Berkeley Nuclear Engineering
UNIVERSITY OF CALIFORNIA

The Chemistry of Graphite in FHRs and MSRs

Raluca O. Scarlat
scarlat@berkeley.edu

Advanced Non-Light Water Reactors - Materials & Component Integrity

U.S. NRC
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Protecting People and the Environment

FLiBe-Graphite | Wetting and Surface Tension

MSRE Considerations for Graphite Integrity

- > 4% salt permeation leads to operational challenges
- Radiation-induced changes in surface tension of salt
- Radiation-induced changes in surface energy of graphite
- Heat deposition in surface voids, if salt intrudes, leading to hot spots and cracking
- Fission fragment damage at graphite surface
- Chemical attack by FP. E.g. graphite halogenation by I, Br.
- Chemical attack by radiolytic F_2 at low temperature – production of CF_4 was observed
- Fuel condensate in graphite pores.

W. R. Grimes, "Molten Salt Reactor Program Semi-annual Progres Report for Period Ending July 31, 1964," ORNL-3708. 1964. p. 255.

Salt intrusion in cylindrical pores

$$\boldsymbol{D = -\frac{4\gamma cos\theta}{\Delta P}}$$

$$D = pore\ diameter$$
$$\gamma = surface\ tension$$
$$\theta = contact\ angle$$
$$\Delta P = pressure\ differential\ at\ pore\ entrance$$

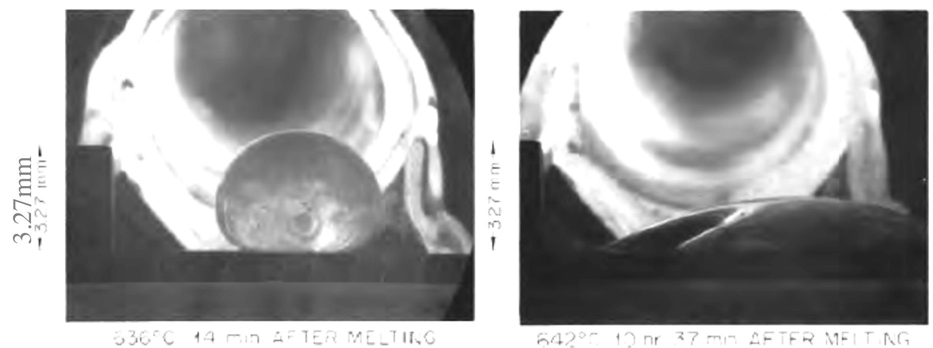
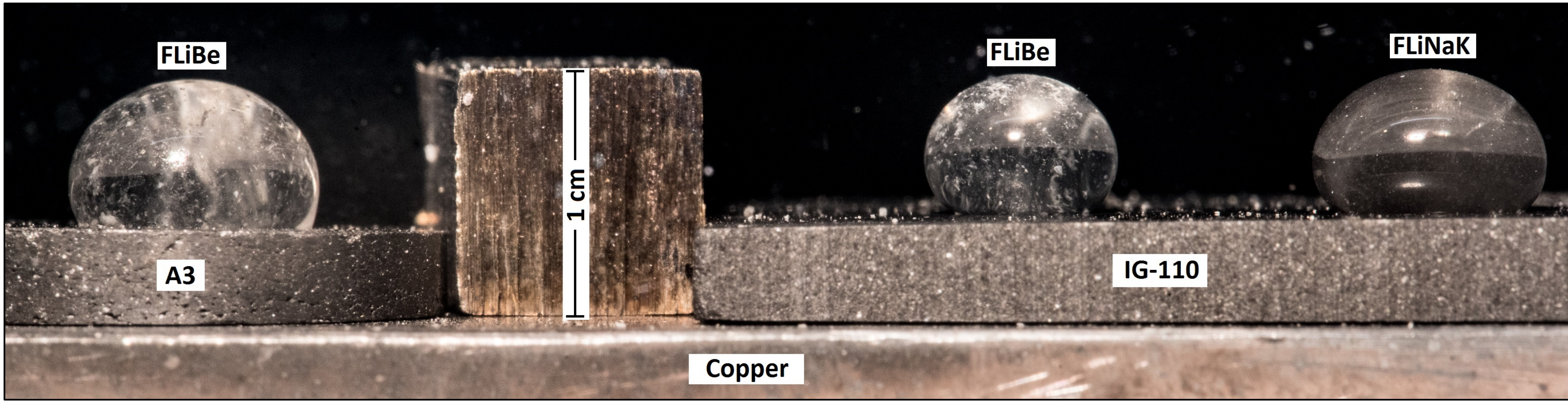


