Understanding salt intrusion and wear behavior of graphite

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Graphite – Molten Salt Interactions Workshop
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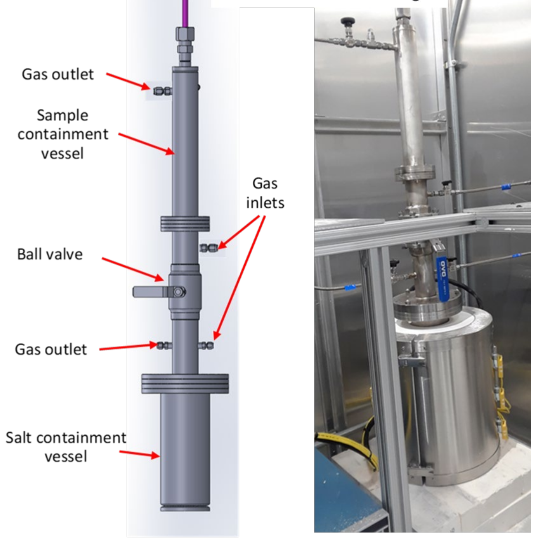
ORNL Graphite Salt Studies - Impact / Accomplishments / Capabilities

- **Understanding salt intrusion and the impact on graphite properties**
  - ✓ Developed salt-intrusion capabilities
    - Designed and built current system: approved for FLiNaK, < 10 bar, < 750ºC
    - Conducted measurements on various graphite grades and intrusion conditions
    - Developing a better understanding of graphite pore structure via Hg intrusion
    - Plan to study wetting behavior of molten salts on graphite surfaces
    - Using neutron imaging to understand salt intrusion and penetration depth profile
    - Participation in ASTM and ASME
  - ✓ Designed and built a second salt-intrusion system, approved for FLiBe, located inside a new 4-glove glovebox (not commissioned due to lack of funds)

- **Understanding wear behavior of graphite**
  - ✓ Completed initial scoping studies in dry Argon and with FLiNaK
  - ✓ Completed procurement of new glovebox (delivered and installed) and tribometer (to be delivered soon) for wear testing studies in controlled environment

FLiNaK Intrusion testing

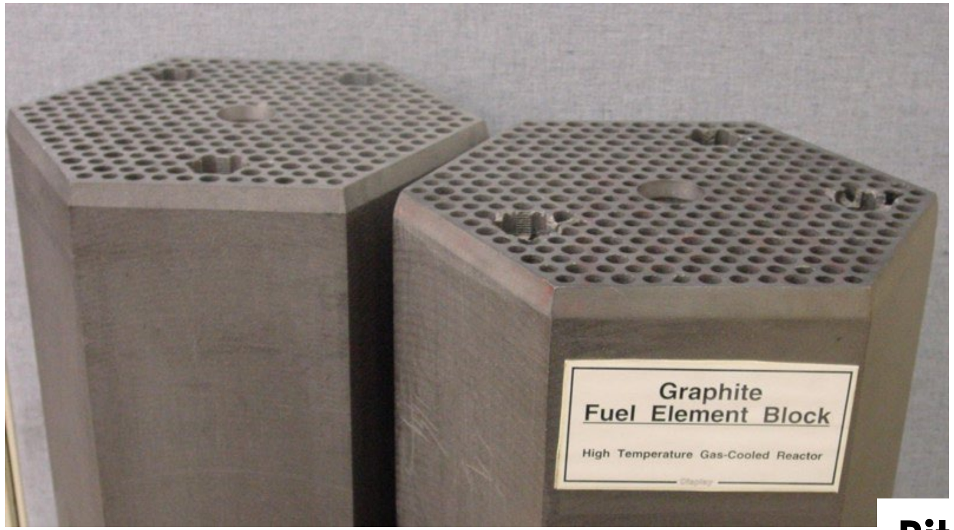


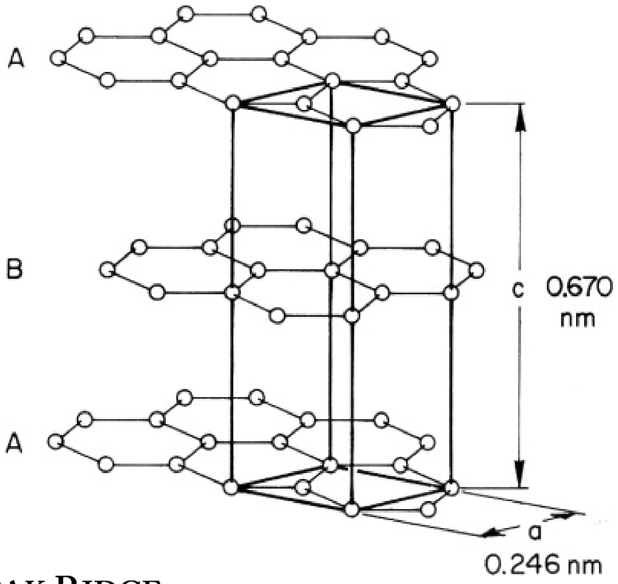
Glovebox and FliBe Intrusion testing

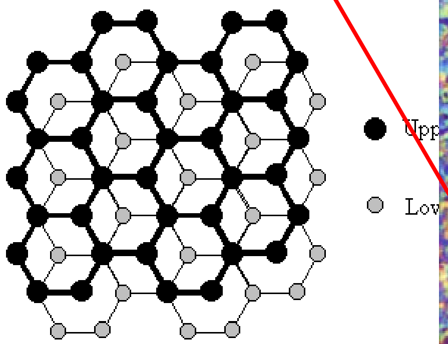
Glovebox for wear testing

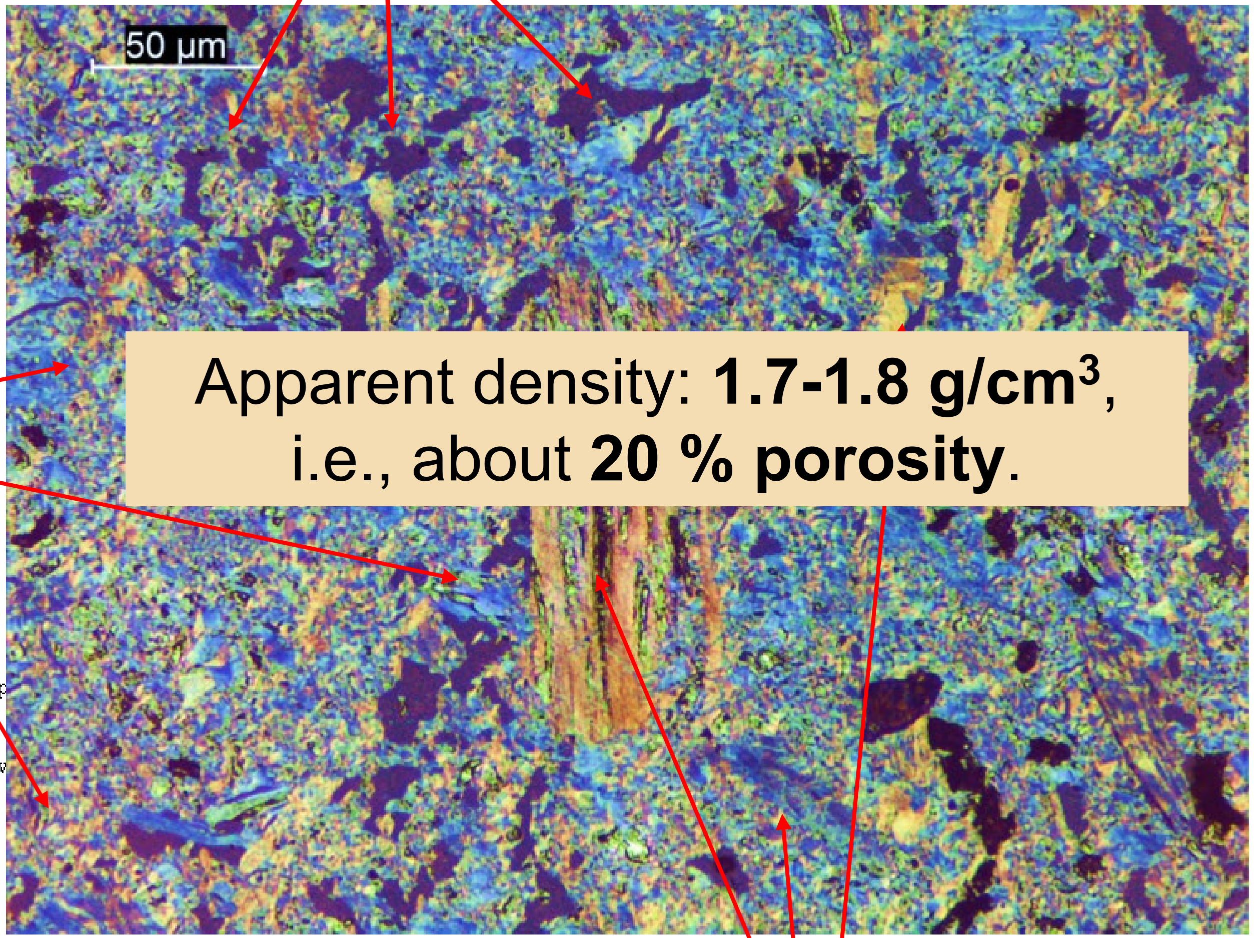
- **Understanding salt intrusion and the impact on graphite properties**

