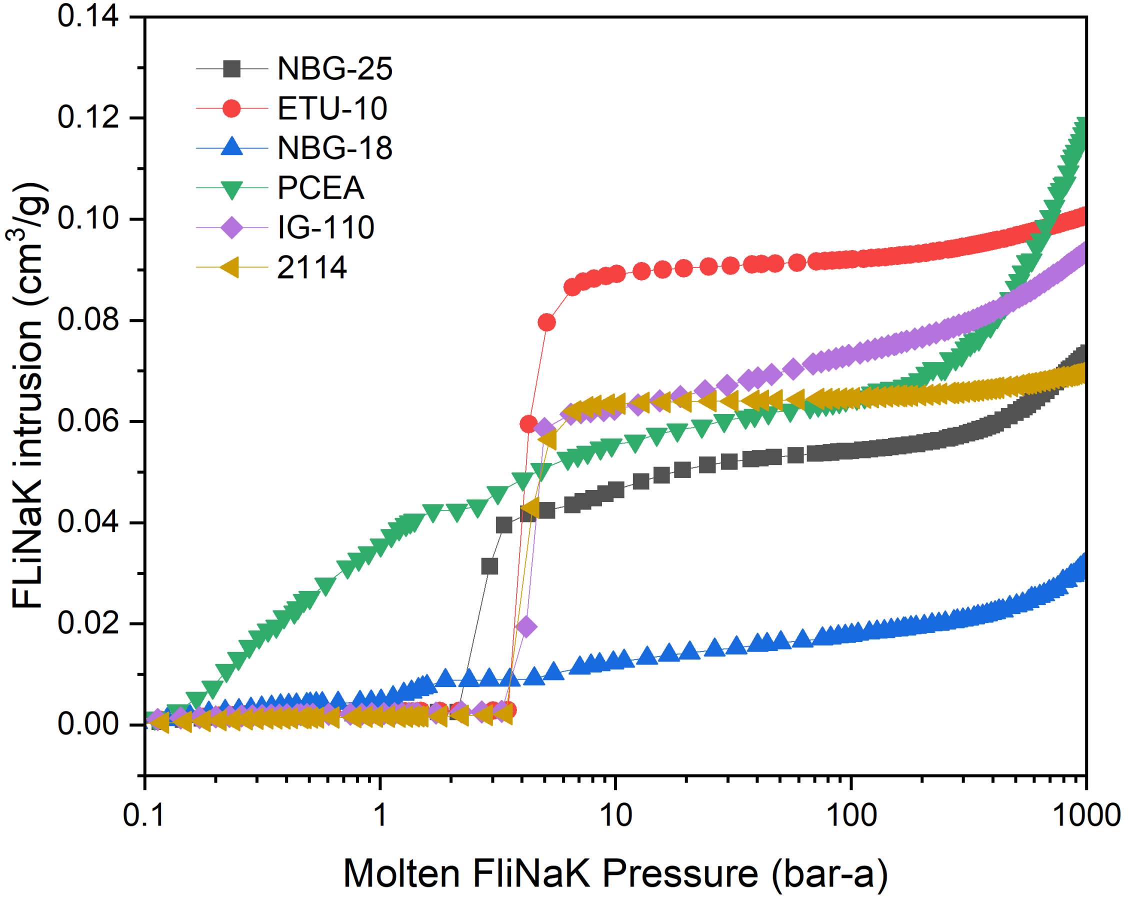


Contact angle measurement condition
- Salt : 3mm diameter salt(~8 mg)
- Graphite dimension: 10mm diameter with 2mm thickness

Salt properties
- FLiNaK Melting point 454 ^{o}C

Can we predict salt intrusion?