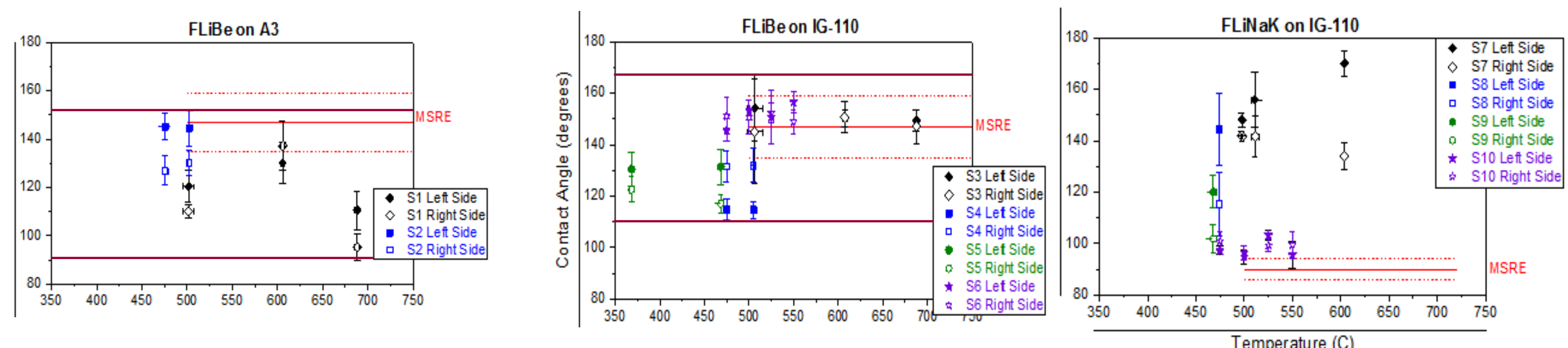
Figure 2: FLiBe is non-wetting on graphite in dry helium (left) but wets graphite at 10 ppm H_2O in helium (right)[3].

W. R. Grimes, "Reactor Chemistry Division Anuual Progres Report for Period Ending January 31, 1964," ORNL-3591. 1964.

FLiBe-Graphite | Contact Angle

Measured contact angle: large scatter in measured data points.





$$D = -\frac{4\gamma\cos\theta}{\Delta P}$$

Salt intrusion is not expected at 1.1 kPa-gauge:

95° contact angle, 0.2 N/m surface tension => Intrusion pore diameter > 60 um

120° contact angle, 0.25 N/m surface tension => Intrusion pore diameter > 400 um

[1] A. R. Delmore, W. Derdeyn, R. Gakhar, R. O. Scarlat. Wetting of Nuclear Graphite by Molten Fluoride Salts: Initial Experiments. American Nuclear Society Annual Meeting. Philadelphia, PA. June 17-21, 2018. [2] W. R. Grimes, "Reactor Chemistry Division Anuual Progres Report for Period Ending January 31, 1964," ORNL-3591. 1964. [3] Briggs. ORNL-3529, p.125.(1965).