Graphite







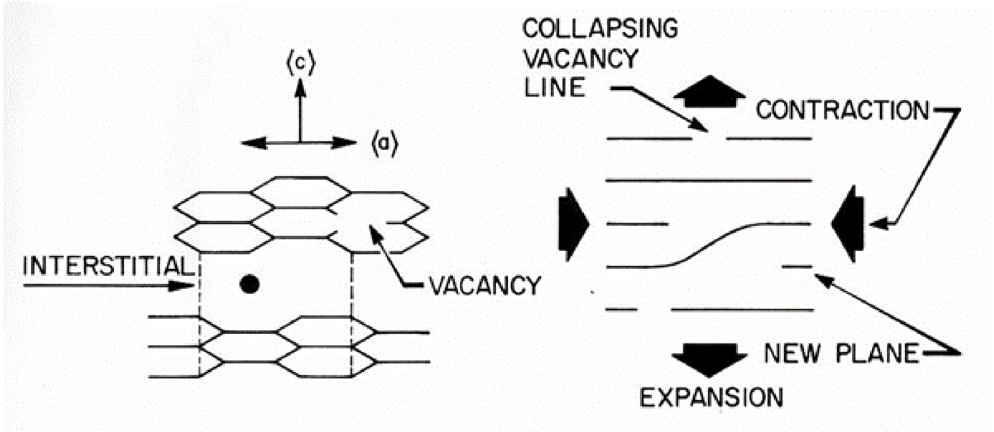


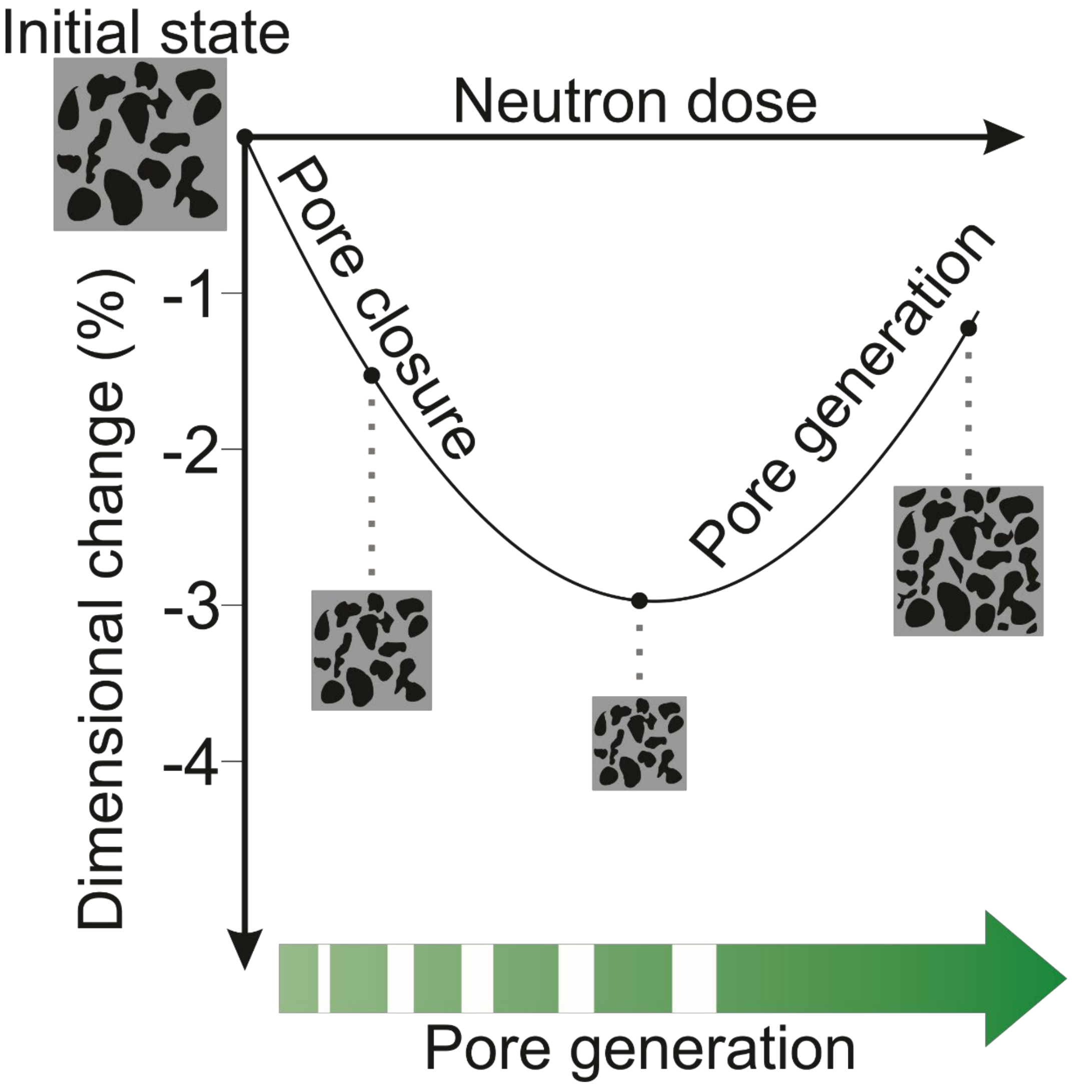
Apparent density: **1.7-1.8 g/cm^3**, i.e., about **20 % porosity**.

Why is porosity important in Graphite?

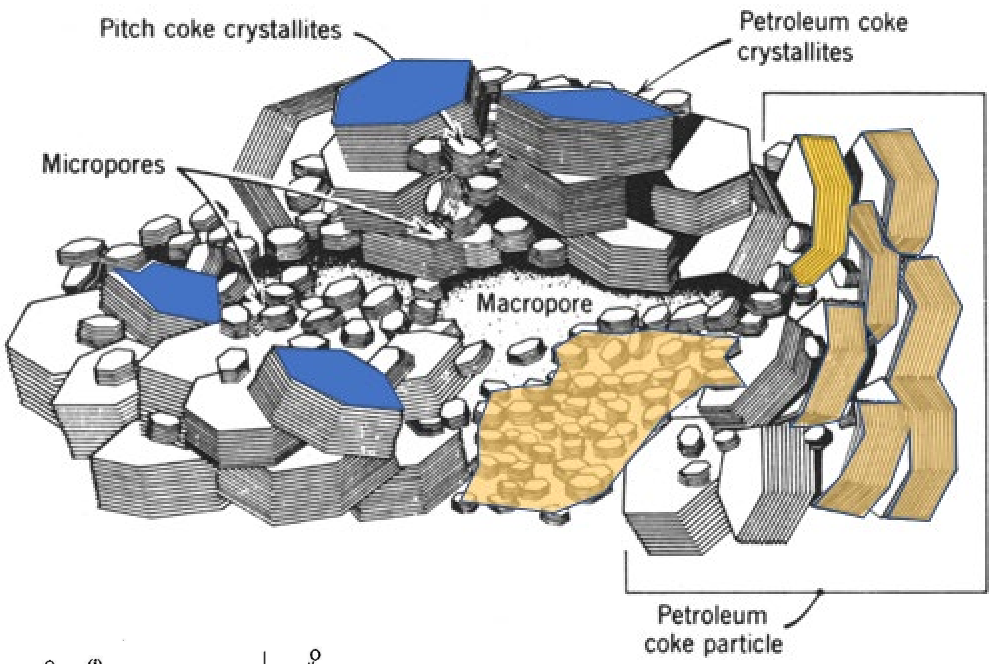
Microstructure and **Porosity** Defines the Properties and Irradiation Behavior of Graphite

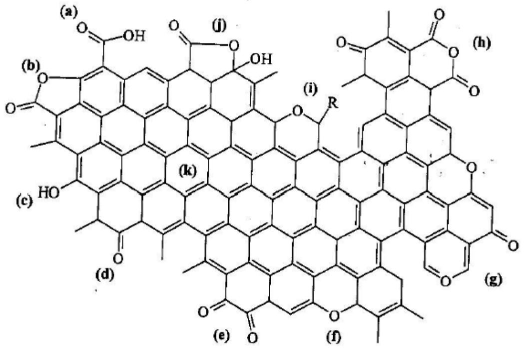
- Graphite contains pores at multiple length scales
- Neutron irradiation affects the size of the porosity in graphite
- The irradiation effects on graphite contribute to the generation of new porosity



