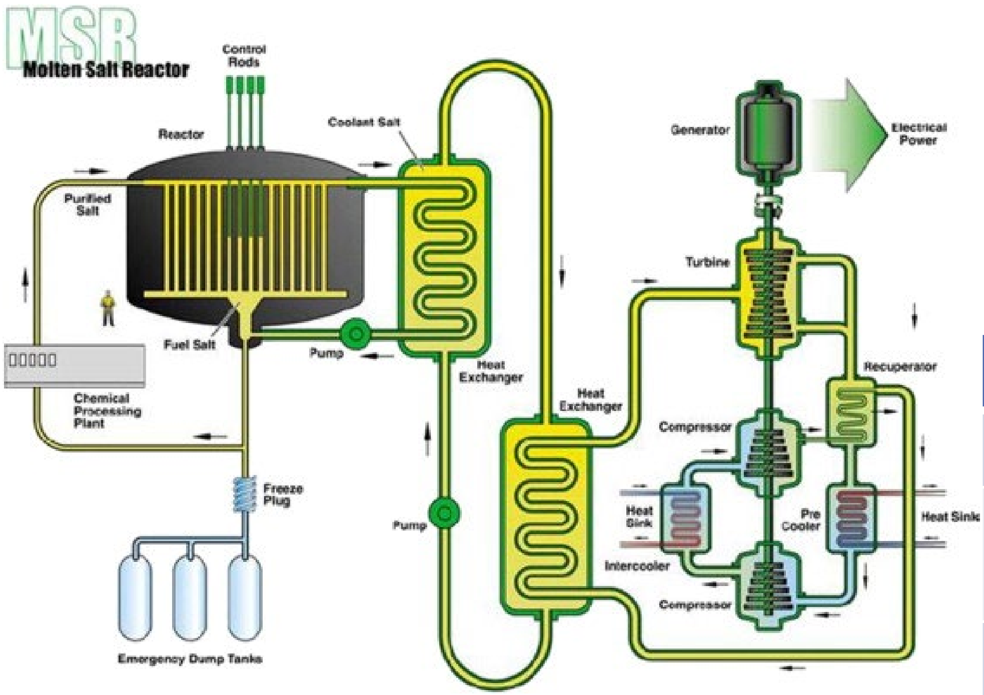
Graphite for Molten Salt Reactors

Derek Tsang

SINAP

Contents

Introduction



Schematic Diagram of Molten Salt Reactor (Abram and Ion 2008)

Table 1: Design parameters of TMSR-LF/TMSR-SF in SINAP (Zhang, Liu et al. 2018)

Design Parameters	TMSR-LF/TMSR-SF
Salt	FLiNaK/FLiBe
Operation temperature	650°C
Operation pressure	Near atmospheric pressure
Core	Graphite

