July 14, 2021

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MSRs: Graphite testing status, ASME support

ART Gas-Cooled Reactor Program Review

Advanced Reactor Technologies

DOE MSR Campaign – Long Term Objective/Goals

- **Objective:**
  - Assist in the near-term deployment of salt-cooled and salt-fueled molten salt reactors

- **Goals:**
  1. Establish viability
  2. Facilitate needed research and enabling technology
  3. Work to reduce cost and accelerate development

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
- Change in chemical resistance to environmental effects

Chemical environment effects and surface reactivity

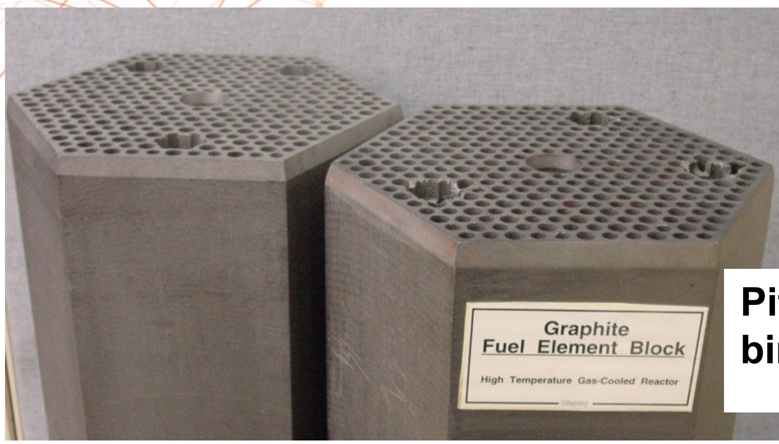
Gas-cooled reactors

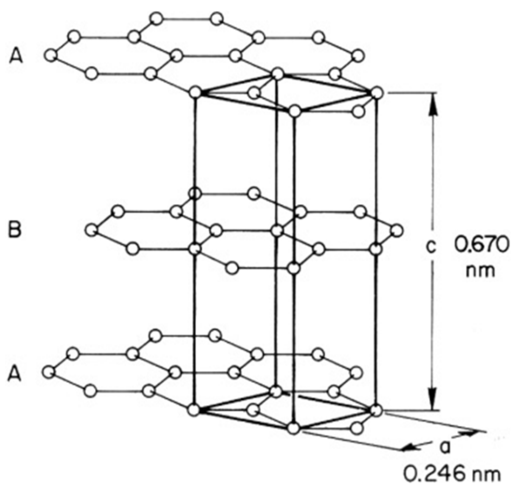
- ❖ Chronic oxidation
- Moisture in coolant will cause slow by continuous oxidation during normal operation – will always happen
- ❖ Acute oxidation
- Air or water ingress (accident conditions) – should never happen