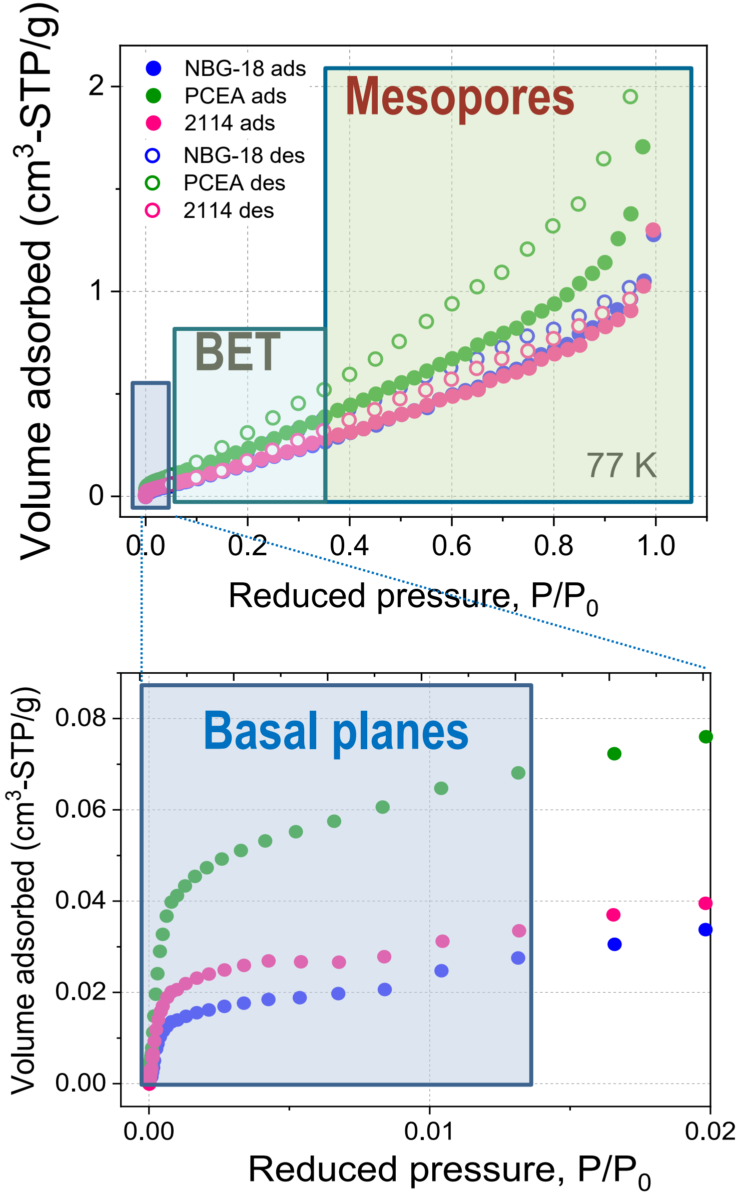


Porosity (edge / basal sites) Determines Reactivity



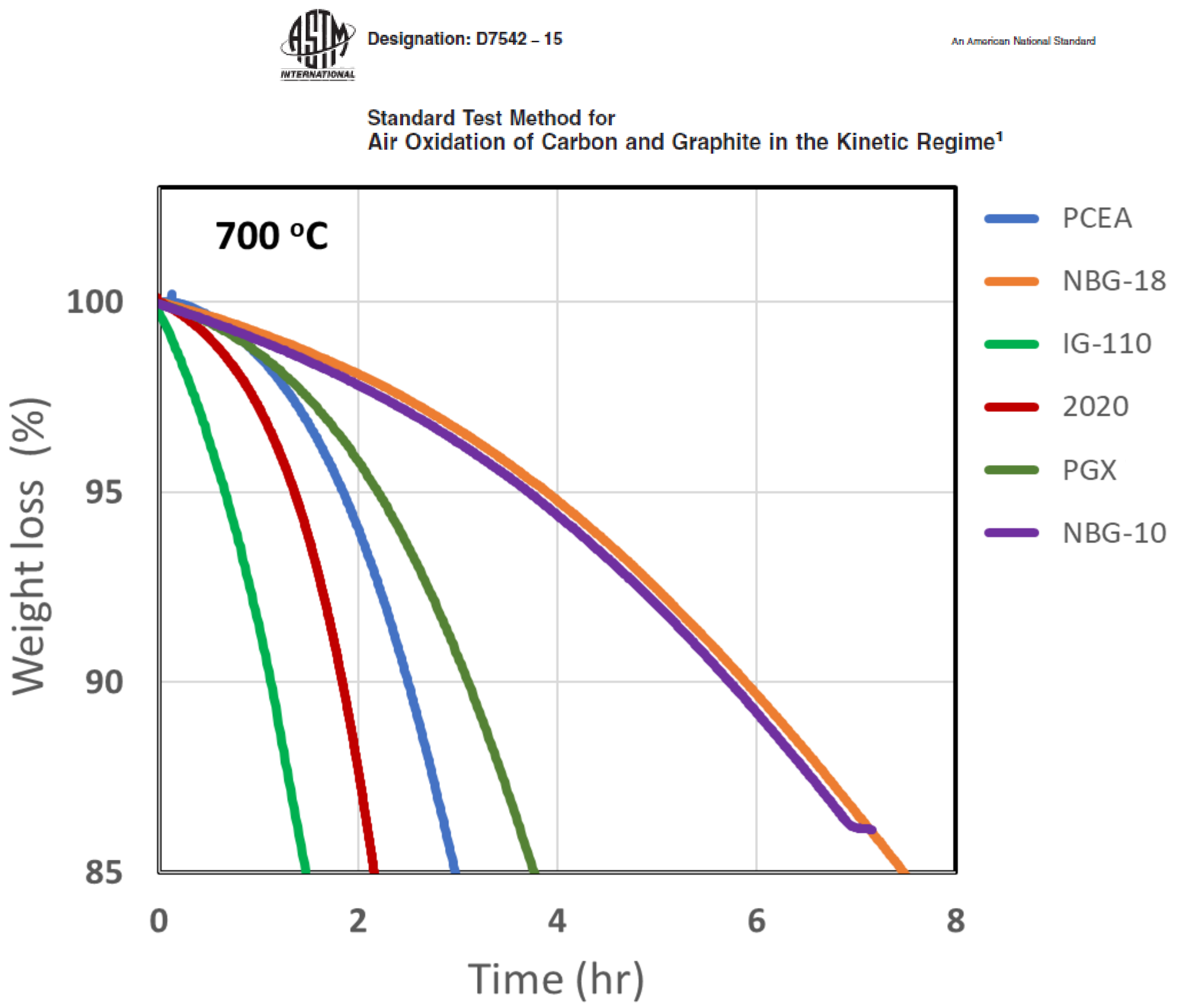


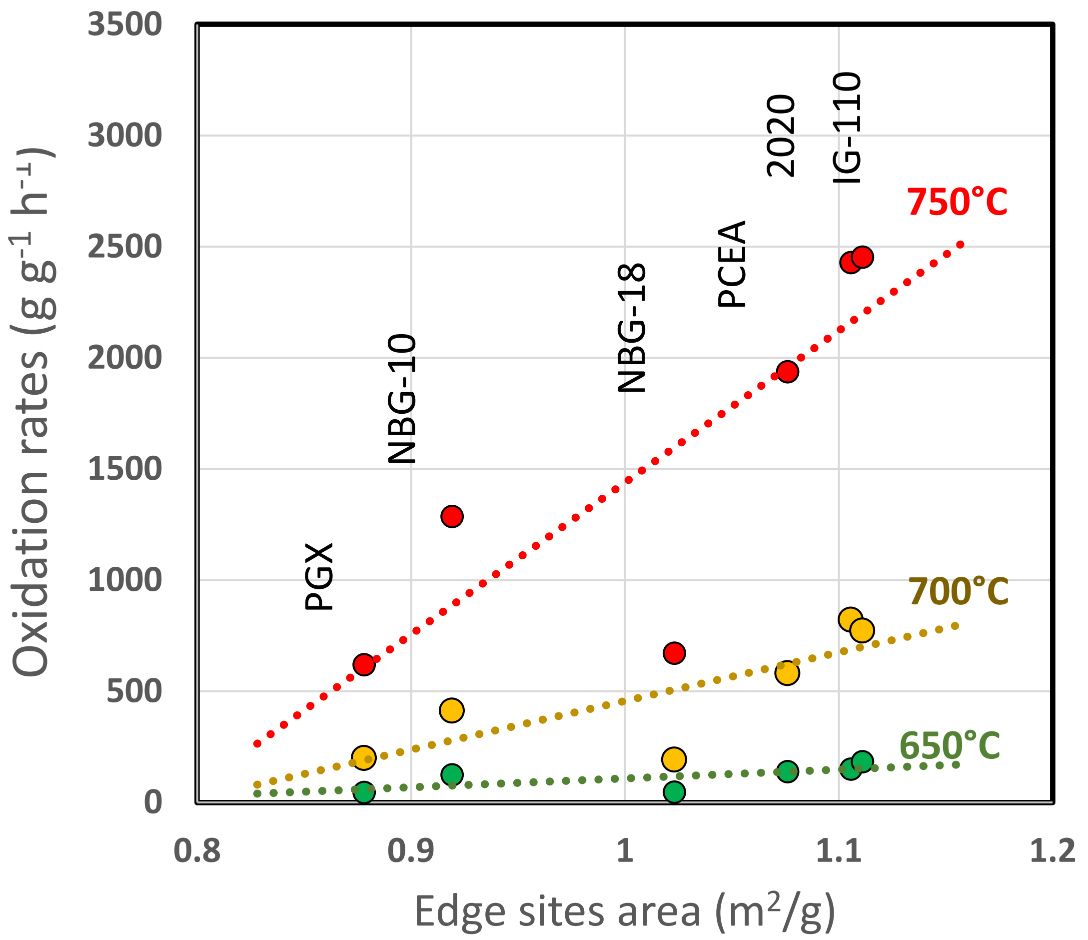
$$S_{BET} = S_{edge} + S_{basal\ sites}$$



H E McCoy et al, Nucl. Applic. Technol. 8 (1970) 156

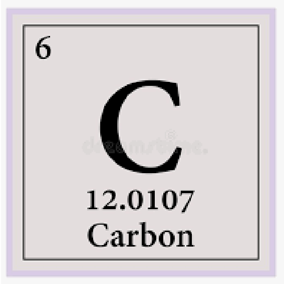
Oxidation Rates Correlates with Edge Sites (Porosity)





What does Porosity in Graphite Mean to MSRs?

