Graphite materials for molten salt reactors (MSR)

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ORNL Graphite Activities

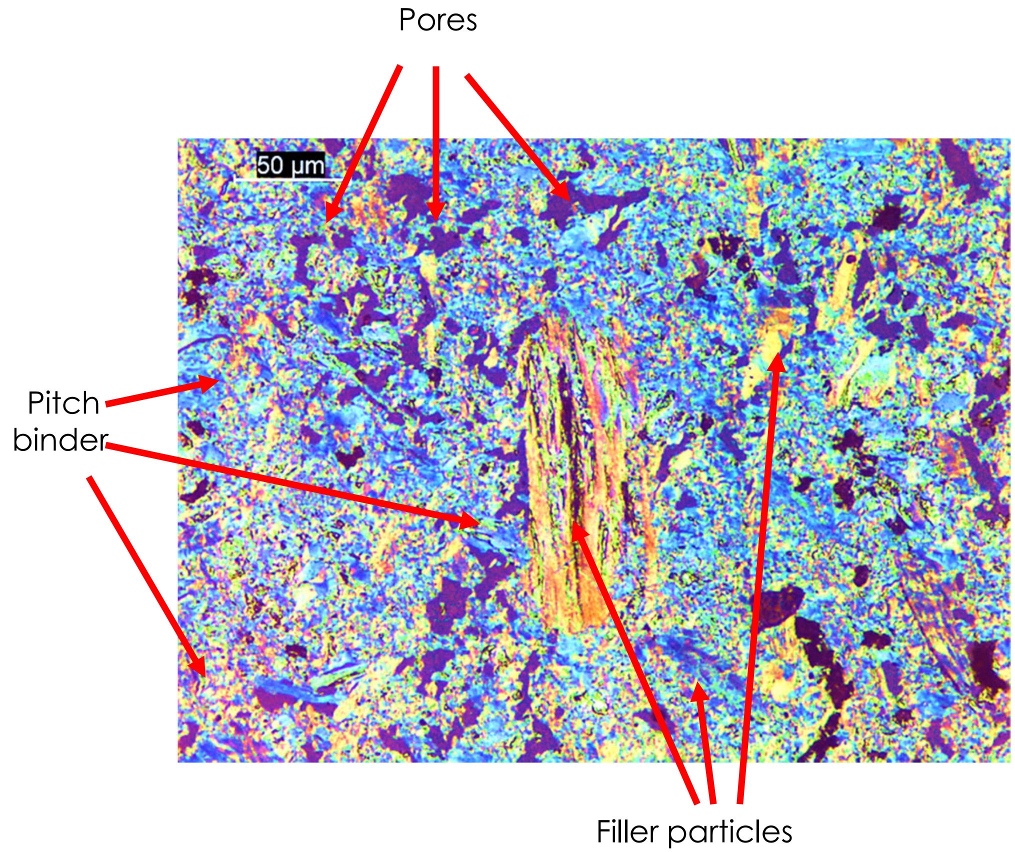
Salt intrusion in selected graphite grades:

- ✓ ORNL's experimental facility for high pressure salt intrusion
- ✓ Examination of porosity properties of multiple graphite grades
- ✓ Salt intrusion experiments (FLiNaK at 750 °C)
- ✓ Correlating salt intrusion with mercury porosimetry data
- ✓ Characterization of salt-exposed graphite samples

Funding: US Department of Energy, Office of Nuclear Energy
Advanced Reactor Technologies (ART) Program

Manufactured Graphite

- Polygranular nuclear graphite is a synthetic composite obtained by molding or extruding a paste made from **coal tar pitch** or **petroleum coke filler** grains and a **pitch binder**, followed by thermal treatments and reimpregnation for densification.
- The last step is graphitization at **2500-2800 C** (or even higher temperature).
- XRD shows a crystalline structures with and average d_{002} spacing just a little larger than of perfect graphite
- The resultant material has an apparent density in the range of **1.7-1.8 g/cm³**, i.e., about **20 % porosity**.