FLiBe-Graphite | Salt-Intrusion

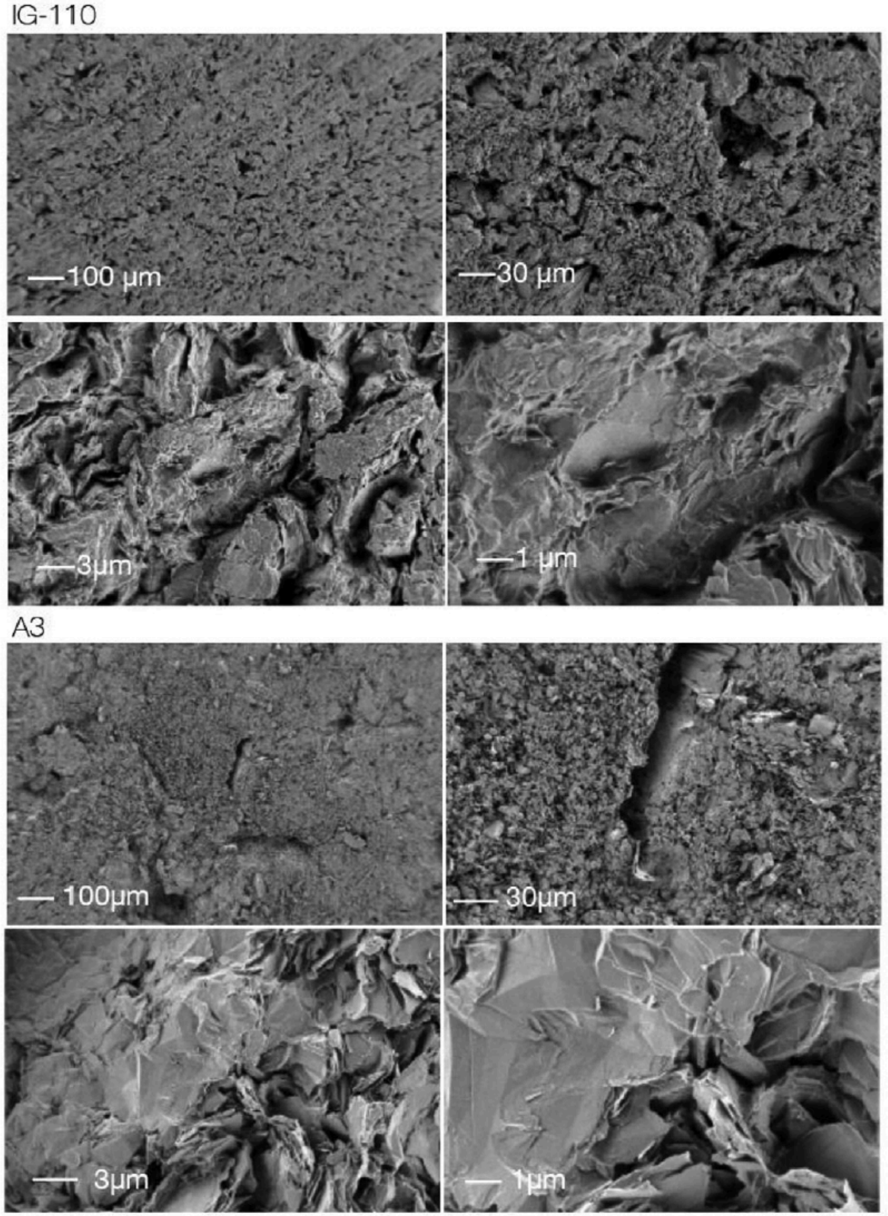
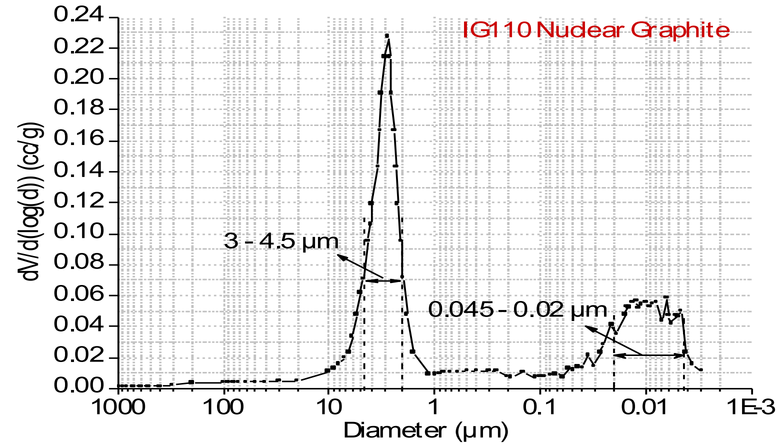
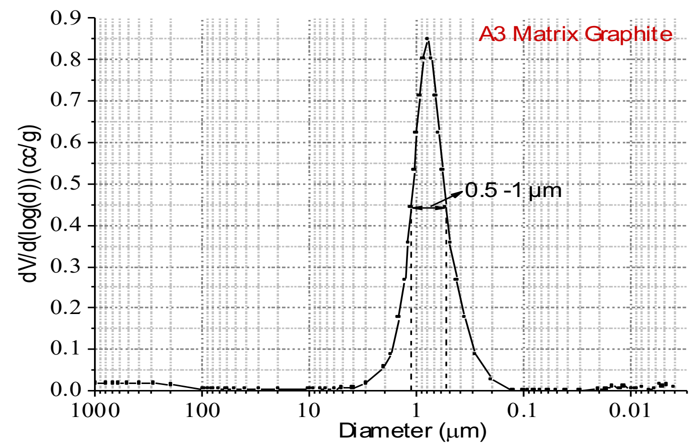


Fig. 1. SEM images of IG-110 and A3 (diamond-blade cut, unpolished), illustrating heterogeneity at several scales. XRD sampling ~100 s µm diameter and ~100 s µm depth, Raman sampling ~1 µm diameter and ~10 s nm depth, hydrogen uptake 500 µm cubic samples.