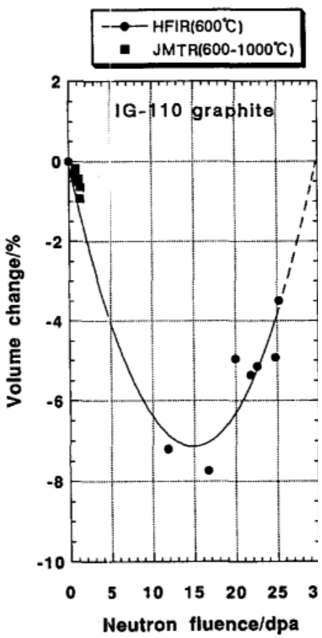
Material Challenges

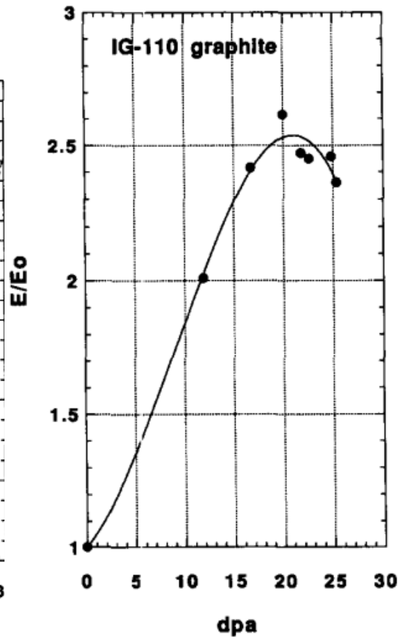
- Molten salt penetration (ASTM)
- Testing at high temperature (ASTM)
- Molten salt permeability (ASTM)
- Life time of a graphite core

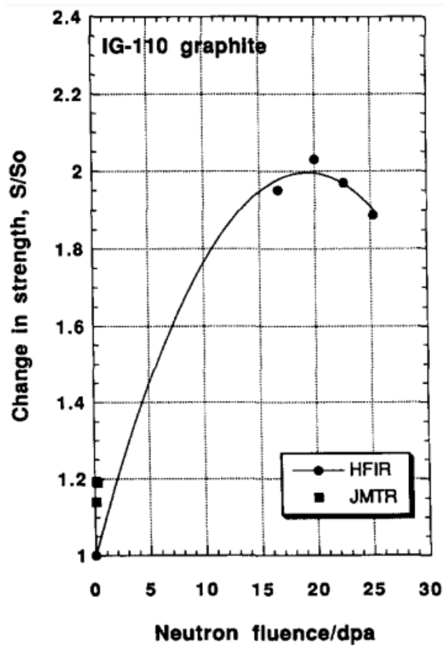
Molten salt impregnation

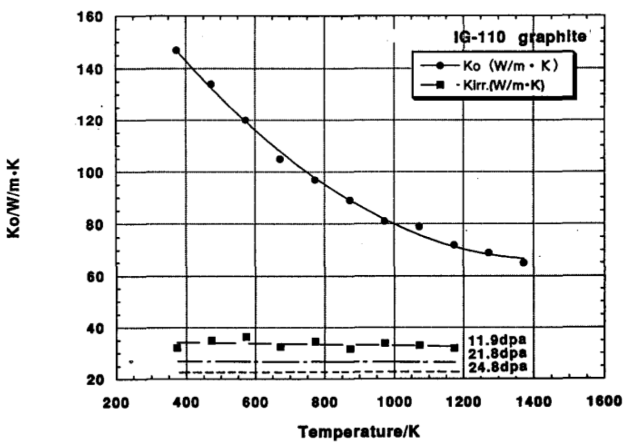
Neutron irradiation (Ishiyama, Burchell et al. 1996)