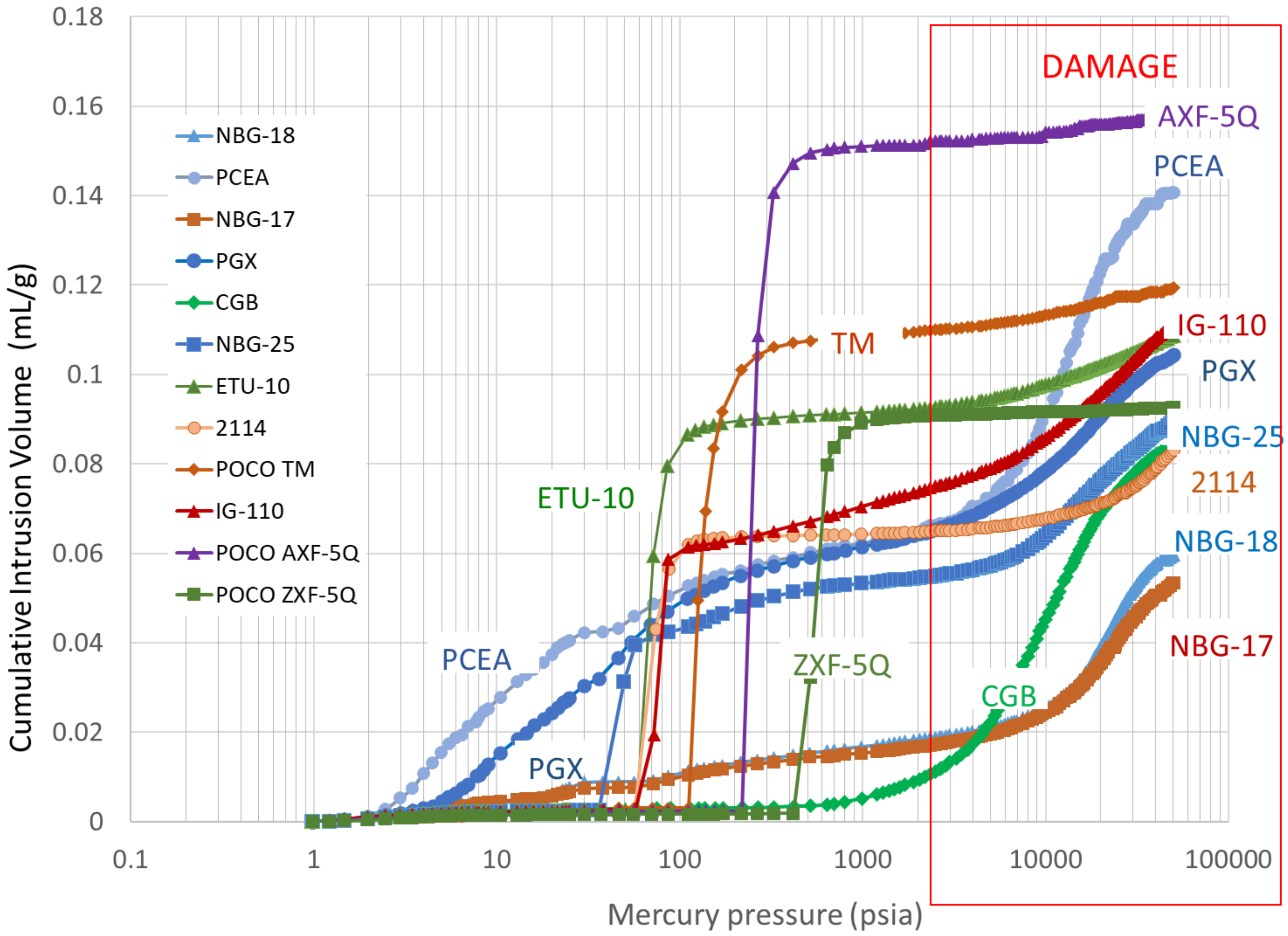
- Salt intrusion into pores?
- Effect of that salt intrusion on graphite properties? (mechanical, thermal)
- Chemical Interaction between salt and graphite?
- Edge sites for tritium retention?

One carbon 

… many graphites!

Porosity in graphite comes in different shapes, sizes and connectivity

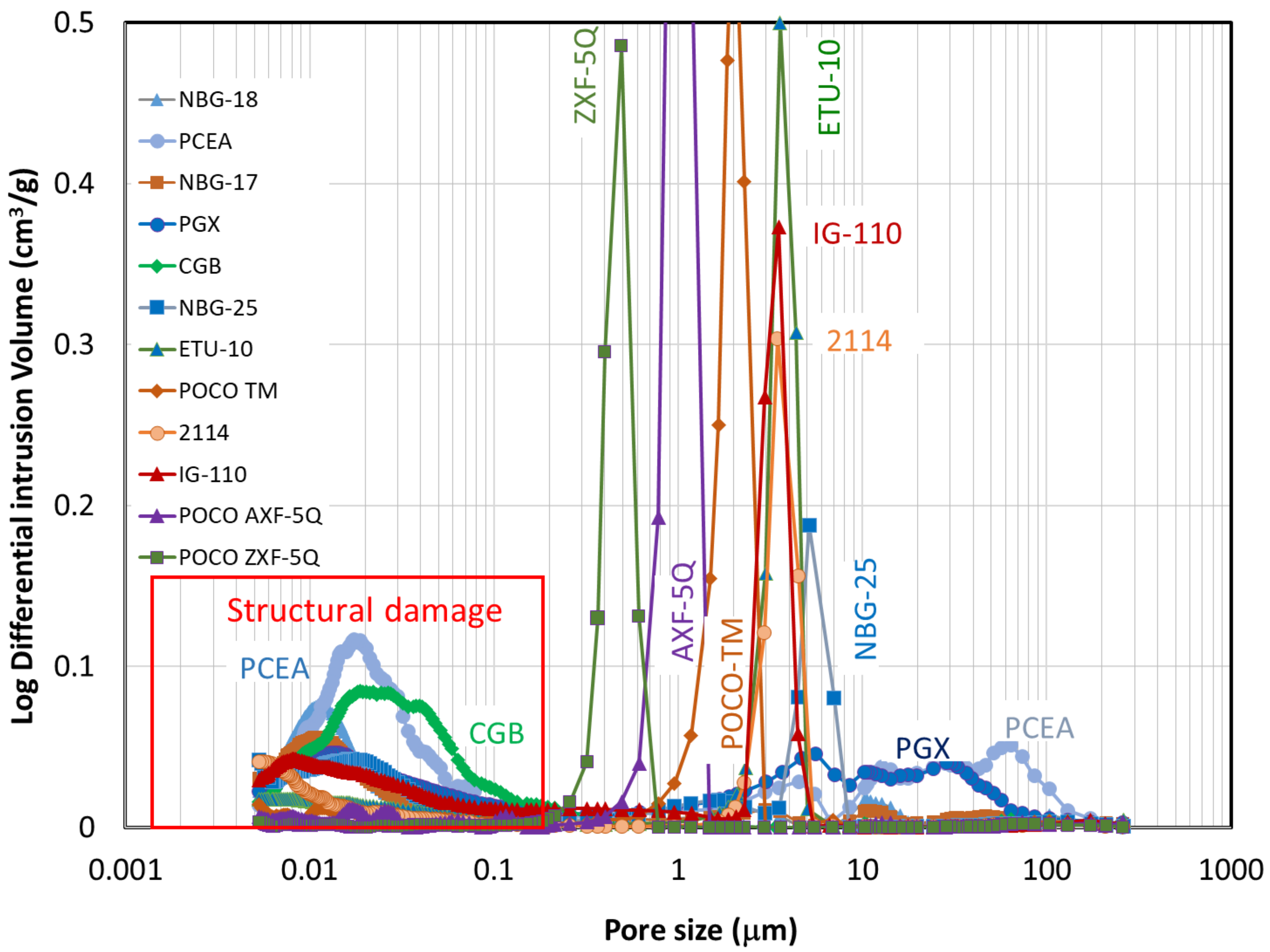
Mercury intrusion showed a wide range of porosity distributions for a variety of graphite grades



- 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

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



ORNL/TM-2020/1621

Can we quantify salt intrusion in graphite?