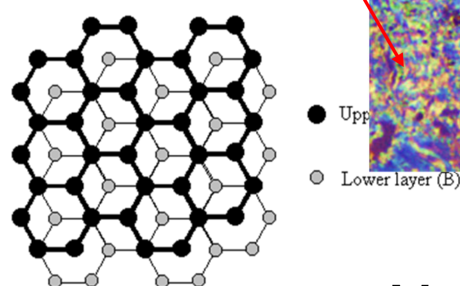
Fluoride salt-cooled reactors

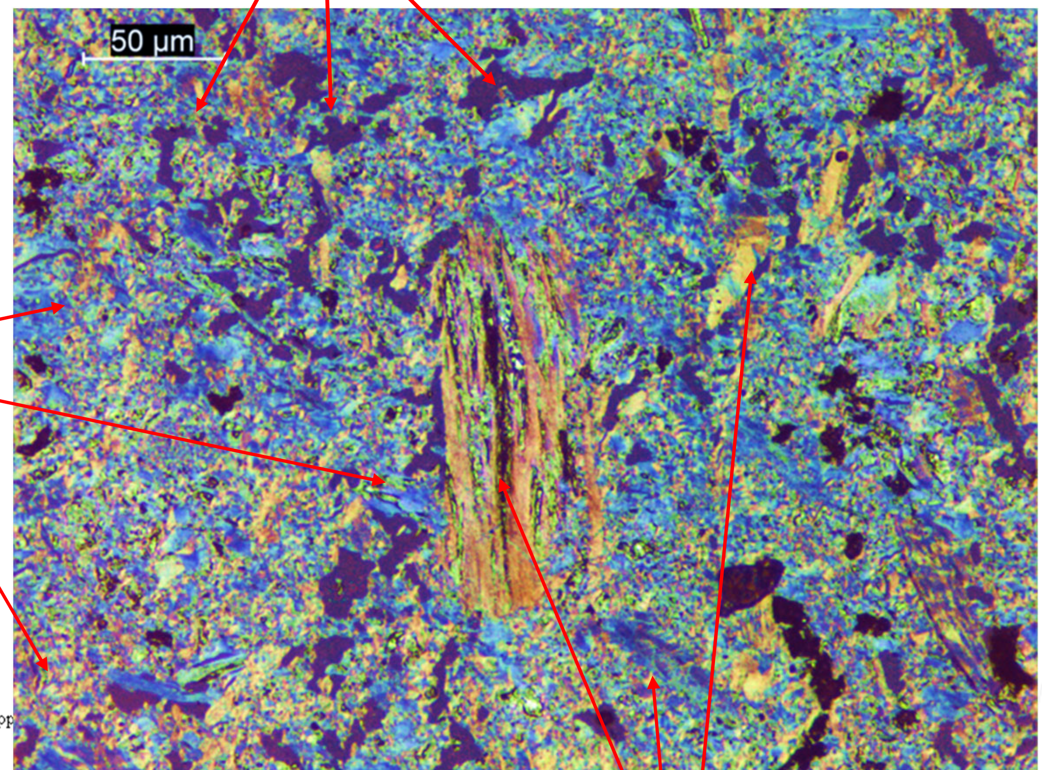
- ❖ Chemical Interactions: Salt-graphite interaction that may affect structural or physical properties of graphite
- ❖ Salt infiltration in graphite: May cause structural changes, hot spots in graphite
- ❖ Wear and erosion
- ❖ Tritium control: May accumulate in graphite

Graphite









Manufactured Graphite has about
20 % porosity

One carbon, many graphites

		Class	Density [g/cm^3]	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)			

Graphite - Salt Intrusion studies: Highlights

- Developed capabilities for high-pressure salt intrusion studies using FLiNaK (based on ASTM D8091)
- On-going FLiNaK intrusion measurements on selected graphite grades
- Completed porosity characterization of 12 graphite grades using mercury porosimetry
- Correlated mercury porosimetry results with FliNaK intrusion using Washburn equation
- Published TM describing system and preliminary results