Dimension changes | Young's modulus | Strength | Thermal conductivity



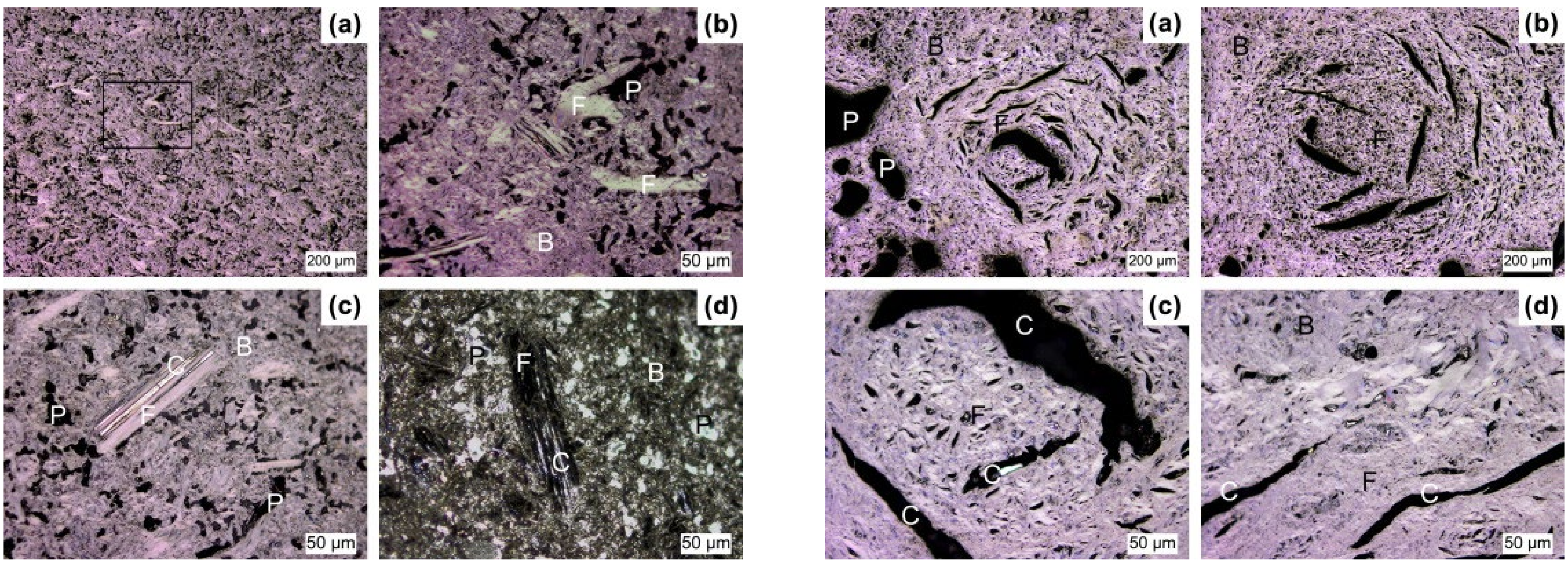






Molten salt impregnation

Nuclear graphite is a porous material



Optical micrographs of IG-110 and NBG-18. (P-Porosity, F-Filler, B-Binder, C-Calcination crack. Kane, Karthik et al. 2011)

Molten salt impregnation

Parameters of nuclear graphite

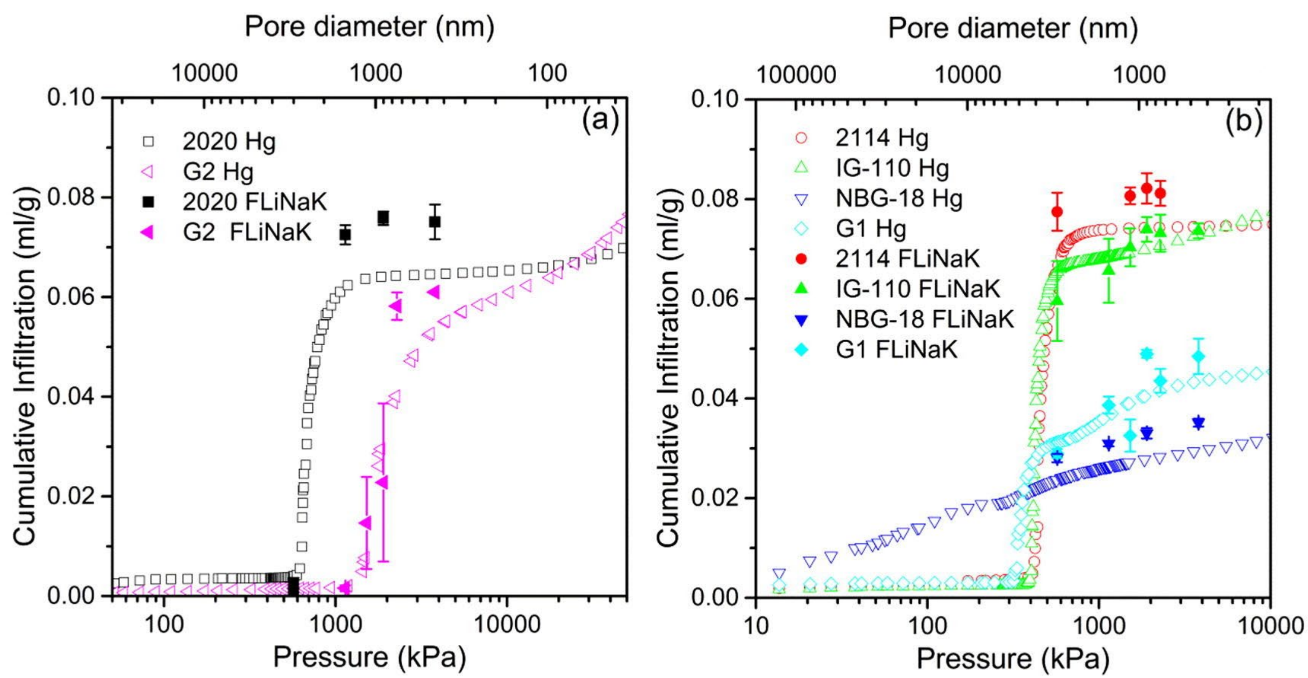
Grade	Coke source	Forming process	Grain size (μm)	Density (g/cm3)	Porosity (%)	Vendor
IG-110	Petroleum	Isostatic pressed	20	1.77	21.7	Toyo Tanso, Japan
NBG-18	Pitch	Vibration molded	300	1.85	18.3	SGL, Germany
T-220	Pitch	Isostatic pressed	Superfine	1.87	17.1	SINOSTEEL, China
NG-CT-10	Pitch	Isostatic pressed	25	1.89	16.4	Chengdu Carbon, China
NG-CT-50	Pitch	Isostatic pressed	Superfine	1.79	20.7	Chengdu Carbon, China