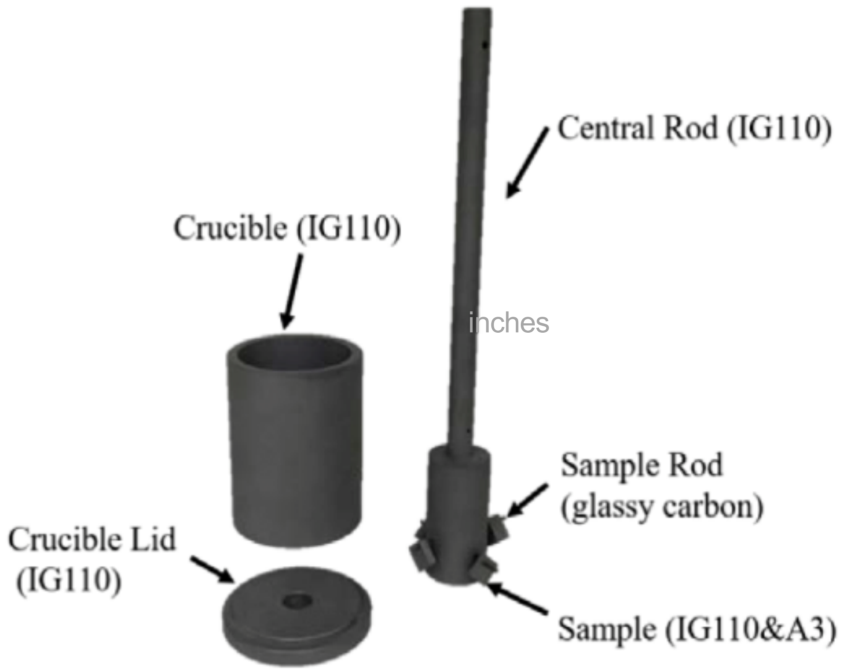


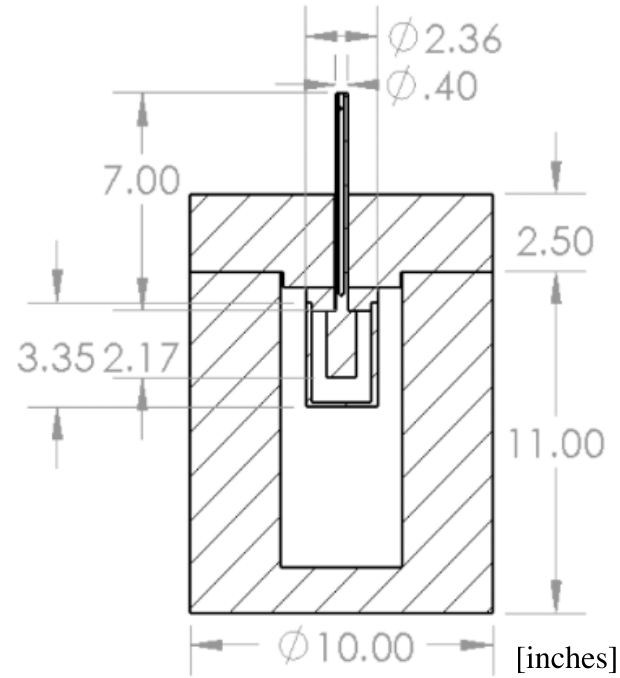


We do not expect 2LiF-BeF_2 (FLiBe) to intrude in the pores of graphite, at ambient pressure.

[1] H. Wu, F. Carotti, N. Patel, R. Gakhar, R. O. Scarlat. Fluorination of Nuclear Graphite IG-110 in Molten FLiBe salt at 700 oC. Journal of Fluorine Chemistry. 211 (2018) 159-170. **[2]** H. Wu et. al. Comparative analysis of microstructure and reactive sites for nuclear graphite IG-110 and graphite matrix A3. *Journal of Nuclear Materials*. 528 (2020) 151802.

FLiBe-Graphite | Salt-Exposure Experiment





12h exposure at 700 ^{o}C

<1ppm O_2, <1ppm H_2O in Ar

no observable weight change of salt-exposed graphite: < 0.016 % [2]

H. Wu, F. Carotti, N. Patel, R. Gakhar, R. O. Scarlat. Fluorination of Nuclear Graphite IG-110 in Molten FLiBe salt at 700 oC. Journal of Fluorine Chemistry. 211 (2018) 159-170.

FLiBe-Graphite | Salt-Exposure Experiment

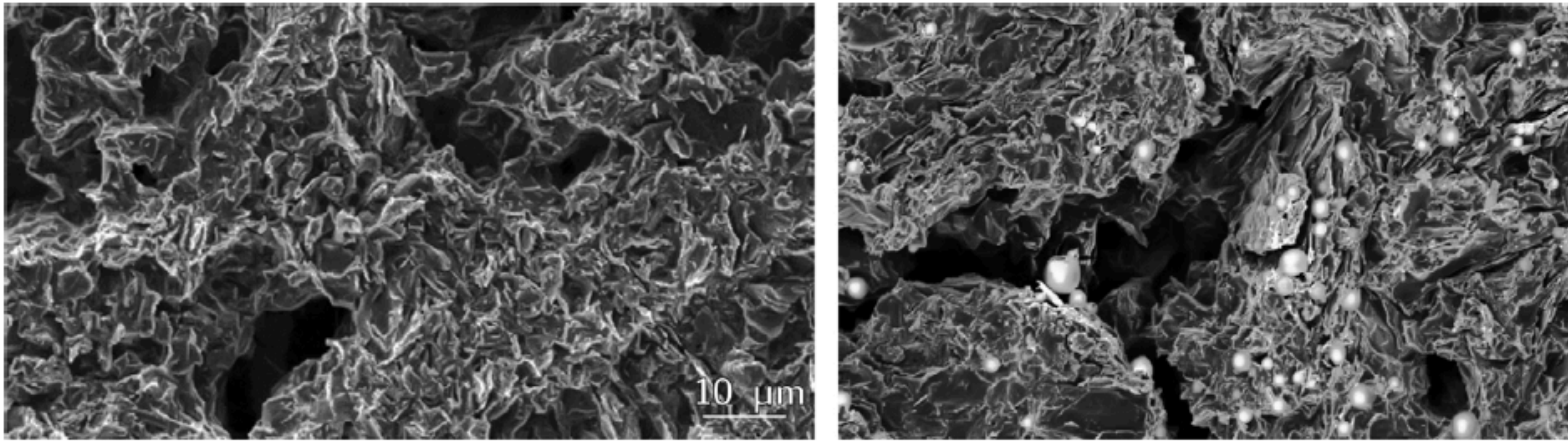


Fig. 3. SEM of IG-110 graphite surface, before (left) and after (right) FLiBe exposure.

No Salt Intrusion Observed
Fluorination was observed

H. Wu, F. Carotti, N. Patel, R. Gakhar, R. O. Scarlat. Fluorination of Nuclear Graphite IG-110 in Molten FLiBe salt at 700 ºC. *Journal of Fluorine Chemistry*. 211 (2018) 159-170.