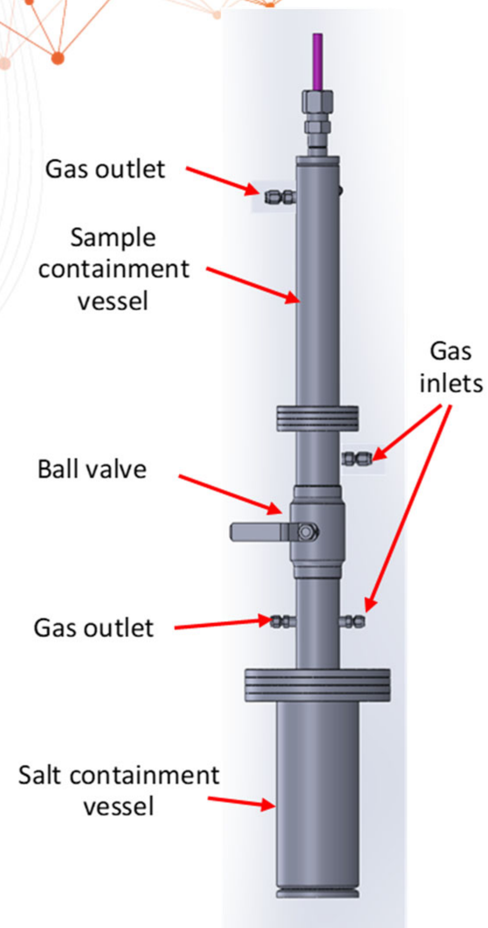
Graphite-Salt Intrusion Studies

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

ASTM INTERNATIONAL Designation: D8091 – 16

An American National Standard

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



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

Standard Guide ASTM D8091 - limitations

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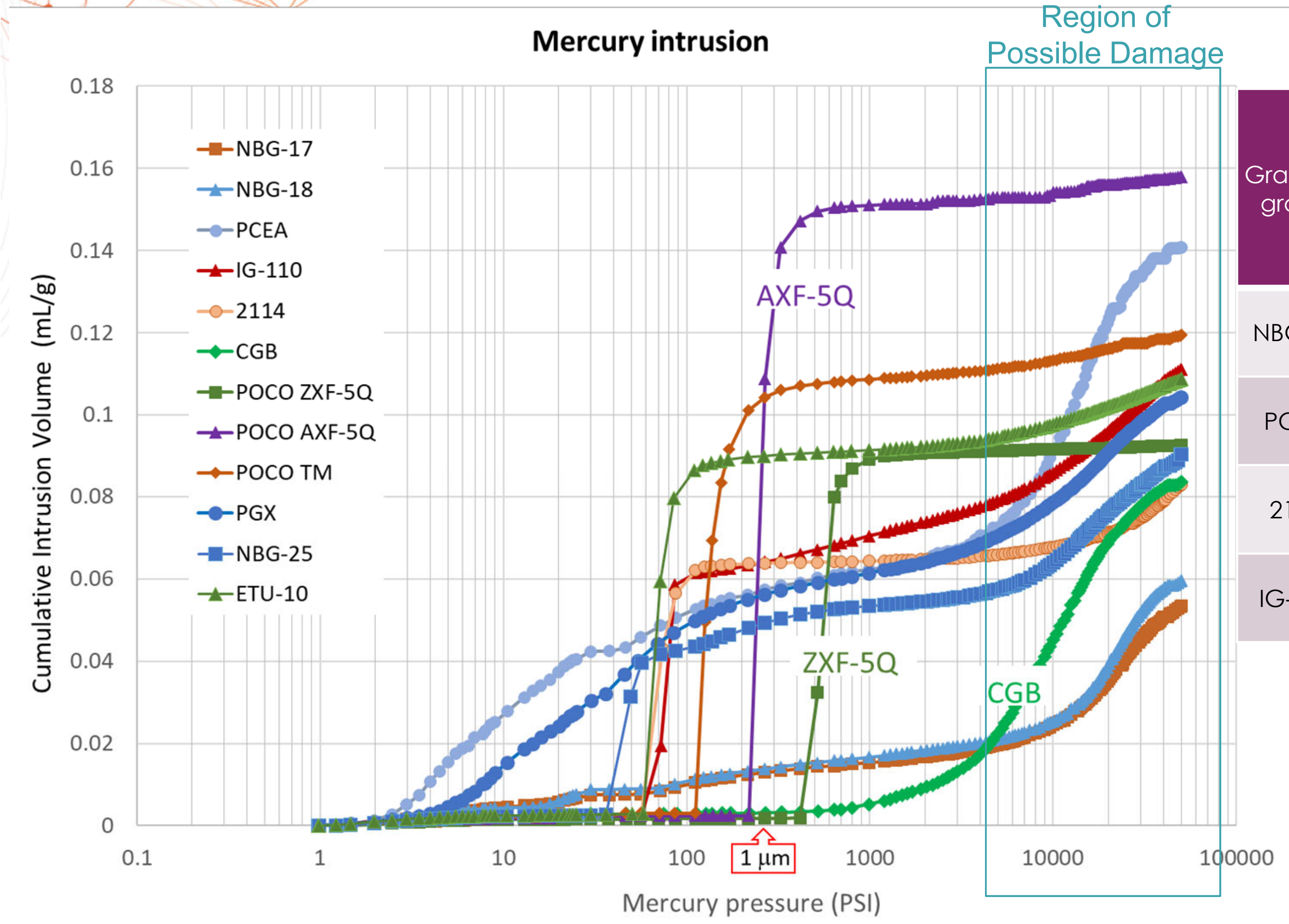
Designation: D8091 – 16 An American National Standard

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

This standard is issued under the fixed designation D8091; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

- Sample size and geometry are not defined
- Equilibration conditions are not defined
- Literature results should be reviewed carefully