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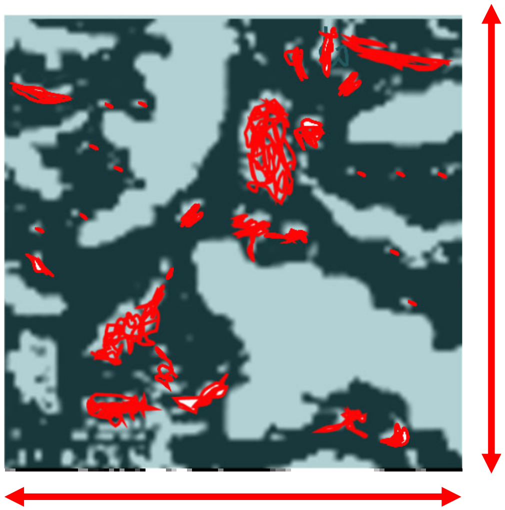
One carbon, many graphites

		Class	Density [g/cm³]	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)			

Open Pores, Closed Pores and Graphite Densities



- Apparent density $\rho_{app} = \frac{m}{V_{app}}$ Includes open and closed pores
- Skeletal/He density $\rho_{sk} = \frac{m}{V_{sk}}$ Includes closed pores
- Crystal density $\rho_{cryst} = 2.24\ \text{g/cm}^3$

$$V_{open} = \frac{1}{\rho_{app}} - \frac{1}{\rho_{sk}}$$

$$V_{closed} = \frac{1}{\rho_{sk}} - \frac{1}{\rho_{cryst}}$$

m = 1

$$V_{total} = V_{open} + V_{closed}$$

ASTM International D8091-16 "Standard Guide for Impregnation of Graphite with Molten Salt"

Recommends a consistent procedure for controlled and reproducible impregnation of graphite with molten salts at constant temperature and pressure