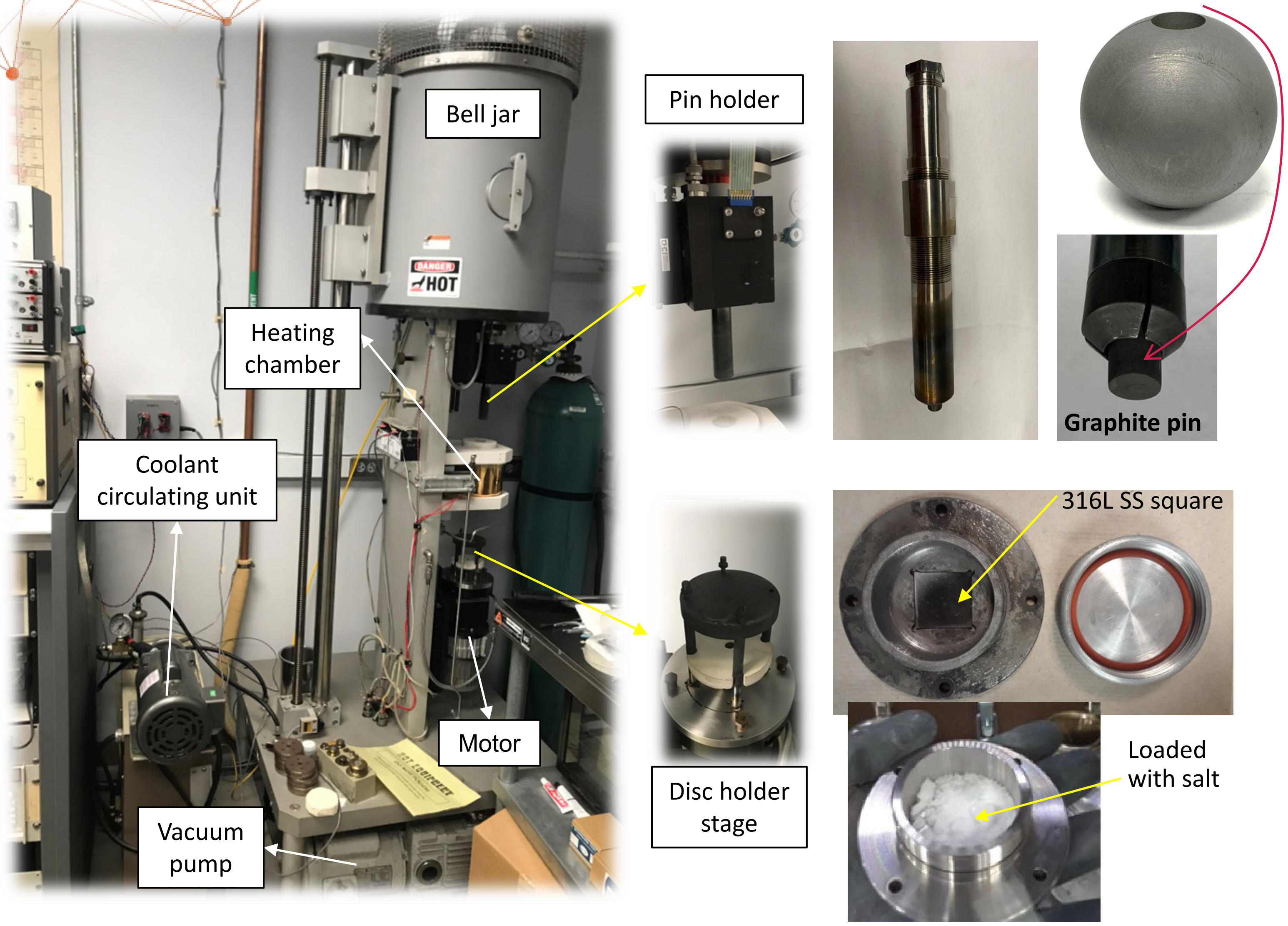


Notes:

- Surface tension from literature (M. S. Sohal et al, 2010)
- Pore size distribution from mercury intrusion

❖ Wear and abrasion of graphite in a molten salt

Feasibility Study of Graphite Wear Testing in Molten FLiNaK Salt



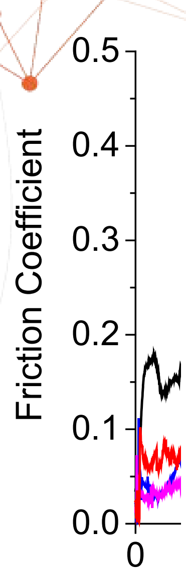
Experimental:

- 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)

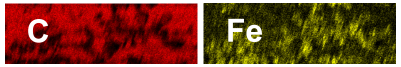
In-situ friction measurement combined with post-test wear quantification and surface characterization to investigate:

- 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)

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



Salt test1 - Wear scar on graphite pin



Wear 522 (2023) 204706

Contents lists available at ScienceDirect

Wear

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

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WEAR

Check for updates

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

We
Gra
316

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

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

Observations:

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salt

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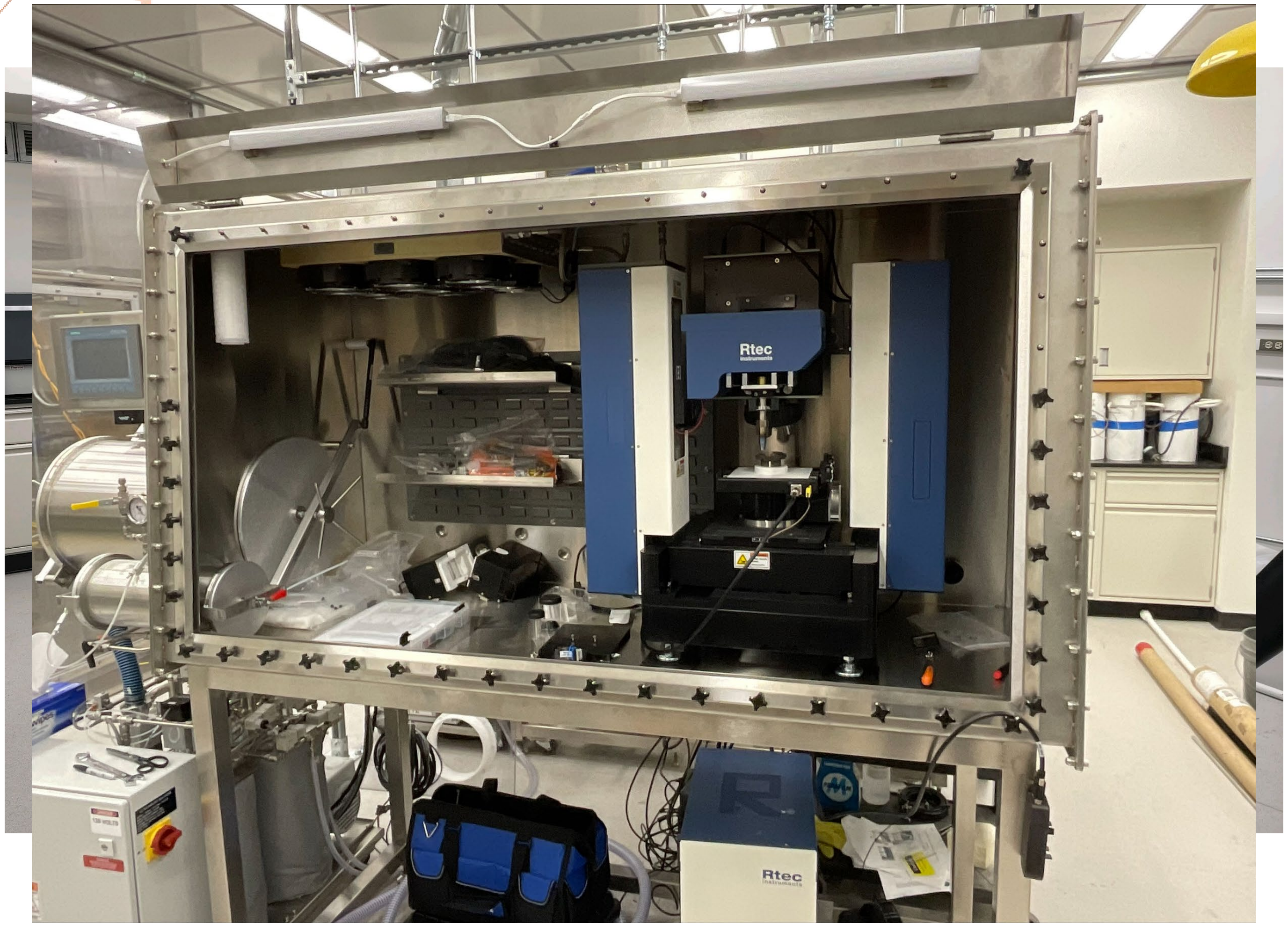
worn

t of

tribocorrosion.

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
- Neutron tomography is a non-destructive method suitable for visualization of impregnated salt distribution in graphite.
- Graphite microstructure (pore structure) is the prime factor that determines distribution of impregnated salt.
- 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 (Carbon 213, 2023, 118258).

Thank you!!