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



Graphite grade	Grain size	Average grain size [µm]	Density [g/cm^3]	SPECIFIC PORE VOLUMES		Porosity fraction [%]
				Total pore [cm^3/g]	Open pore [cm^3/g]	
NBG-18	medium -coarse	1600	1.86	0.092	0.044	17.1
PCEA	medium -fine	800	1.77	0.119	0.065	21.0
2114	super-fine	13	1.81	0.105	0.071	19.0
IG-110	super-fine	10	1.76	0.120	0.079	21.2

- 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

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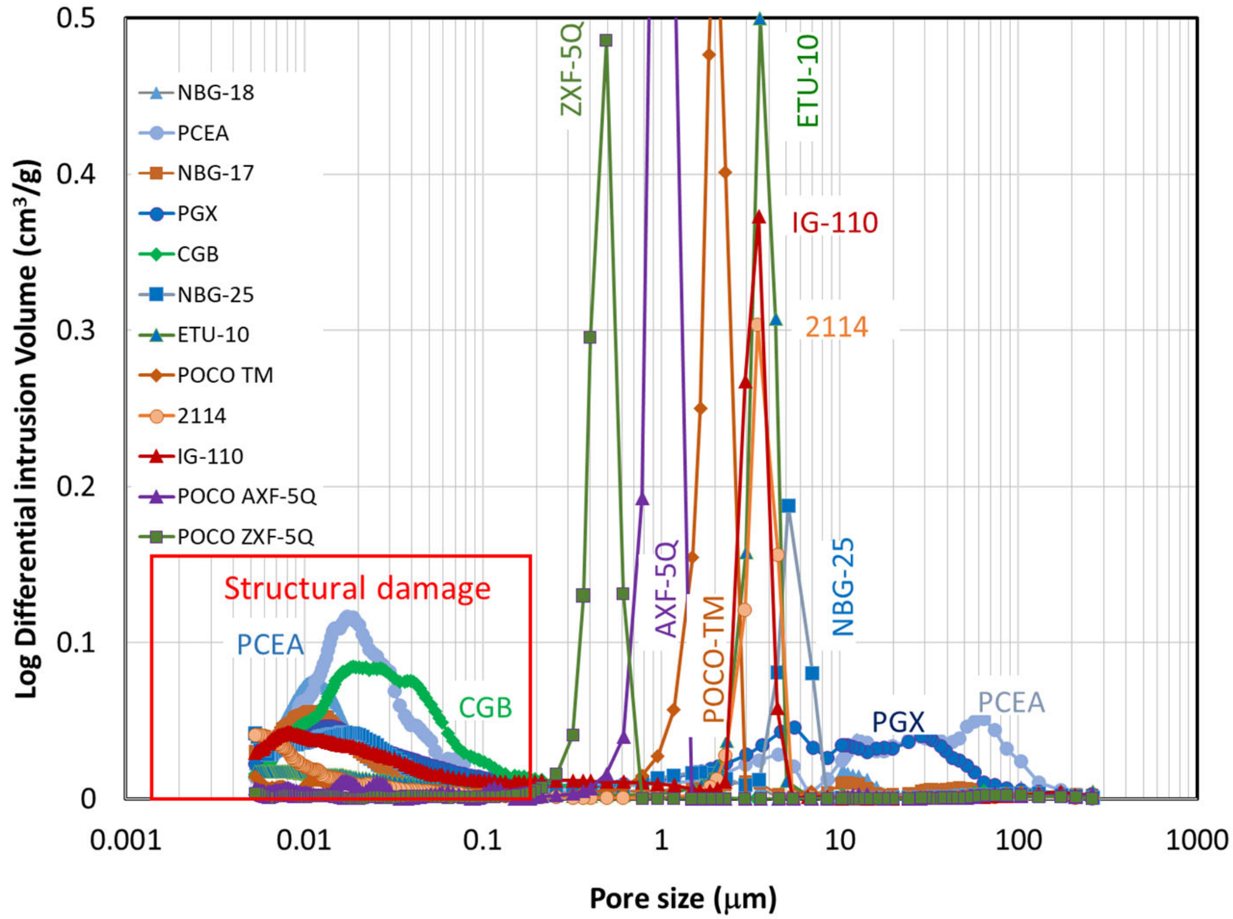