$$D_0 = \frac{w_2 - w_1}{\rho \, V_{open}}$$

$$D_1 = \frac{w_2 - w_1}{\rho \, V_{total}}$$

w_1 = initial weight

w_2 = weight after impregnation

V_{open} = open pore volume

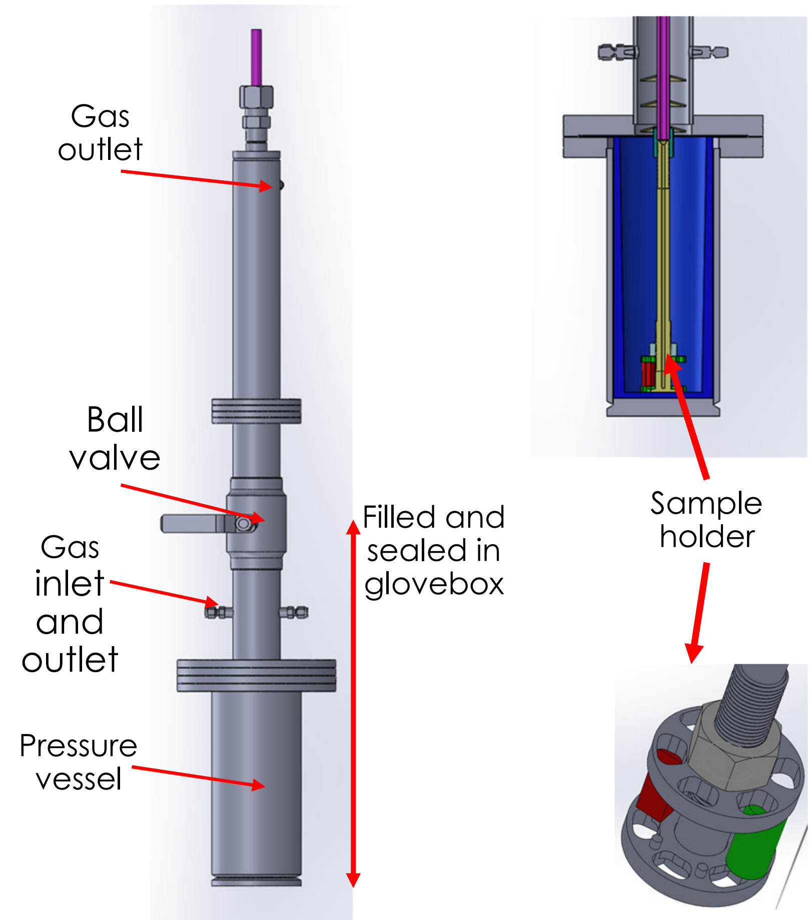
V_{total} = total pore volume

ρ = salt density at impregnation temperature

ASTM INTERNATIONAL https://www.astm.org/

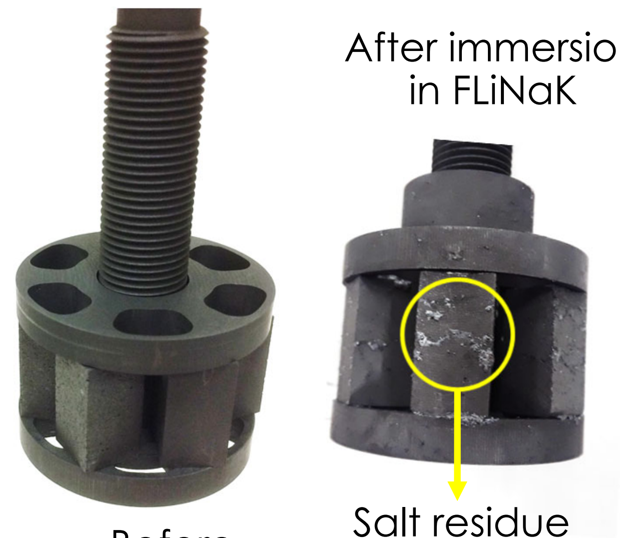
ORNL's Salt Intrusion System

- System can operate at pressures as high as 10 bar and temperature of at least 750°C
- System can expose up to six samples in each test
- The initial tests have been conducted with FLiNaK salt
- No metallic materials contact the salt during the test – only graphite