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

Designation: D8091 – 21

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

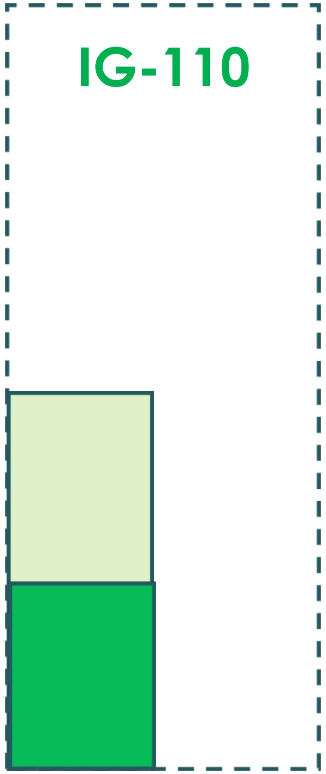
$$D_o = \left(\frac{W_2 - W_1}{V_o \rho} \right)$$

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

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.

Understanding the meaning of D parameter

	IG-110	NBG-18
Sample volume (cm^3)	**1.00**	**1.00**
Sample weight (g)	**1.76**	**1.86**
Specific open pore volume(cm^3/g)	**0.079**	**0.044**
Open pore volume in graphite sample (cm^3)	**0.139**	**0.082**
Pore filling fraction (D_o)	**D_0 = 0.5**	**D_0 = 0.5**
Salt % by volume (D_v)	**D_v = 7.0 %**	**D_v = 4.1 %**
Salt % by weight (D_w)	**D_w = 7.9 %**	**D_w = 4.4 %**



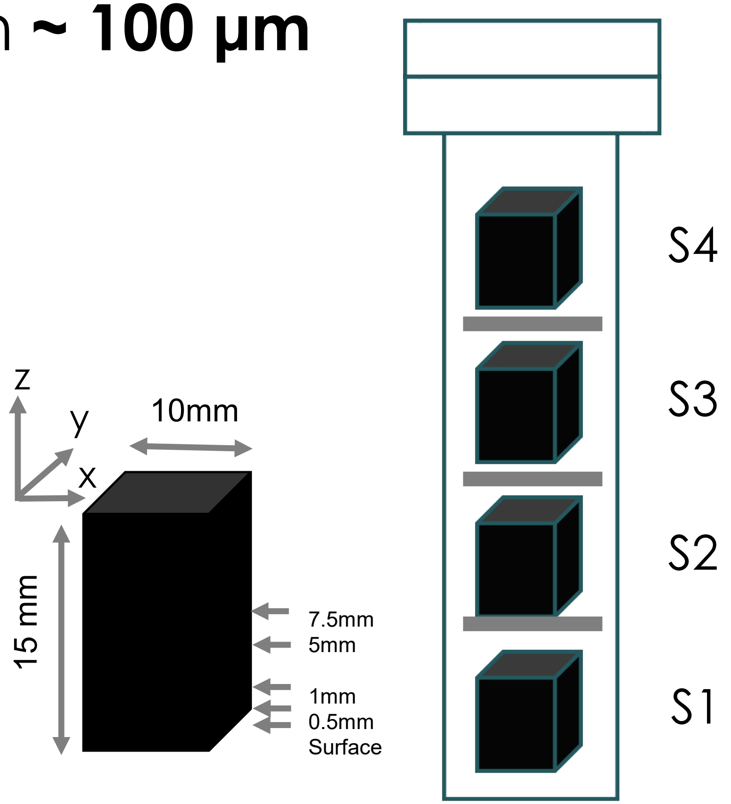
What about **salt distribution** across the cross-section of sample?

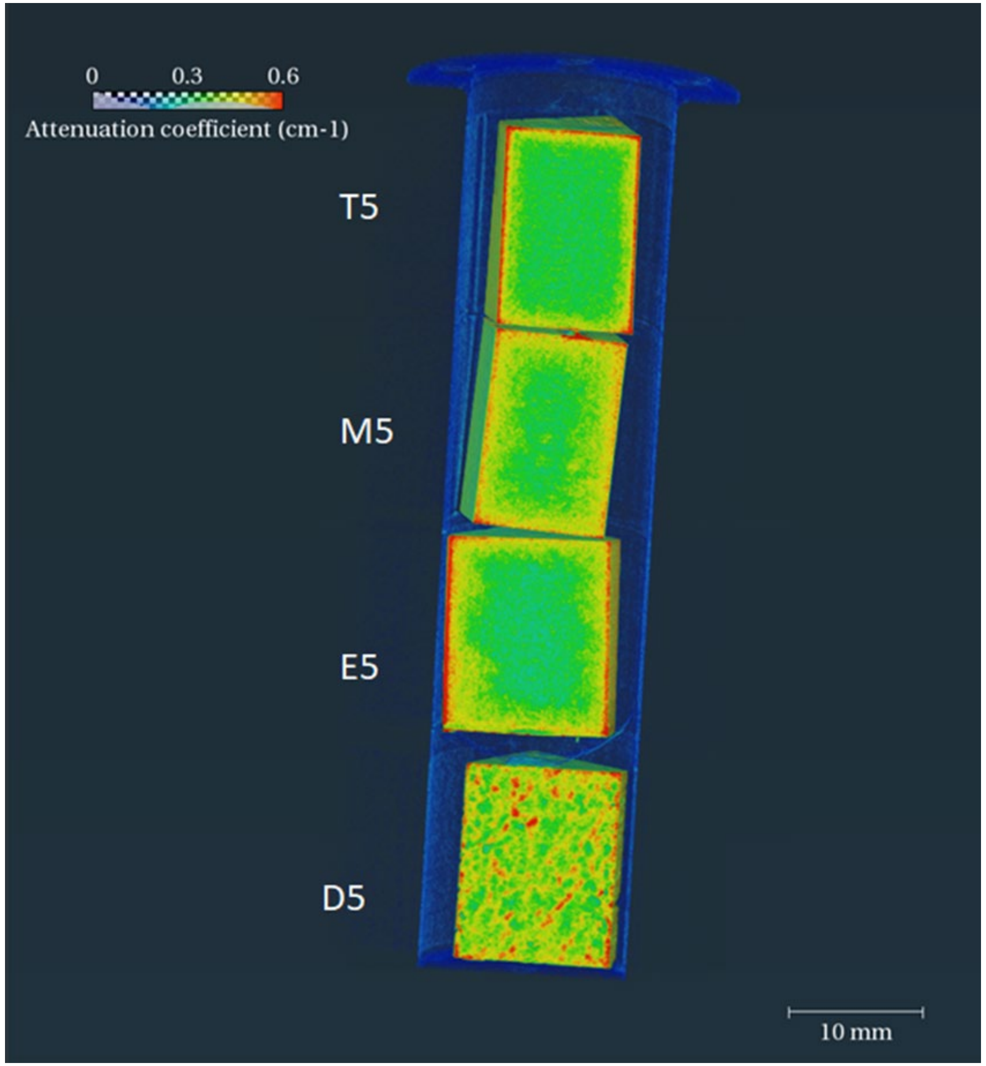
Using neutron imaging to study ***salt distribution***

- Proof of principle experiment at Neutron Imaging Beamline CG-1D (ORNL's HFIR)
- Image resolution **~ 100 µm**