Connecting mercury and FLiNaK pressure scales

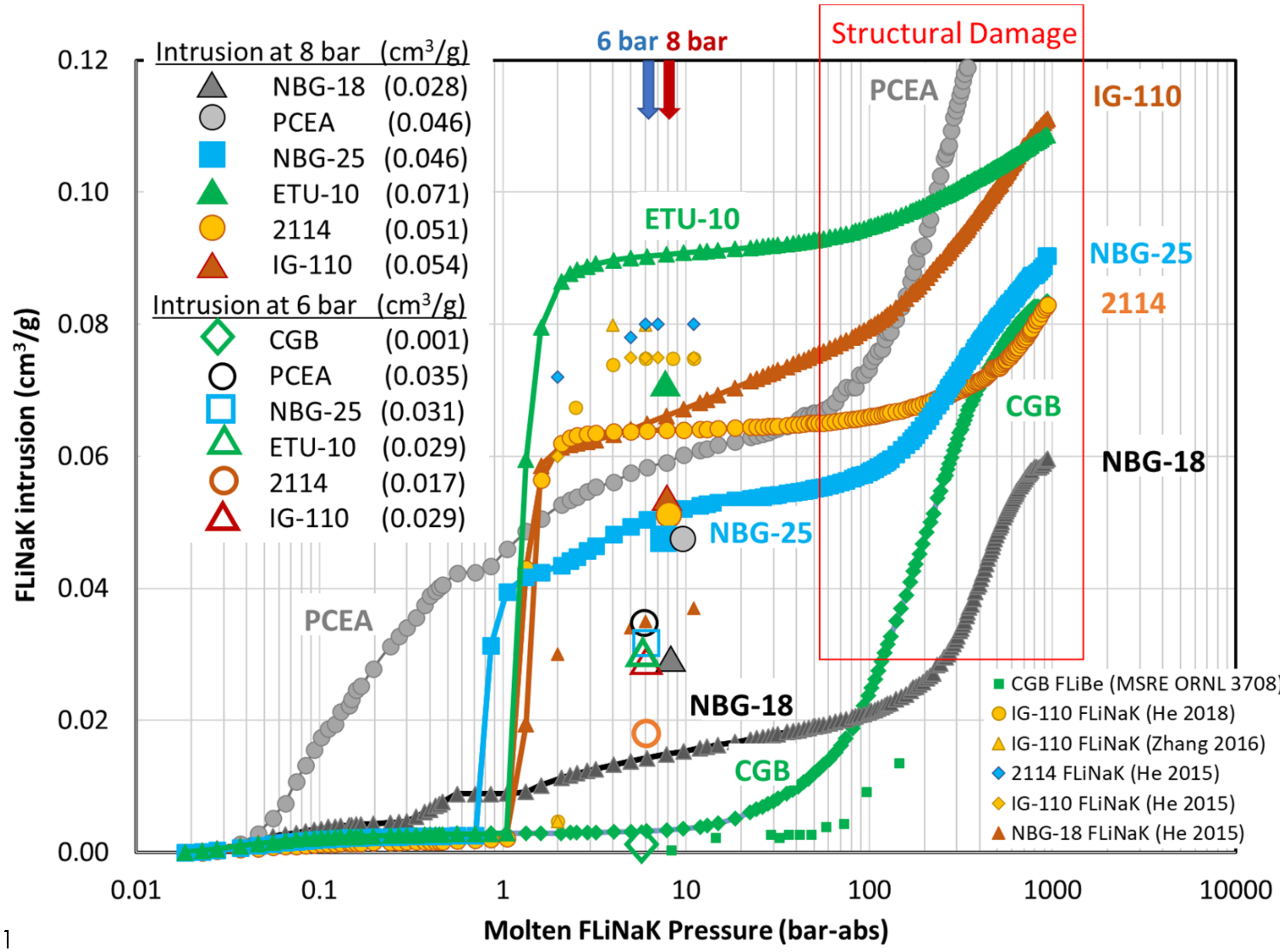
$$D = \frac{4\,\gamma_S \cos\theta_{G/S}}{P_S} = \frac{4\,\gamma_{Hg}\cos\theta_{G/Hg}}{P_{Hg}},$$

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

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



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Progress Report on Graphite-Salt Intrusion Studies

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Cristian I. Contescu
James R. Keiser

July 2020

Approved for public release.
Distribution is unlimited.