Molten salt impregnation

1. Threshold pressure: It is inversely proportional to open pore size,

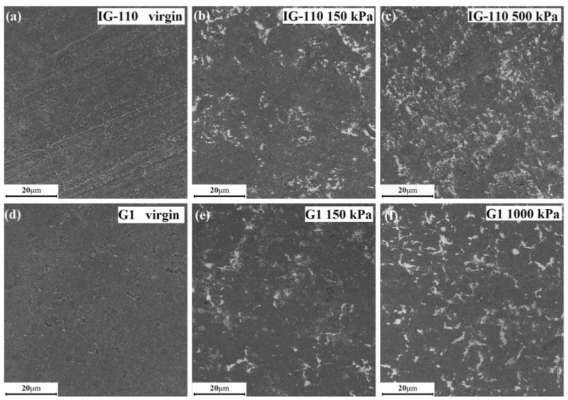
2. Cumulative impregnation: It is proportional to external pressure,

3. Saturation quantity of cumulative impregnation: It is proportional to porosity.

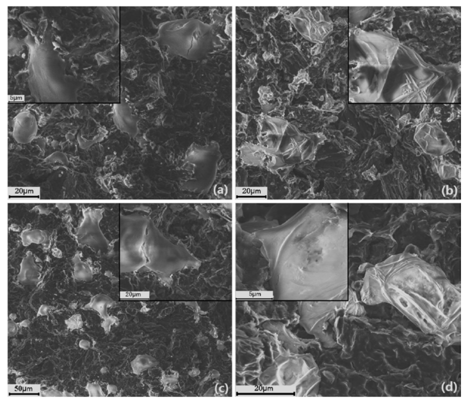


Cumulative infiltration for molten FLiNaK salt and mercury into various graphite(He, Gao et al. 2015)