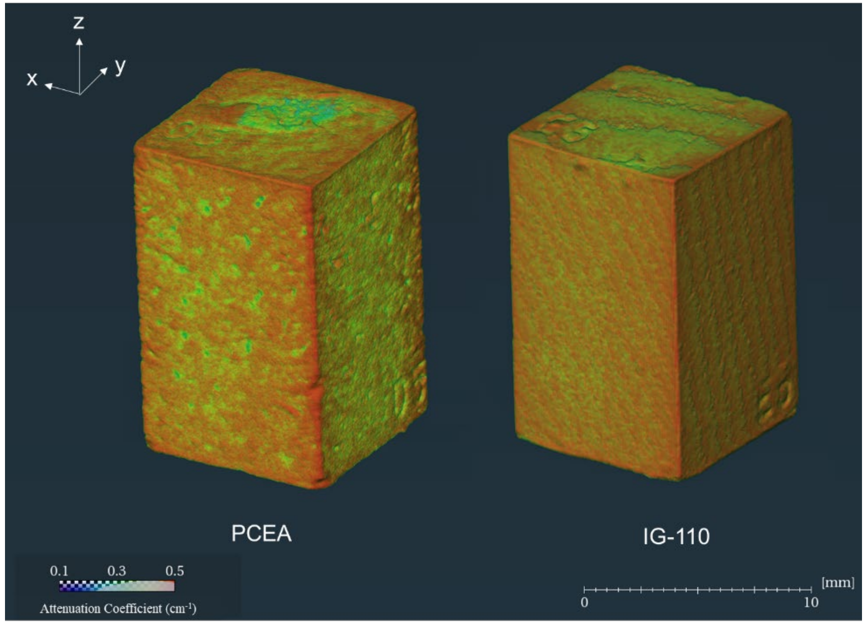
FLiNaK impregnated graphite samples

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



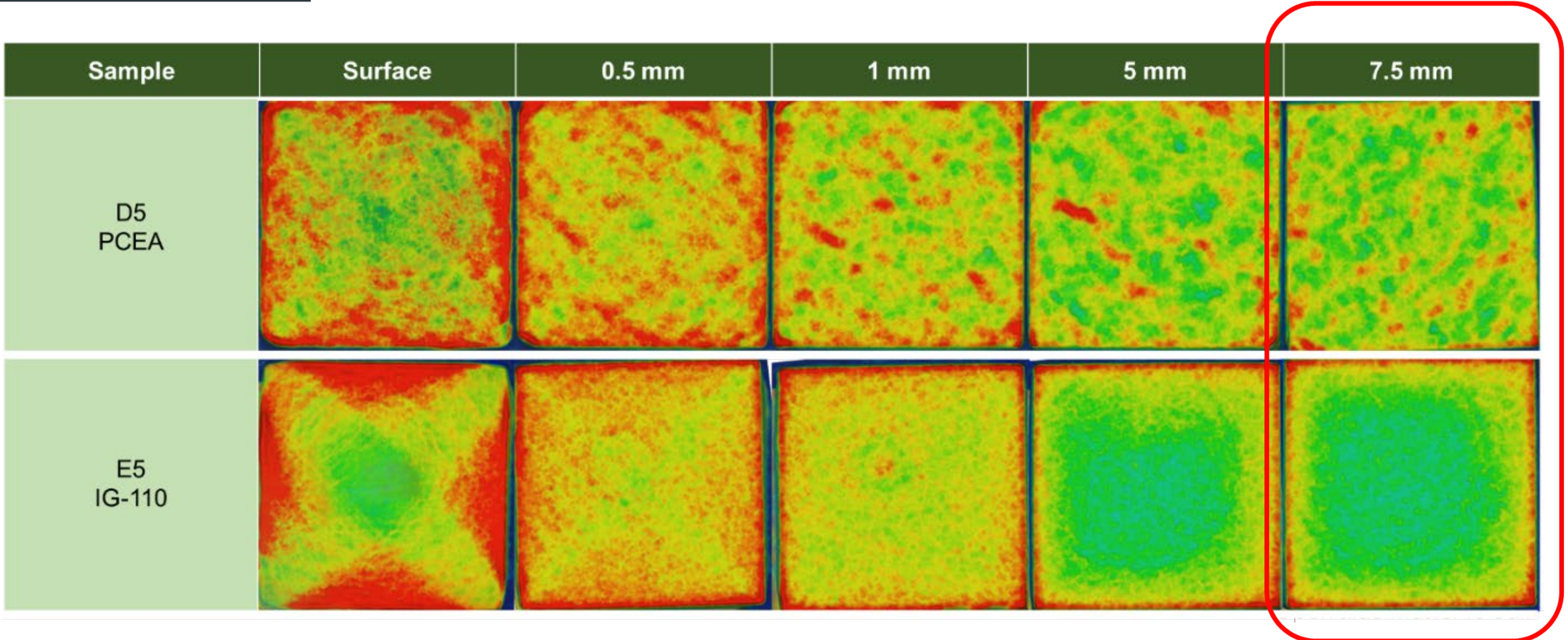


XY axis images were captured at the surface, from 0.5, 1, 5, 7.5mm from the surface

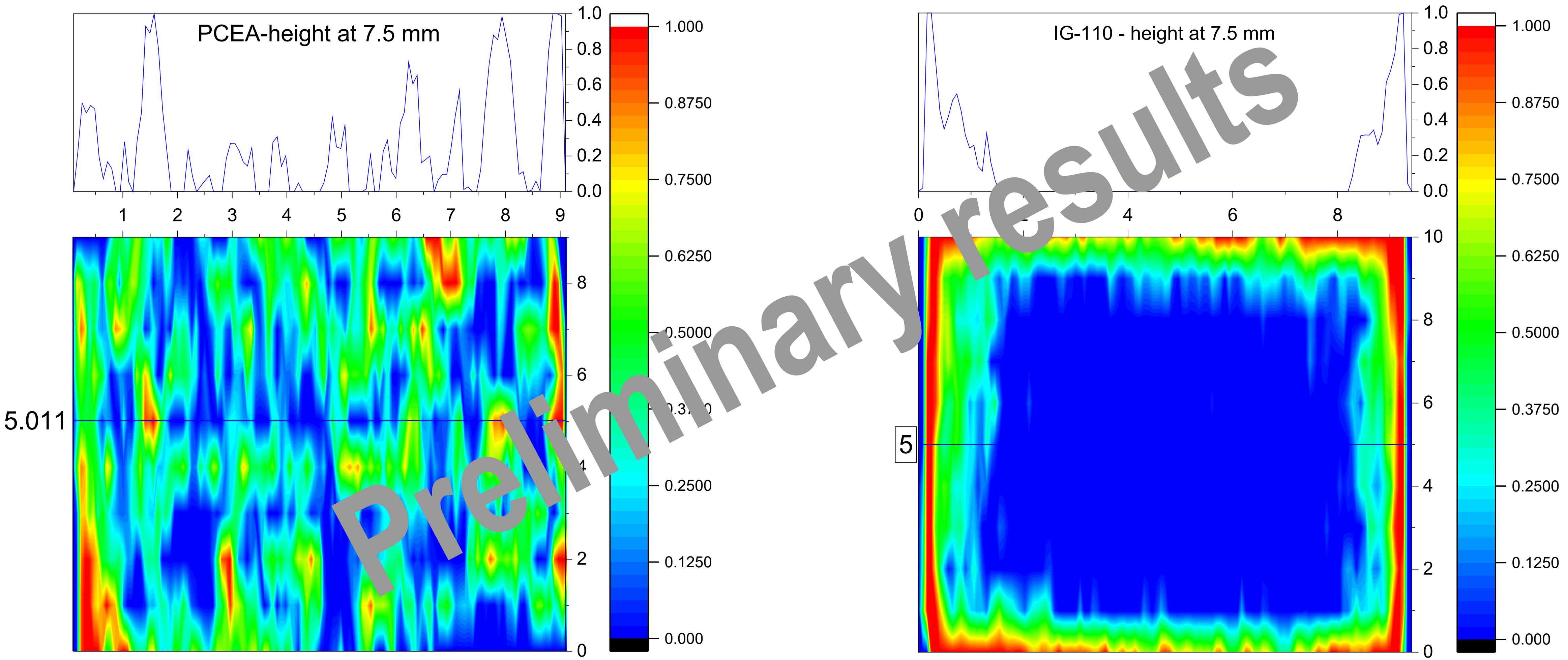


P: 5 bar ; T: 750°C; t: 12 hours

Graphite grade	Grain size (µm)	Pore Φ (µm)	Bulk density (g·cm^{-3})	Open pore volume (cm^3·g^{-1})	Total pore volume (cm^3·g^{-1})	Porosity (%)	Wt. uptake (%)	Do
IG-110	10	3.9	1.76	0.079	0.120	21	5.7	0.36
PCEA	800	64	1.77	0.065	0.119	21	6.9	0.53



Salt **distribution profile** is significantly different between grades



- **What can we say about salt intrusion in graphite**?
  - It is real, at least at the conditions presented here.
  - Salt distribution and penetration is highly dependent on pore structure
- On-going work to further analyze the data collected on other graphite grades
- **Future analysis**:
  - New samples prepared – will do neutron imaging of samples before and after pre-salt infiltration – better baseline; will utilized cylindrical samples, potentially performing compression tests on samples after imaging
  - Want to evaluate lower pressures at **various times**

Can we measure the effect of salt intrusion on graphite properties?