- Summary of capabilities and results published last year.
- TM Report available at OSTI
- https://www.osti.gov/biblio/1651304-progress-report-graphite-salt-intrusion-studies
- An update report will be published by end of FY

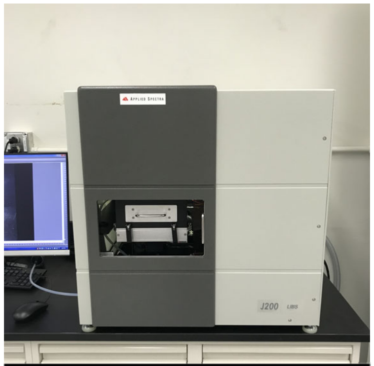
Expanding capabilities to handling FLiBe

- Installed and commissioned a 3-glove glovebox for welding of Be-containing static capsules
- Designed and currently building a second salt-intrusion system, to be located inside a glovebox
  - Procured a new 4-glove glovebox for intrusion system
  - Pressure system being built- expect completion by end of FY
  - Kairos will provide FLiBe for system

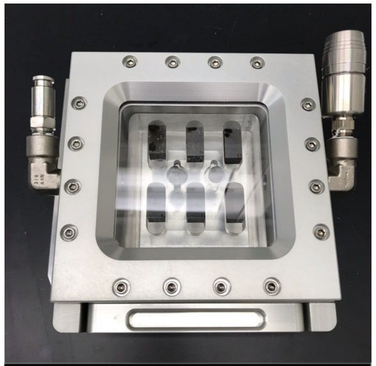
- Additional characterization of salt-exposed graphite samples to understand the effect of salt on mechanical and structural properties
  - Including LIBS, FTIR, Raman, XRD, Microscopy
- Compression testing and split-disk testing of salt-exposed sample

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

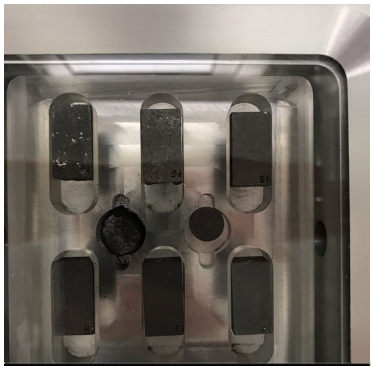
- All elements of interest measured in FLINAK exposed graphite samples
- Inert atmospheres maintained using sealed sample chamber
- Multivariate analysis techniques explored to process 3D data