FLiBe-Graphite | Graphite Fluorination

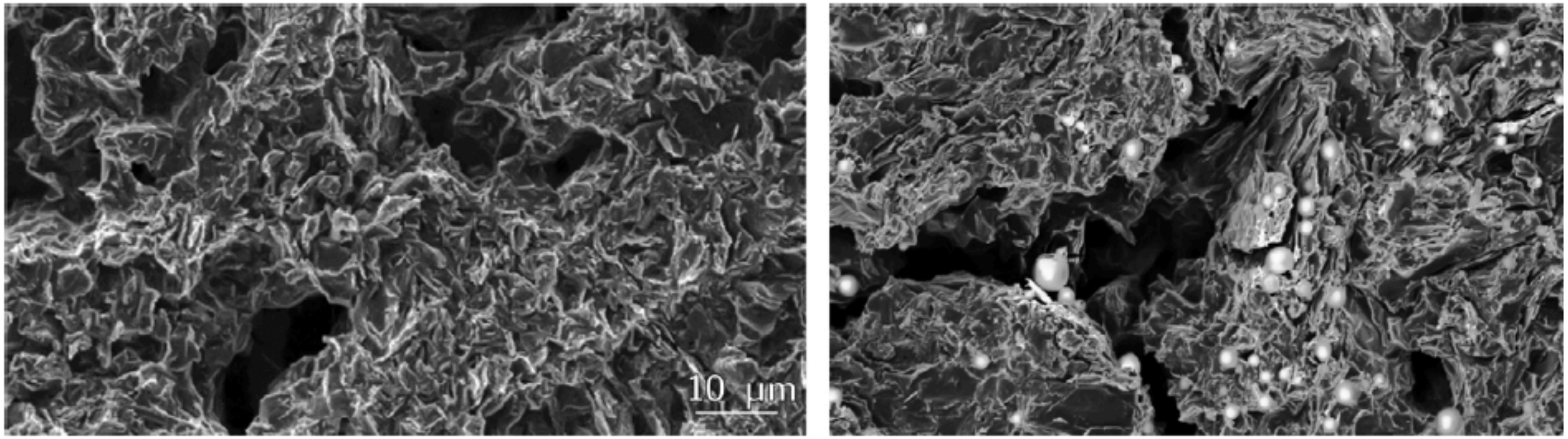
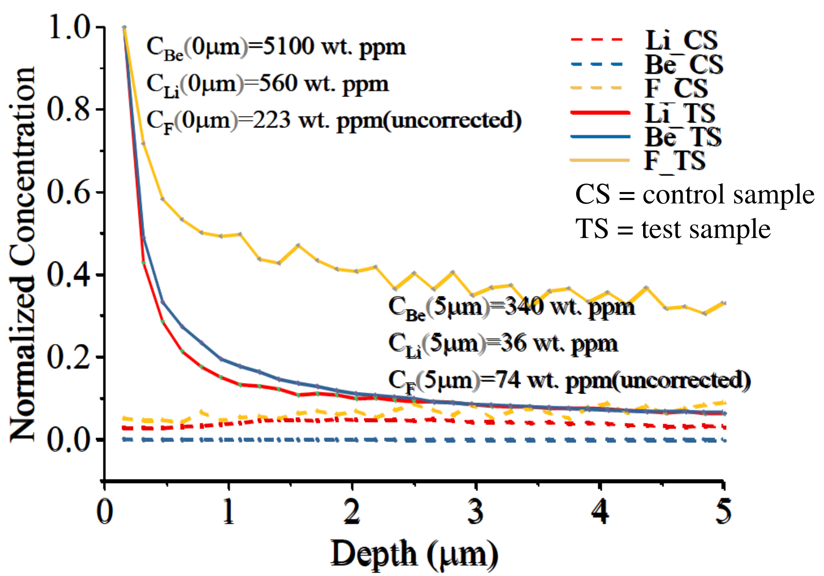


Fig. 3. SEM of IG-110 graphite surface, before (left) and after (right) FLiBe exposure.

$$n\,C^* + x\,MF_n \leftrightarrow n\,CF_x + x\,M$$

MF_n = metal fluorides
C^* = reactive carbon sites in graphite
M = reduced metal
CF_x = fluorinated carbon sites in graphite