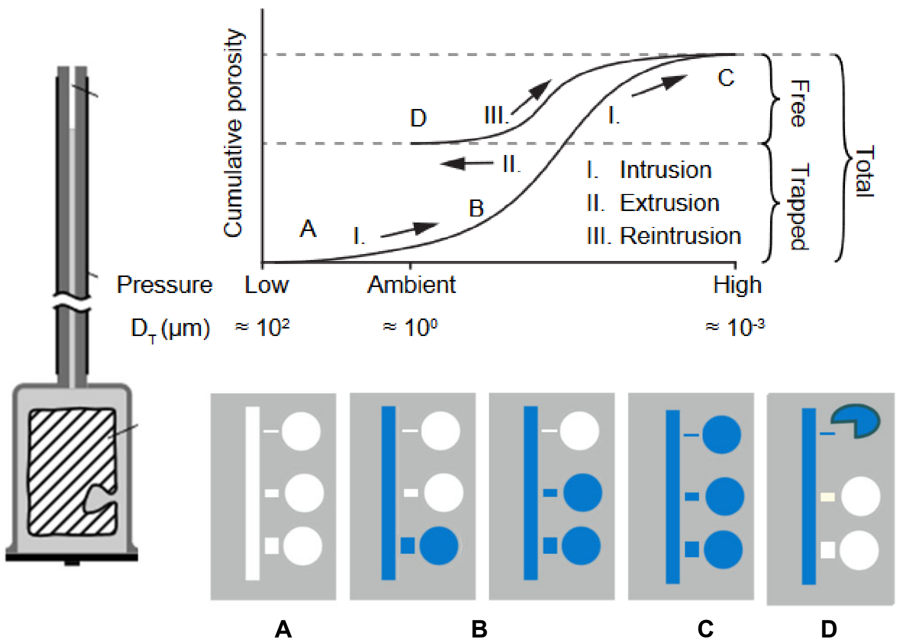
Pressure-Vessel Testing Apparatus

After immersion in FLiNaK



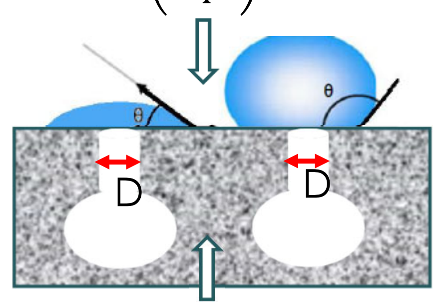
Before immersion in FLiNaK

Graphite Porosity from Mercury Intrusion Porosimetry



Mercury does not wet graphite

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



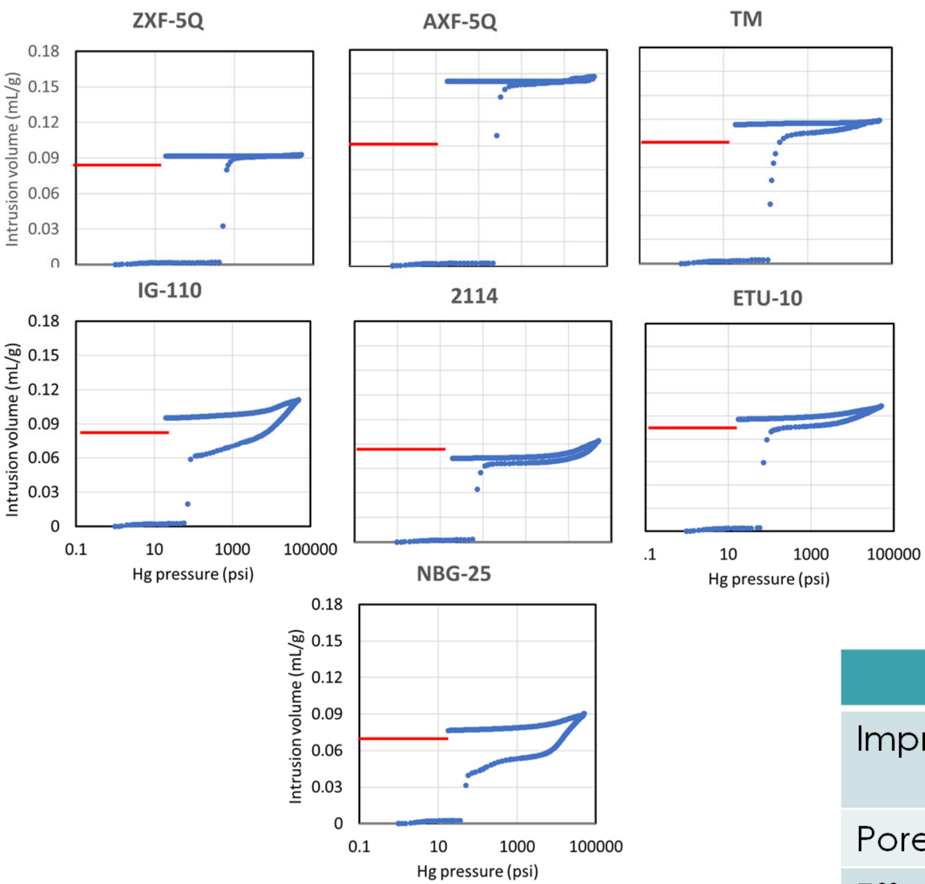
$$-\sigma * \cos(\theta) * \pi D$$

Washburn eq.