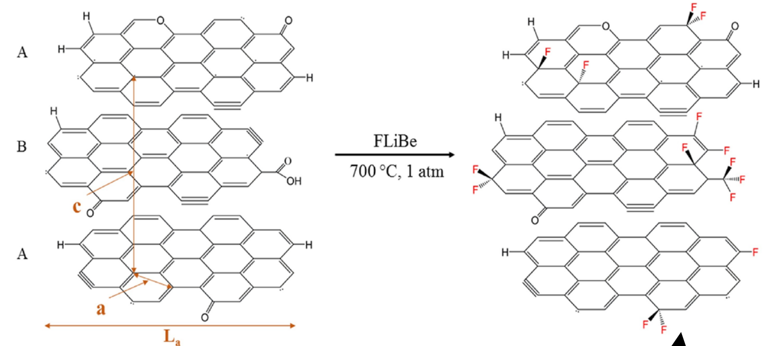
Molten salt impregnation



Cross-sectional SEM images molten FLiNaK salt impregnated grades IG-110 and G1 graphite at different pressures(He, Gao et al. 2015).



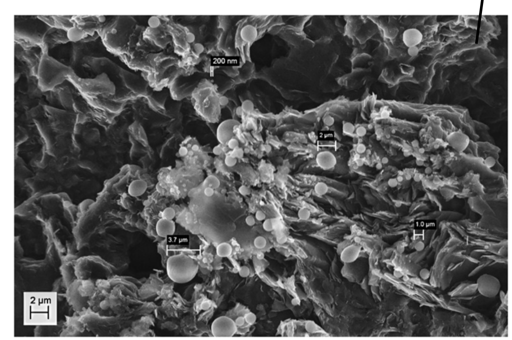
Fracture surface FLiNaK salt impregnated graphite (He, Gao et al. 2015).



Representative ABA (hexagonal) crystallite in graphite, including edge sites with typical edge functionalities, dangling bonds at zigzag and armchair sites, and triple bonds at the armchair sites.

Fluorination at the reactive carbon sites after salt exposure, leading to the formation of different types of C-F groups, observed with XPS. An increase in content of ABC (rhombohedral) graphite is also observed with XRD.

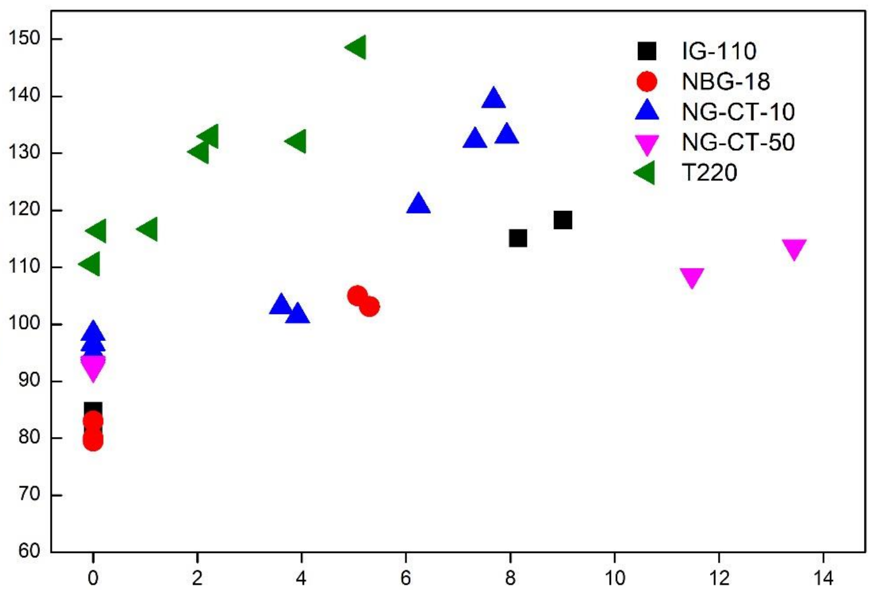
Fracture surface FLiBe salt impregnated graphite(Wu, Carotti et al. 2018).