$$nC^* + nx\,BeF_2 \leftrightarrow nCF_{2x} + xBe$$

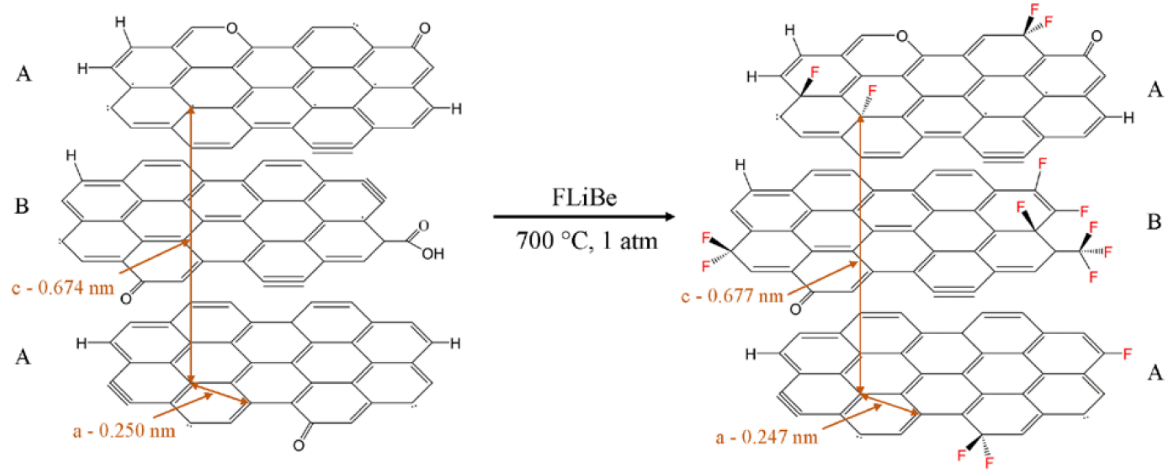


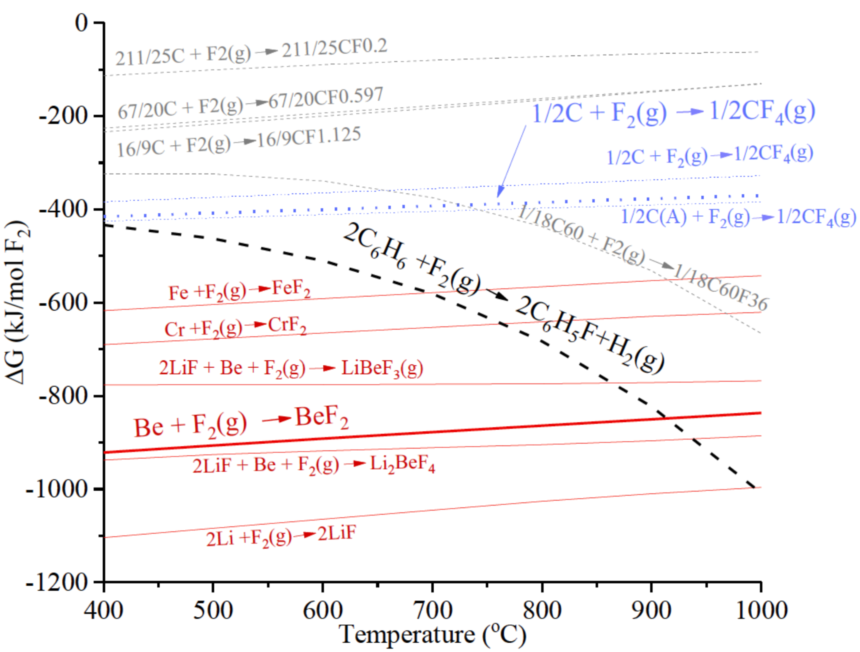
H. Wu, F. Carotti, N. Patel, R. Gakhar, R. O. Scarlat. Fluorination of Nuclear Graphite IG-110 in Molten FLiBe salt at 700 oC. Journal of Fluorine Chemistry. 211 (2018) 159-170.

FLiBe-Graphite | Reactive Carbon Sites

$$n\,C^* + x\,MF_n \leftrightarrow n\,CF_x + x\,M$$

MF_n = metal fluorides
C^* = reactive carbon sites in graphite
M = reduced metal
CF_x = fluorinated carbon sites in graphite





Reactive carbon sites (C*) in graphite, enable this reaction.

Otherwise, the following reaction does not proceed spontaneously:

FLiBe + C -> metal + fluorinated carbon

[1] H. Wu, F. Carotti, N. Patel, R. Gakhar, R. O. Scarlat. Fluorination of Nuclear Graphite IG-110 in Molten FLiBe salt at 700 oC. Journal of Fluorine Chemistry. 211 (2018) 159-170. [2] HSC 9.2.

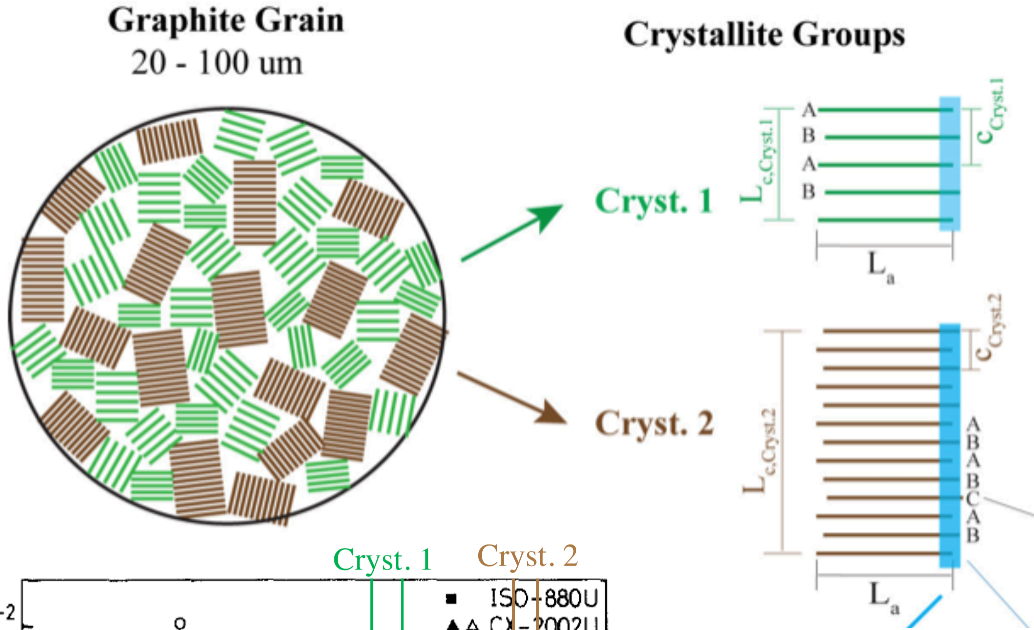
Raw Materials: Nuclear Graphite and Graphite Matrix