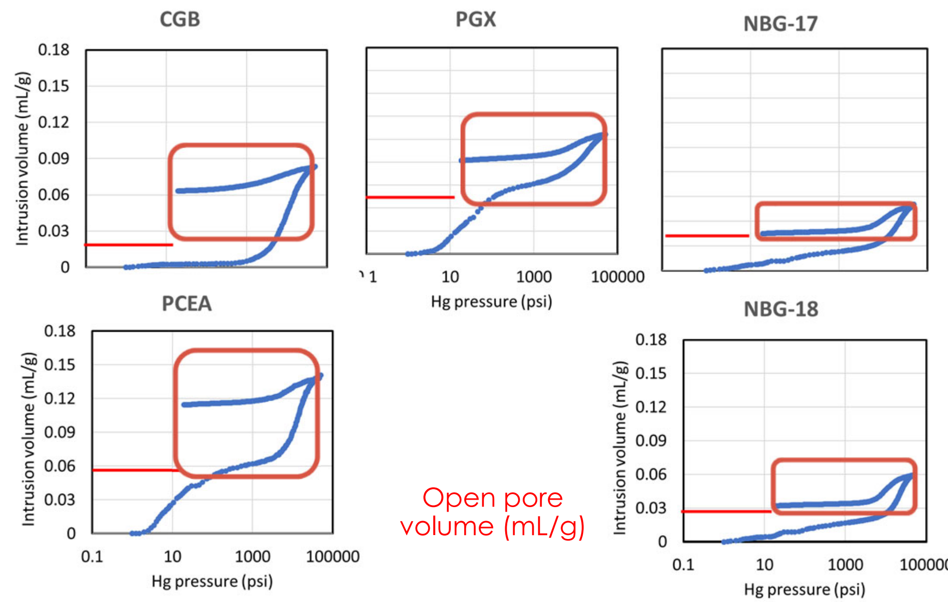
$$D_P = -\frac{4\,\sigma\cos\theta}{P}$$

Mercury intrusion: fine-grain vs. medium-grain graphites

Fine grain (< 50 μm)



Medium grain (50 – 1600 μm



	Fine grain	Medium grain
Impregnation	Well-defined pressure	Broad pressure range
Pore size distribution	Narrow	Wide
Effect of high pressure	None	Structural damage

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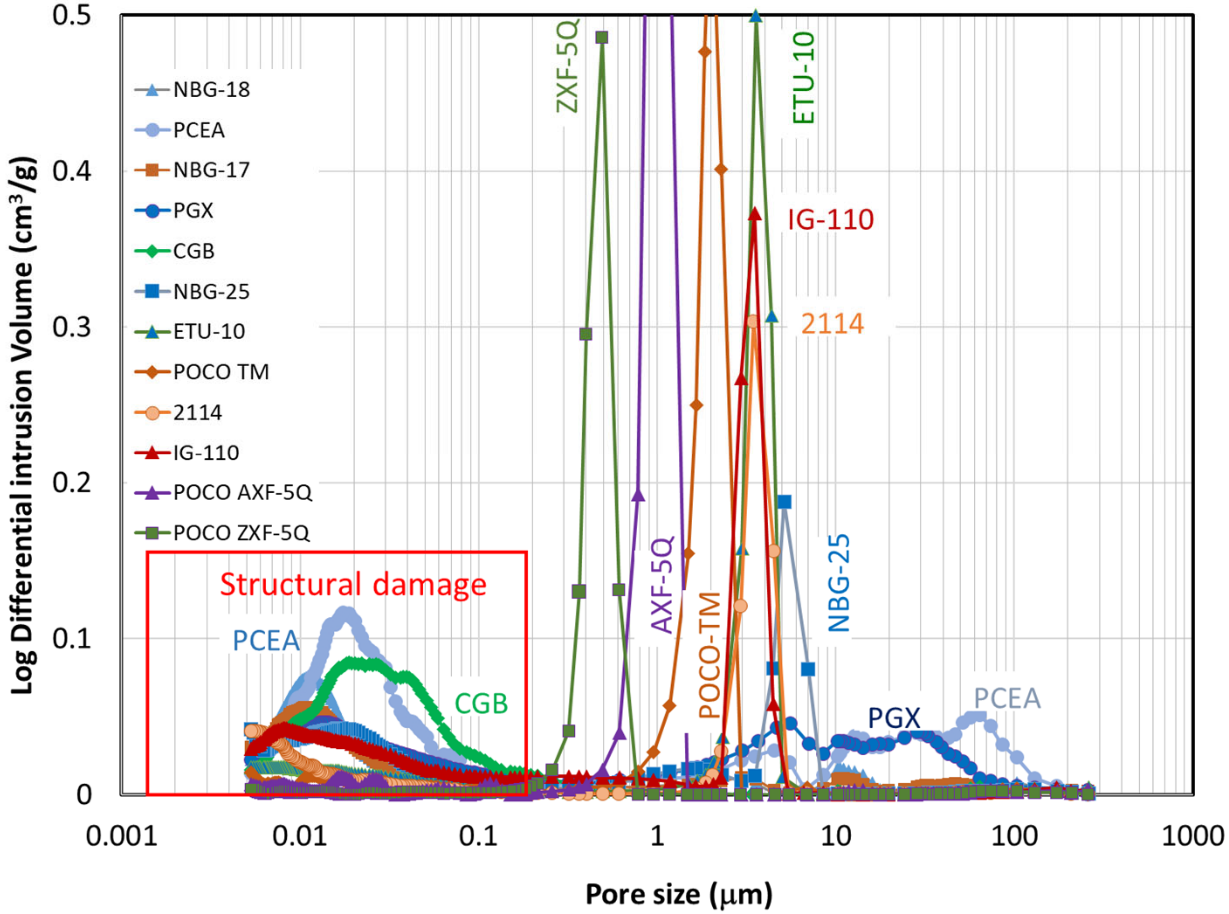
Pore size distribution from mercury intrusion porosimetry