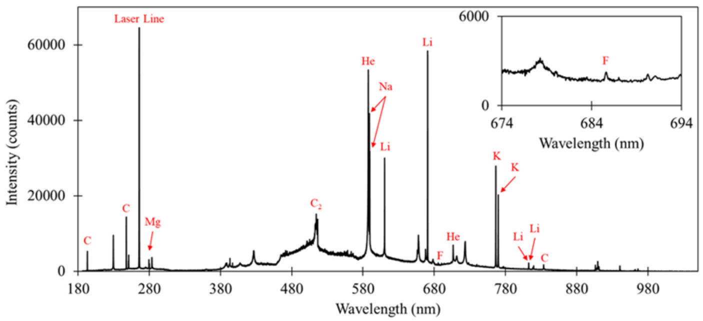
J200 LIBS instrument



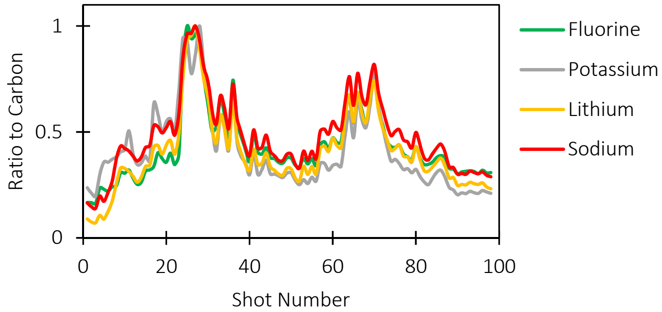
Inert sample carrier



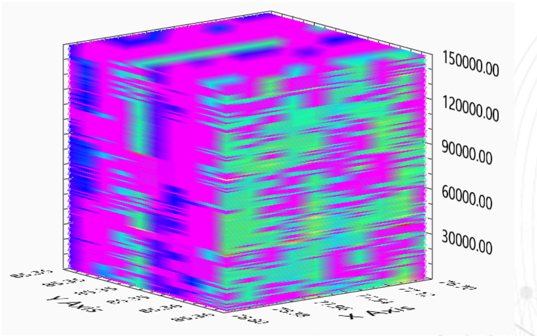
FLiNaK exposed samples



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

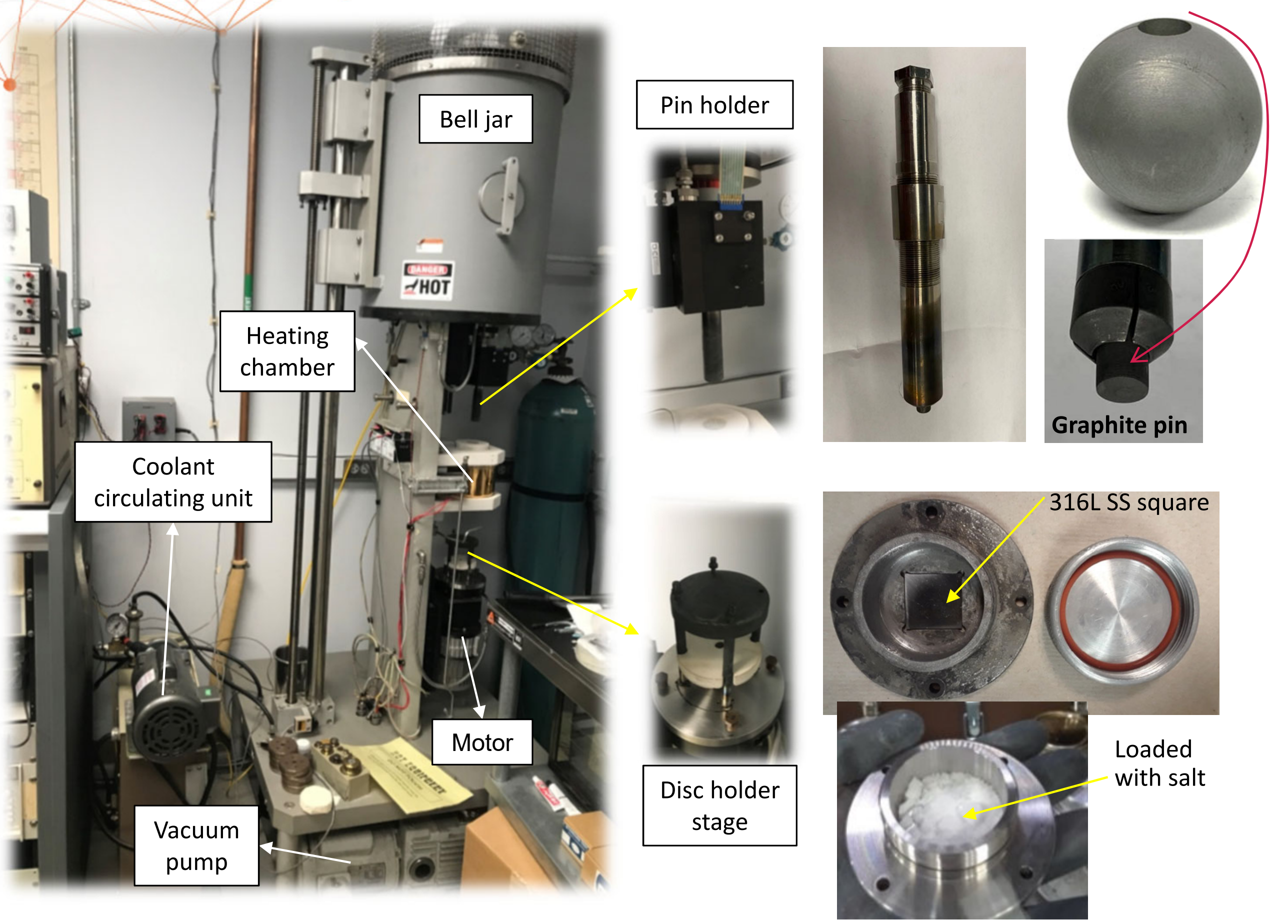


Depth profile of F, K, Li, and Na relative to C in graphite as measured by LIBS.



3D reconstruction of hyperspectral data showing fluorine distribution relative to carbon in FLiNaK exposed sample.