Item	A3	IG-110
Raw Materials	Natural Graphite-64 wt%, Synthetic Graphite-16 wt%, High purity Novolac resin-20wt% (pre-bake weight basis)	Petroleum Coke/Coal tar Pitch
Formation	Hot Pressing	Cold Isostatic Pressing
Heat Treatment Temperature	~1800°C	~2900°C
Grain Size	100 µm	20 µm

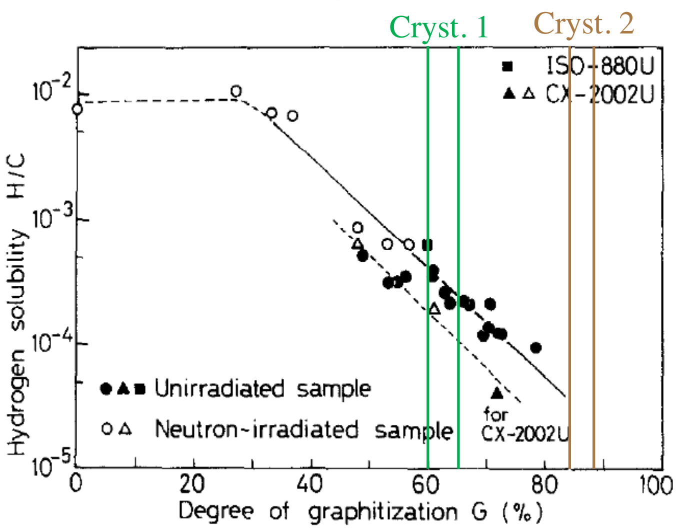
J. D. Hunn and M. P. Trammell. "Data Compilation for AGC-2 Matrix-only Compact Lot A3-H08." ORNL/TM-2010/304. Oak Ridge National Laboratory, Oak Ridge, TN. (2010).

P. J. Pappano, T. D. Burchell, et al., "A novel approach to fabricating fuel compacts for the next generation nuclear plant (NGNP)," *J. Nucl. Mater.*, **vol. 381**, no. 1–2, pp. 25–38, (2008).

Variability Among Graphite Grades | Reactive Carbon Sites



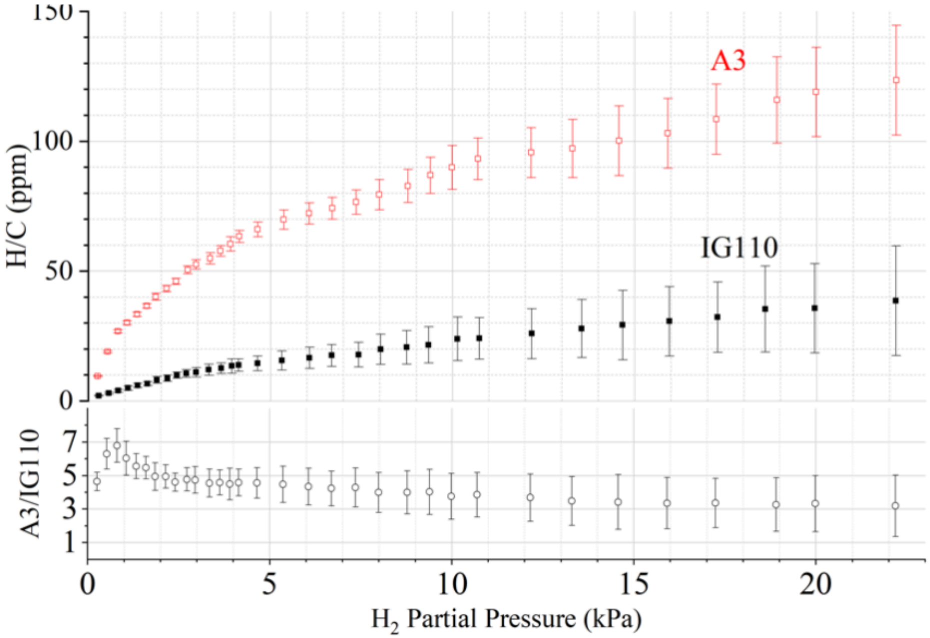
	IG110	A3
Cryst. 1	abundance = 57(9)	61(12) %
	g = 60(7)	65(5) %
	c = 0.6778(6)	0.6768(8) nm
	layers=L_c/c: 53	50
	B = 1.100(3)	B = 1.391(8)
Cryst. 2	g = 84(4)	88(2) %
	c = 0.6734(6)	0.6730(2) nm
	layers=L_c/c: 71	132
	B = 1.166(4)	B = 1.174(8)
	stacking fault ABC, rhombohedral content 14(4)	19(1) %
	FWHM(D) = 46(2)	54.2(1.0) cm^{-1} (Raman)