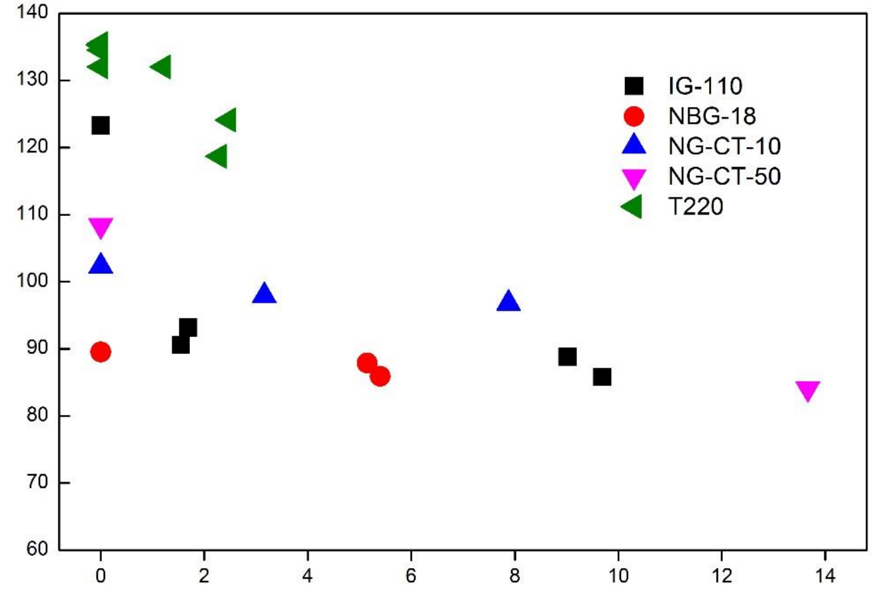
Molten salt impregnation

At room temperature:
The compressive strength is positively correlated with the penetration of molten salt.

At 700℃ :
The compressive strength is negatively correlated with the penetration of molten salt



Molten FLiBe salt at room temperature (wt.%)

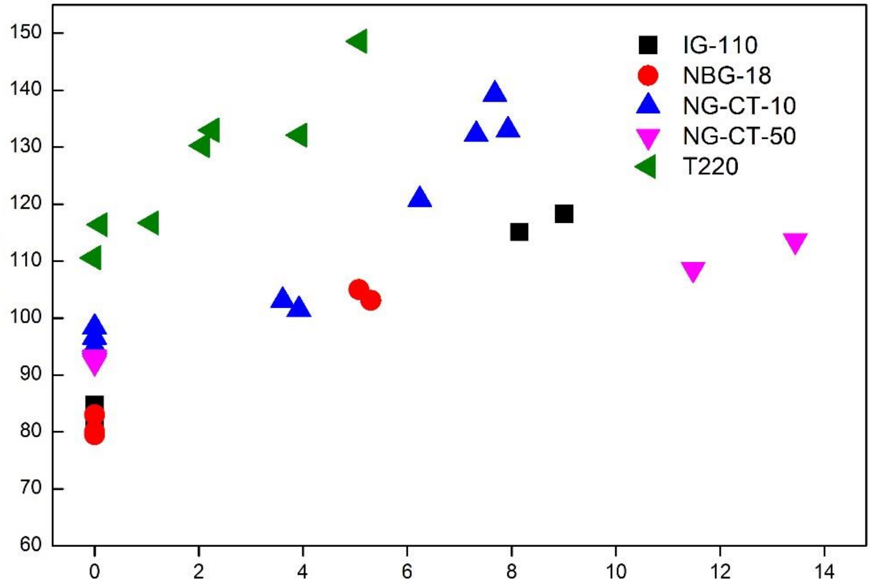


Molten FLiBe salt at 700℃ (wt.%)

The effect of molten salt penetration on compressive strength
at room temperature and 700℃ (Tang ,He et al. 2017)

Molten salt impregnation

- Careful to compare impregnation data from different grade of graphite by using weight percent!
- Higher values of wt. % may due to it has smaller density.