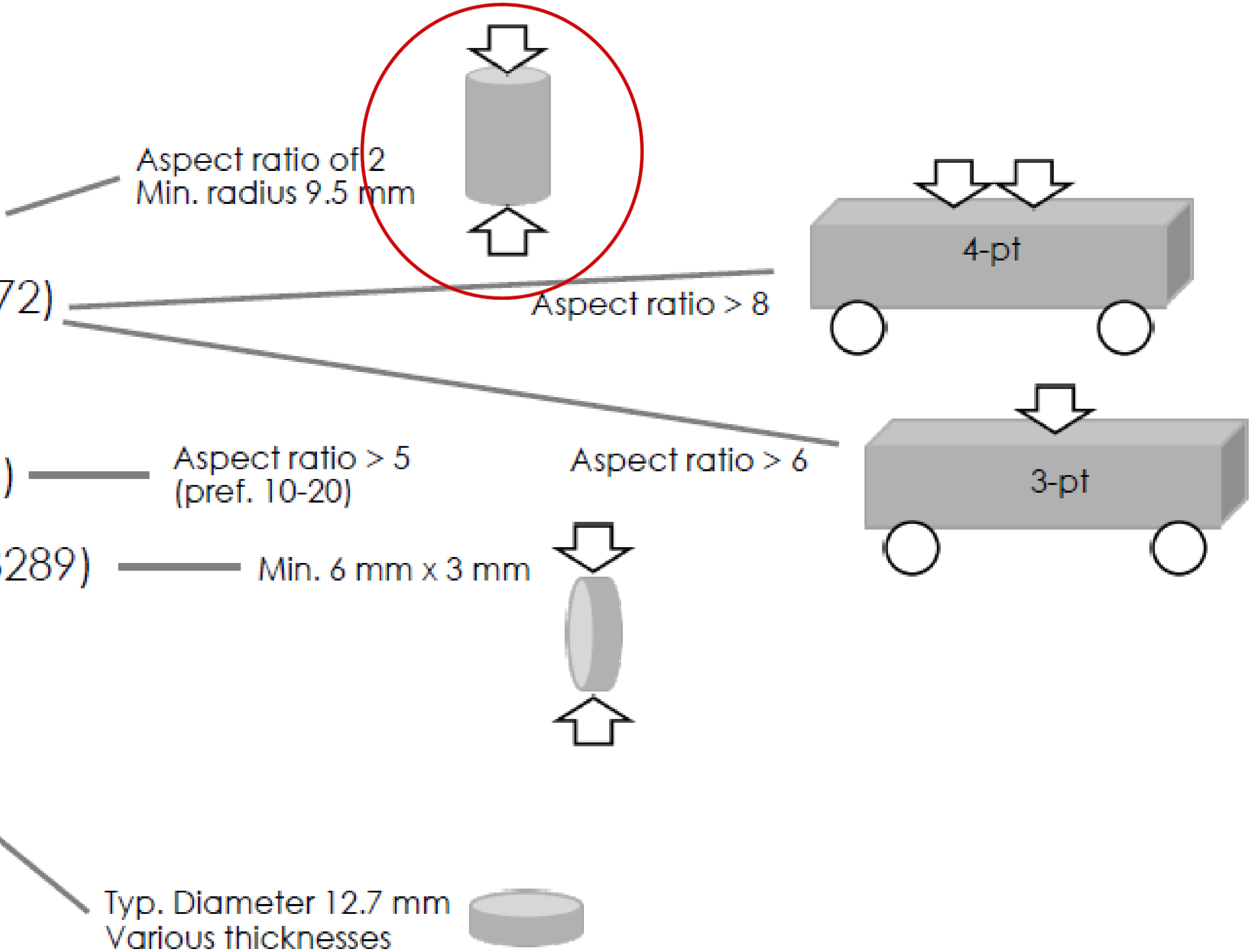
Diverse sample size and geometries for various testing

<u>Mechanical</u>

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

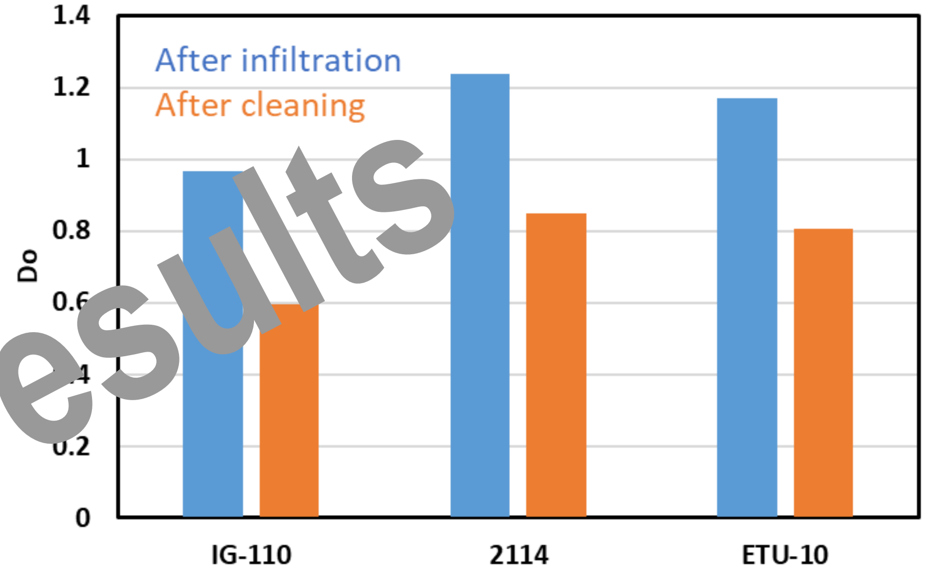
<u>Thermal</u>

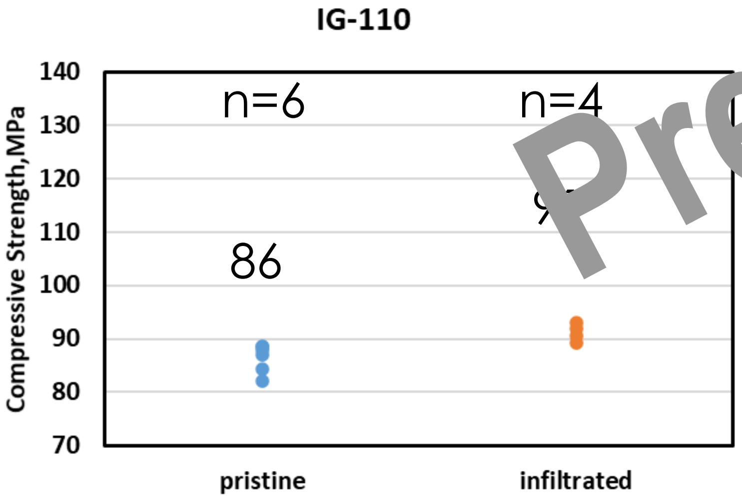
- CTE (E228)
- Conductivity (C714)

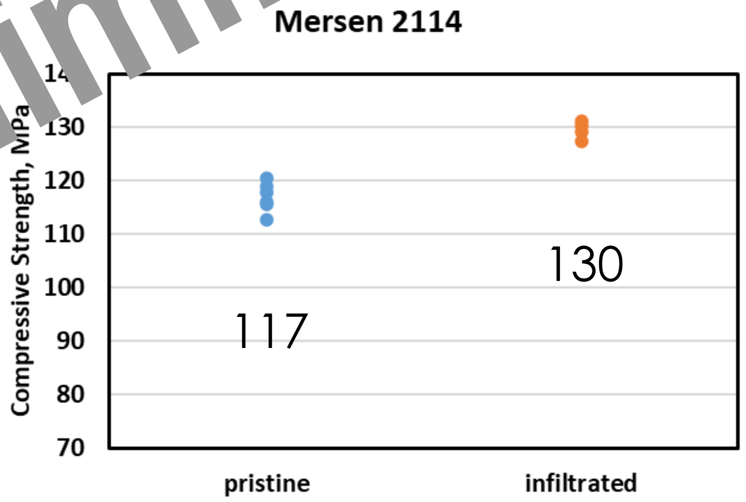


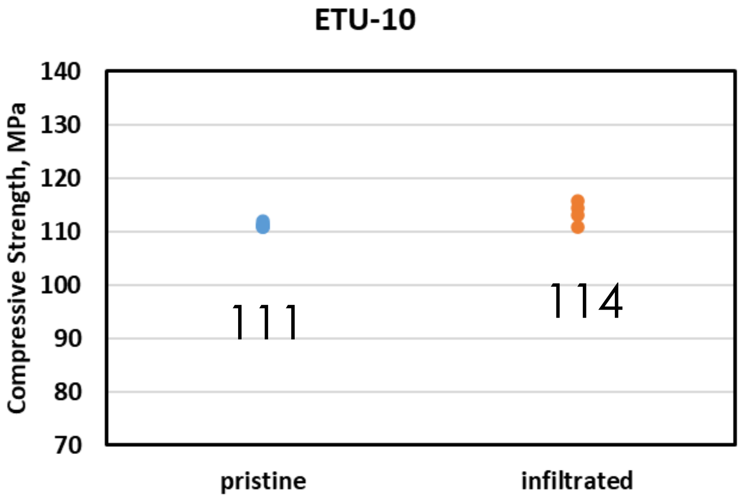
Overview – Compressive Strength of Infiltrated Graphite

- Nominal dimensions: 10 mm diameter x 20 mm length
- Grades: IG-110, 2114, and ETU-10
- Samples were infiltrated in Flinak molten salt (7 bar gauge; 750 C; 12 hrs)
- Post infiltration, samples were cleaned using: (1) boiling water, (2) sonication in DI water, and (3) vacuum drying.
- Compression testing followed ASTM C695
- Average compressive strength slightly increased









Preliminary results

How do we perform test after intrusion? Salt /no salt?