Feasibility Study of Graphite Wear Testing in Molten FLiNaK



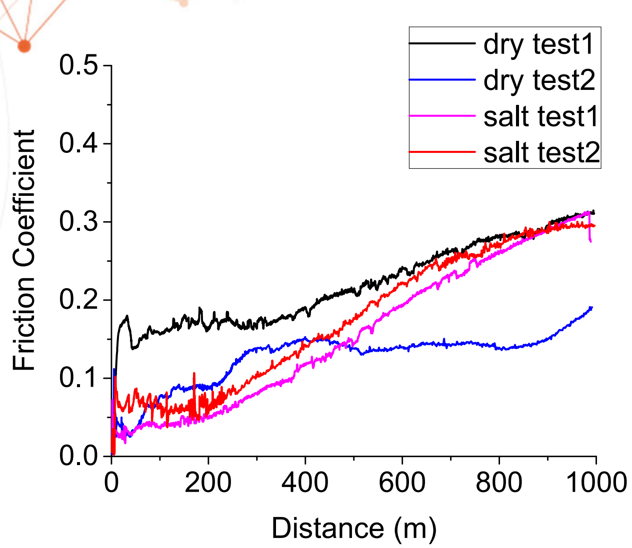
Experimental:

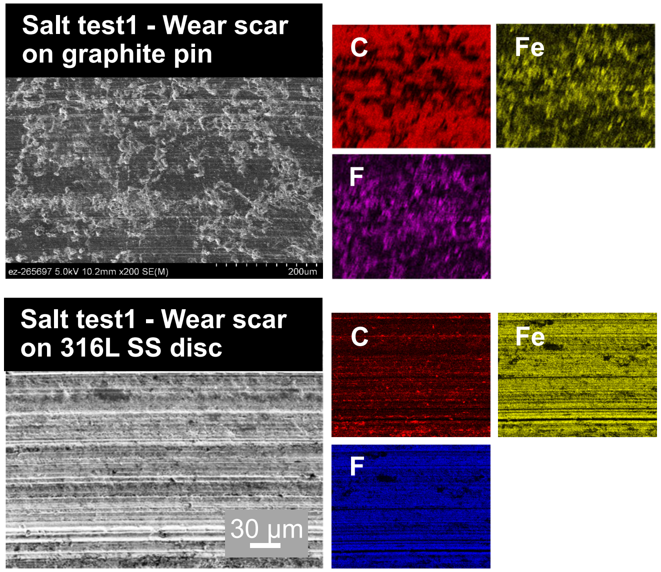
- Graphite pin sliding against 316L SS surface
- Salt: FLiNaK
- Temperature: 650 oC (up to 1000 oC)
- Gas environment: Ar
- Normal load: 20 N (up to 100 N)
- Rotating speed: 120 rpm (up to 1000 rpm)
- Sliding distance: 1000 m (~2 hrs 30 mins)

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

- Graphite pellet rubbing against the container alloy in molten FLiNaK salt
- Collision and rubbing between graphite pellets in molten FLiNaK salt
- Impact of temperature, load, speed, pellet surface roughness, and salt purity.

Initial friction and wear results of graphite pin sliding against 316L SS in 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…*

Additional tests in molten salt are needed to better understand the wear mechanism. Dry testing cannot can not be used as substitute.

ASTM and ASME participation

- Participated on the last two quarterly ASME Working Group Meetings
- ASME committee has requested a Task Group to evaluate code gaps on graphite issues related to MSR and prepare a white paper on MSR conditions and graphite material properties affected as result
- Participation on ASTM Graphite committee – there is a critical need for the development of Standard procedures to be used to study the effect of molten salt on graphite properties
  - Conducting scoping studies on the effect of salt intrusion on graphite mechanical properties
  - Samples have been prepared and will be tested in the next few weeks.

Team effort

- ORNL
  - Nidia Gallego
  - Cristian Contescu
  - Ryan Paul
  - Jim Keiser
  - Jun Qu
  - Kristian Myhre
  - Jisue Moon
  - Adam Willoughby
  - Ashli Clark
  - Many others around ONRL
- INL Graphite team lead by Will Windes
- SNS (VISION)
  - Timmy Ramirez-Cuesta
  - YQ
  - Luke Daemen
- University of Wisconsin
  - Raluca Scarlat (UCB)
  - Huali Wu
- Various Reactor vendors including Kairos and Flibe Energy