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



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Connecting mercury and FLiNaK pressure scales

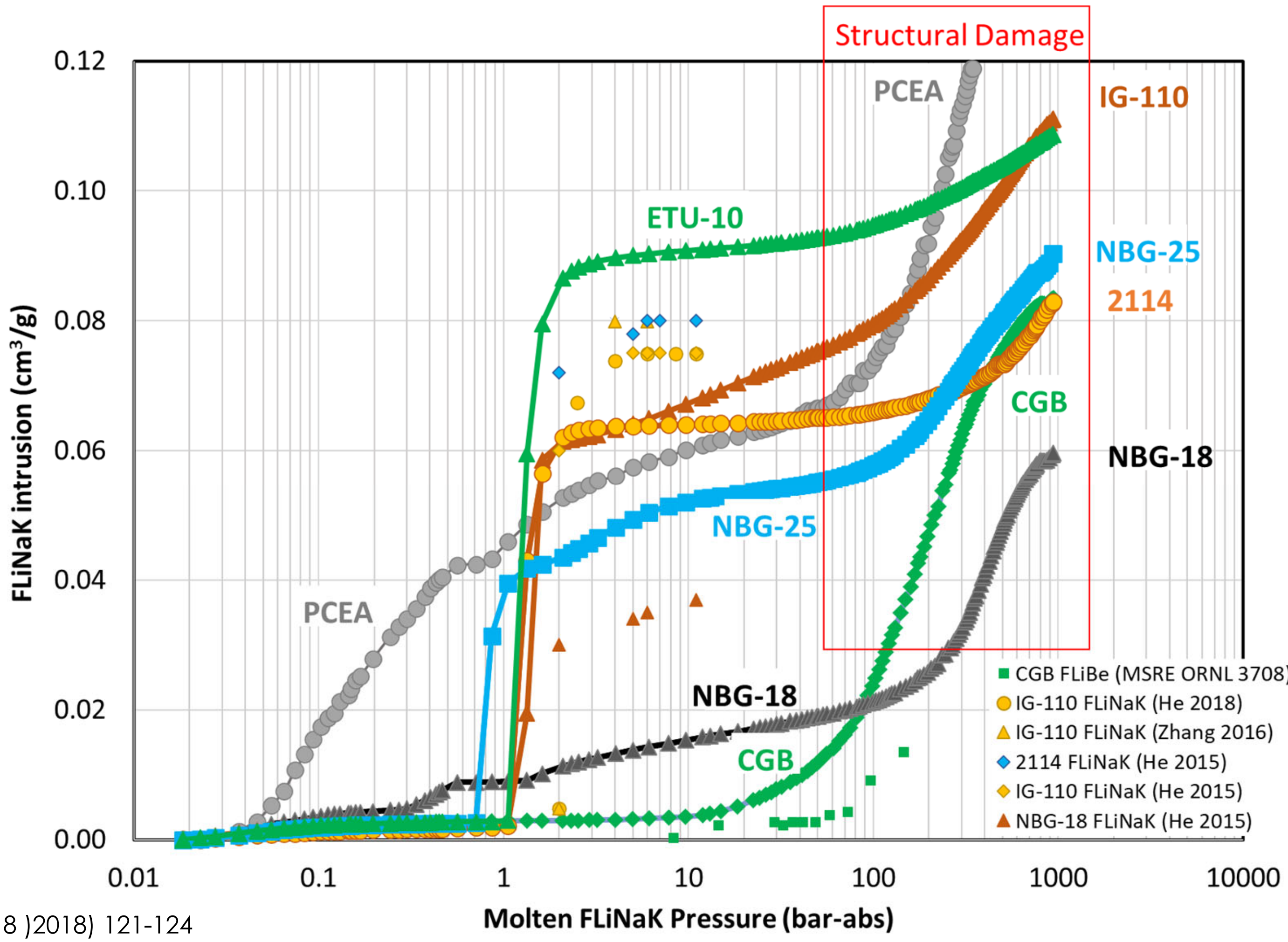
$$D = \frac{4\,\gamma_S \cos\theta_{G/S}}{P_S} = \frac{4\,\gamma_{Hg} \cos\theta_{G/Hg}}{P_{Hg}},$$