- If interested on "material properties", salt should be removed:
  - however, removing salt is not a straightforward process

- If salt is left in graphite sample, then, what are we measuring?
  - system performance? a composite property?
  - Temperature of measurement? Room temp vs temp of intrusion?
  - Handleability? - salt is highly hygroscopic and some are toxic

ASTM D8377-21

Designation: D8377 – 21a

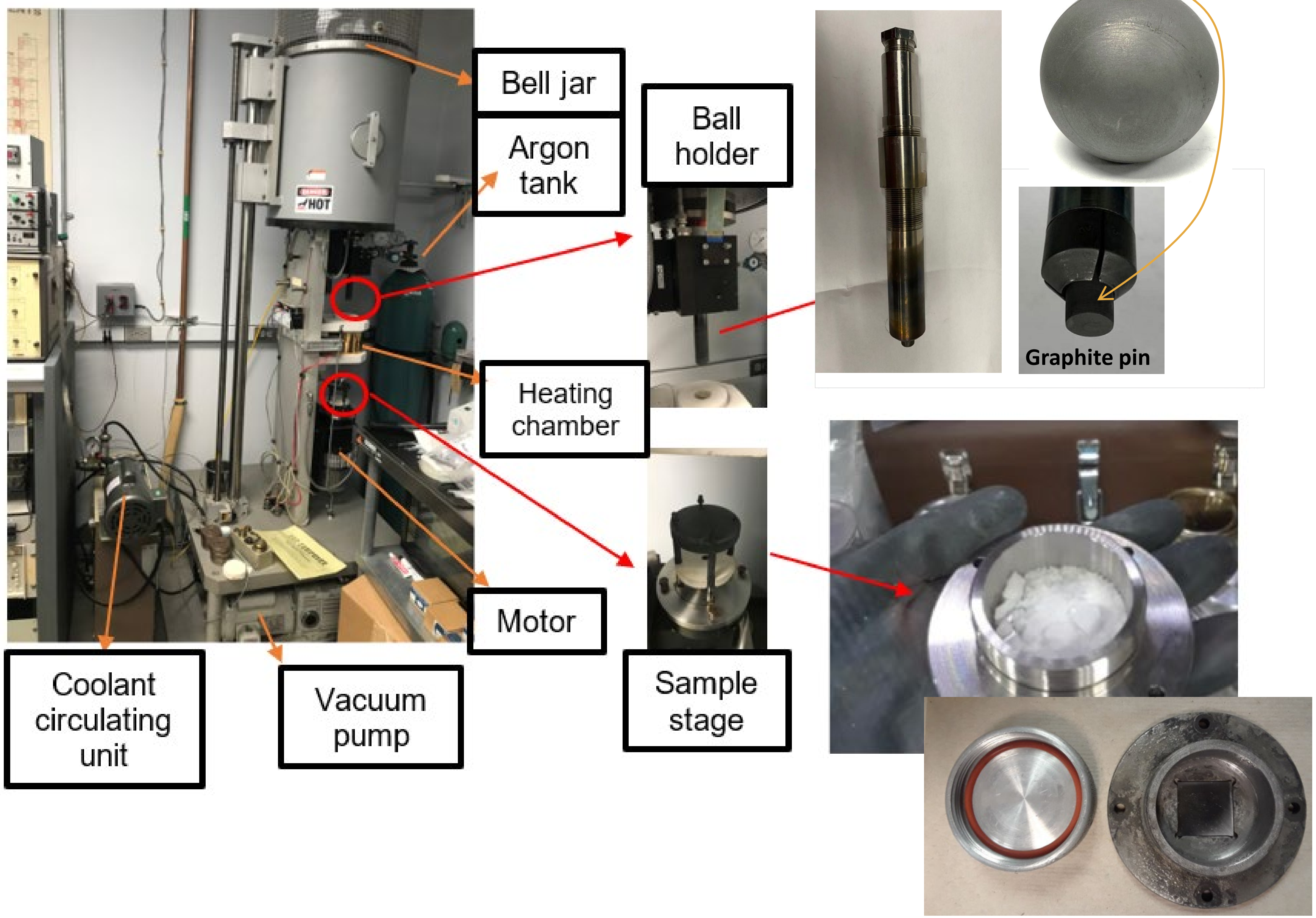
Standard Guide for High Temperature Strength Measurements of Graphite Impregnated with Molten Salt[1]

- Prepared salt-exposed samples following ASTM D8091 – stored samples in glovebox
  - But what intrusion parameters do we use to evaluate effect: P & T? or time? D_o or D_t ? Wt % uptake ? Homogenous intrusion ?
- Testing of graphite sample is done at high temperature with retained salt
- Requires significant modification of equipment to meet the required testing conditions

➢ Understanding wear behavior of graphite

Funded by:
SOLAR ENERGY TECHNOLOGIES OFFICE
U.S. Department Of Energy

Motel salt wear testing setup



Materials pair

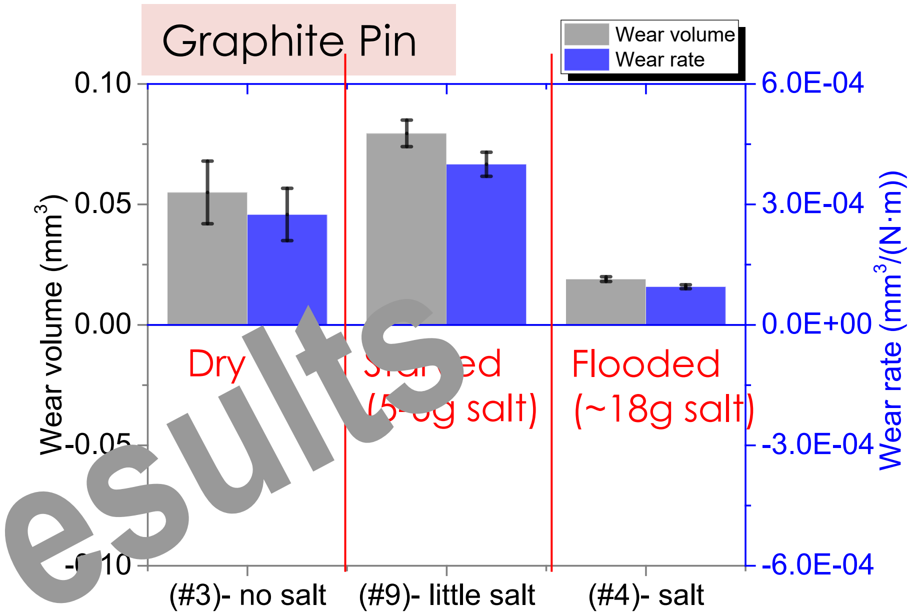
- Graphite pin (from pellet)
- 316L stainless steel disk

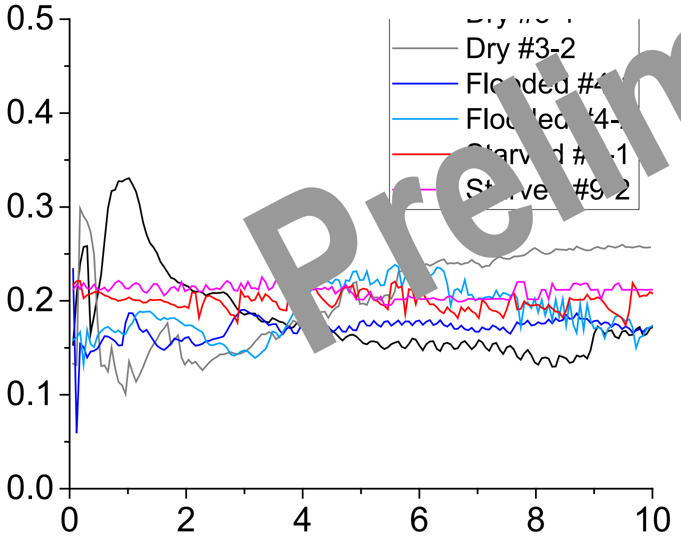
Conditions

- 650°C
- 20 N load
- 120 rpm speed
- 1,000 m sliding distance
- FLiNaK salt

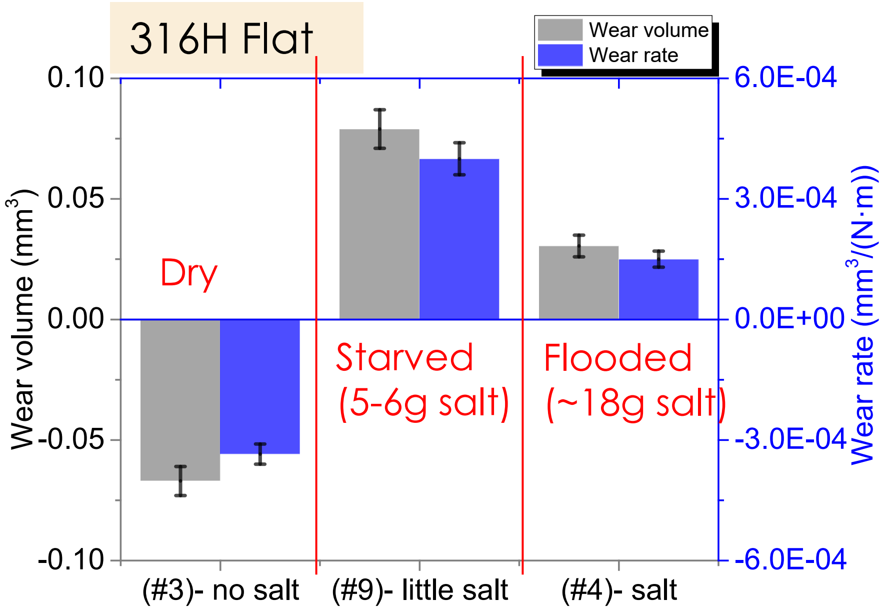
Effect of Salt Presence and Quantity

- **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)



- What is next on wear testing:
  - Commission of new tribometer (inside glovebox) – perform test on more controlled environmental conditions
  - Evaluate graphite-on-graphite
  - Maybe move to matrix carbon

- Evaluate erosion is our next challenge

Team effort

ORNL

- Nidia Gallego
- Cristian Contescu
- Jim Keiser
- Adam Willoughby
- Jun Qu
- Xin He
- Jisue Moon
- Yuxuan Zhang
- Ashli Clark
- Many others around ORNL