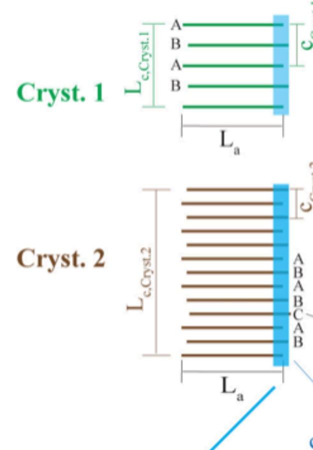
Slightly higher A3 degree of graphitization would predict lower or similar H_2 chemisorption.

[1] Huali Wu, Ruchi Gakhar, Allen Chen, Stephen Lam, Craig P. Marshall and Raluca O. Scarlat. Comparative Analysis of Microstructure and Reactive Sites for Nuclear Graphite IG-110 and Graphite Matrix A3. Journal of Nuclear Materials. 2019. [2] H. Atsumi, T. Tanabe, et al., 'Hydrogen behavior in carbon and graphite before and after neutron irradiation – Trapping, diffusion and the simulation of bulk retention', *J. Nucl. Mater.*, **vol. 417**, no. 1–3, pp. 633–636, (2011).

Variability Among Graphite Grades | Reactive Carbon Sites



Crystallite Groups



	IG110	A3
Cryst. 1: abundance	= 57(9)	61(12) %
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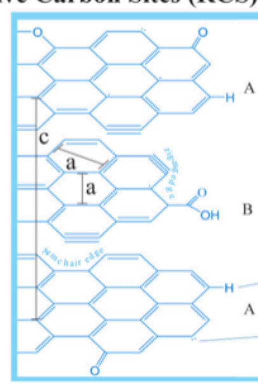
B	= 1.166(4)	B = 1.174(8)
stacking fault ABC, rhombohedral content	14(4)	19(1) %
FWHM(D)	= 46(2)	54.2(1.0) cm^{-1} (Raman)

Crystallite Edge with Reactive Carbon Sites (RCS)



	IG110	A3
a	= 0.24625(3)	0.24617(4) nm
La	= 21(8)	23(2) nm (XRD)
La	= 33(9)	34(14) nm (Raman)
edge area	= 76(6)	65(5) m^2/g (XRD)
C_{edge}/C_{total}	= 3.8(3)	3.3(3) % (XRD)

chemisorbed hydrogen (H-C bond) at RCS

RCS example: dangling bond

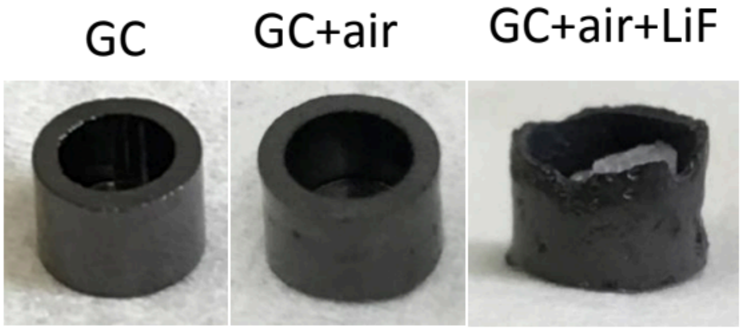
	IG110	A3	
H/C	= 24(8)	90(8) appm,	at 10 kPa H_2 and 700 °C
H/C_{edge}	= 630(50)	2660(260) appm,	at 10 kPa H_2 and 700 °C

Prior correlations (valid across 16 grades of isotropic graphite, 0-0.7 dpa neutron irradiation) assume uniform density of reactive carbon sites at crystallite edges.

Correlations do not extend to graphite matrix.

Huali Wu, Ruchi Gakhar, Allen Chen, Stephen Lam, Craig P. Marshall and Raluca O. Scarlat. Comparative Analysis of Microstructure and Reactive Sites for Nuclear Graphite IG-110 and Graphite Matrix A3. Journal of Nuclear Materials. 528 (2020) 151802.

The Chemistry of Graphite in FHRs and MSRs
Future Questions to Investigate



O2 solubulity in the melt accelerates graphite degradation?

W. Derdeyn, R. Scarlat. 2019 (unpublished)

1. Role of fluorination and salt intrusion on graphite tribology & mechanical properties.
2. Surface tension changes with salt composition & cover gas composition.
3. Impact of fluorination on irradiation; impact of irradiation on fluorination.
4. Impact of tritium + salt presence on irradiation; impact of irradiation ion tritium uptake and fluorination. Consider also formation of volatile organic species.
5. Metal carbide formation: kinetics, impact on tribology, fluorination, wetting.
6. Dust formation and introduction of soluble-carbon species in the salt.
7. Impact of graphite degassing treatment on salt interaction, and on corrosion in salt.
8. Degradation of graphite upon O_2 presence in cover gas.
9. Gas-phase reactions, and degradation at free liquid surfaces (i.e. salt-gas interface).