$$\log P_S = \log P_{Hg} + \log\left(\frac{\gamma_S \cos\theta_{G/S}}{\gamma_{Hg} \cos\theta_{G/Hg}}\right),$$

G = graphite; S = salt; Hg = mercury

	Surface tension (σ) (N/m)	Contact angle (θ) (°)
Mercury (Hg) at 25°C [1]	0.485 N/m	--
FLiNaK at 750°C [2]	0.169 N/m	--
Hg-graphite at 25°C [1]	--	155°
FLiNaK-graphite at 750°C [3,4]	--	135°

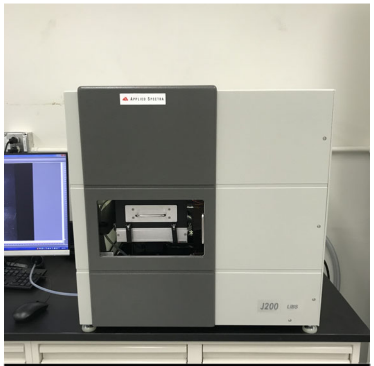
[1] ASTM D4284-12 (2017)
[2] M.S. Sohal et al. INL/EXT-10-18297 (2010)
[3] Z He et al. Carbon 84 (2015) 511-518
[4] A. R. Delmore et al. Trans Amer. Nucl. Soc. 118)2018) 121-124

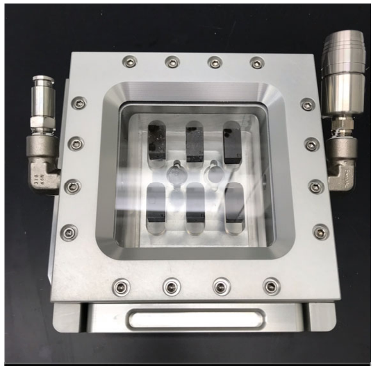


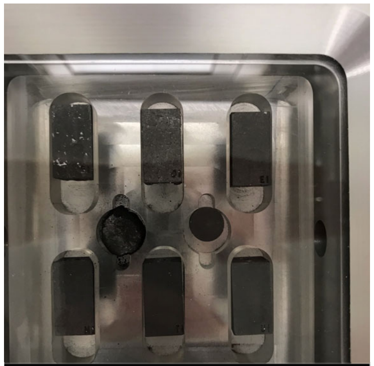
- Continue intrusion tests with FliNaK to add more data points for our predictive model based on Washburn equation
- Design and build FLiBe-dedicated system, hopefully to be available next summer
- Characterization of salt-exposed samples to understand chemical interaction and structural changes in graphites

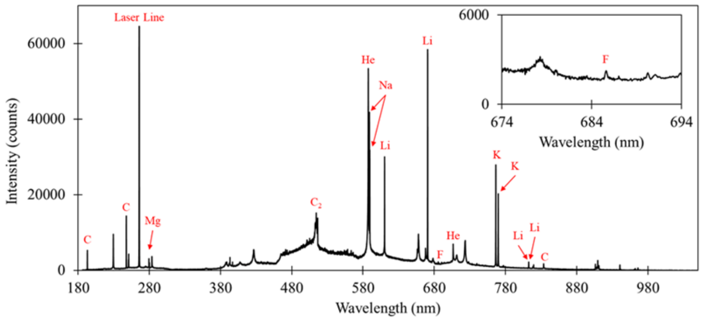
Elemental 3D mapping of salt in graphite was achieved using Laser Induced Breakdown Spectroscopy

- Detection of broad range of elements
- All elements of interest measured in FLINAK exposed graphite samples
  - Carbon, fluorine, lithium, sodium, potassium, oxygen, hydrogen
- Inert atmospheres maintained using sealed sample chamber
- Advanced data analysis to understand correlations and increase sensitivity

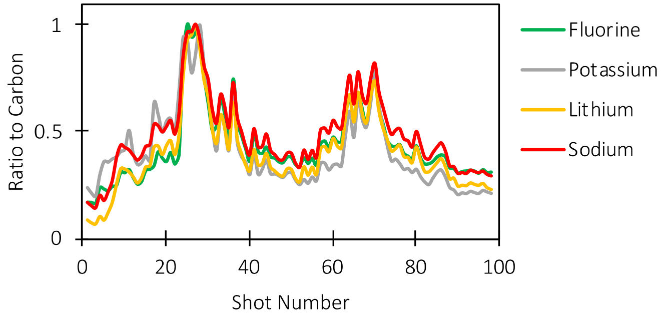

J200 LIBS instrument


Inert sample carrier

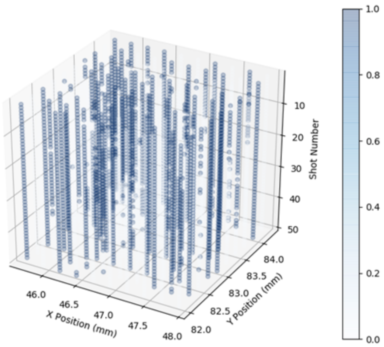

FLiNaK exposed samples



LIBS spectra of graphite exposed to FLiNaK with major emission lines of interest noted.



Depth profile of F, K, Li, and Na relative to C in graphite as measured by LIBS.



3D reconstruction of hyperspectral data showing FLINAK distribution in graphite sample exposed to molten FLINAK.

Emphasizing capability development for MSR community

Suite of characterization techniques

- 3D elemental mapping with laser induced breakdown spectroscopy
- Molecular analysis with FTIR and Raman spectroscopies
- Correlative analysis with scanning probe techniques and spectroscopy

Actively increasing techniques available for **beryllium** and **radioactive** samples

Ongoing work

- Performing LIBS analysis of FLINAK and FLIBE exposed samples with determined measurement methodology
- Exploring correlative analysis between multiple techniques
  - LIBS, Raman, FTIR, XPS, scanning probe microscopies
- Building capabilities to serve the MSR community

Questions?

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