Molten FLiBe salt at room temperature (wt.%)

	Graphite A	Graphite B	Graphite C
Graphite density ρ_g (g/cm^3)	1.7	1.8	1.9
Volume of graphite sample V_g (cm^3)	10	10	10
Weight of graphite sample M_g (g)	17	18	19
Weight of molten salt M_s (g)	1	1	1
Weight percent M_s/M_g*100% (wt. %)	5.88	5.56	5.26

Molten salt impregnation

- ASTM D8091-21 gives a general guide to perform molten salt impregnation test.

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.

INTERNATIONAL

Designation: D8091 – 21

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.

1. Scope*

1.1 This guide covers procedures for the impregnation of graphite with molten salt under a consistent pressure and temperature. Such procedures are necessary if the user wishes to prepare graphite specimens for testing that represent material that has been exposed to a molten salt environment in a molten salt nuclear reactor. The user will need to ensure that impregnation temperature and pressure conditions reflect those pertaining to the molten salt environment, noting that the properties of the material will change once it becomes irradiated.

NOTE 1—The term impregnation is used throughout this guide as this is the correct term for the described process. Other terms such as infiltration and intrusion may be encountered by the user in other texts and the term intrusion is commonly used to describe penetration of open porosity in graphite in a molten salt reactor environment.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this guide.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

B923 Test Method for Metal Powder Skeletal Density by Helium or Nitrogen Pycnometry
C559 Test Method for Bulk Density by Physical Measurements of Manufactured Carbon and Graphite Articles
D7775 Guide for Measurements on Small Graphite Specimens

3. Terminology

3.1 *Definitions:*

3.1.1 *impregnation pressure (P_I), n*—the differential pressure between the cover gas pressure and the pore pressure of the graphite specimen.

3.1.1.1 *Discussion*—If the impregnation starts at a pore pressure of atmospheric pressure, the impregnation pressure is the gauge pressure of the cover gas; if the impregnation starts at a pore pressure of "0" (vacuum), the impregnation pressure is the gauge pressure plus atmospheric pressure. For a pore pressure between 0 and atmospheric pressure, the impregnation pressure is (gauge pressure + atmospheric pressure − pore pressure).

3.1.2 *impregnation temperature (T_I), n*—the system temperature before the graphite specimen has been immersed in the molten salt.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *Parameter D_o, n*—a measure of the extent of penetration of the graphite porosity by the molten salt expressed in terms of the open pore volume of the specimen.

3.2.1.1 *Discussion*—If there was no damage to the microstructure of the graphite during impregnation, then parameter D_o based upon open pore volume would be unity at saturation. This parameter is applicable when damage to the graphite microstructure during impregnation is absent or low. Mercury porosimetry studies indicate that the threshold pressure for microstructural damage is 13.8 MPa to 20.0 MPa (2000 psi to 3000 psi).[3,4] This threshold should be used as a guide by users when evaluating D_o. At high impregnation pressures, closed porosity may be broken into by the molten salt and parameter

[1] This guide is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.F0 on Manufactured Carbon and Graphite Products.

Current edition approved July 1, 2021. Published July 2021. Originally approved in 2016. Last previous edition approved in 2016 as D8091 – 16. DOI: 10.1520/D8091-21.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Dickinson, J. M., Shore, J. W., "Observations Concerning the Determination of Porosities in Graphites," *Carbon*, Vol 6, 1968, pp. 937–941.

[4] Baker, D. J., Morris, J. B., "Structural Damage in Graphite Occurring during Pore Size Measurements by High Pressure Mercury," *Carbon*, Vol 9, 1971, pp. 687–690.

*A Summary of Changes section appears at the end of this standard

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Testing at high temperature

- The working temperature of MSR has to be higher than the melting temperature of salts. Melting temperature of salt > 450°C.
- Graphite strength at high temperature is higher than at room temperature.
- Need to get data at high temperature to correctly represent molten salt environment.
- Try to avoid testing impregnated graphite sample at room temperature with solidified salt inside!

Table 6.14 — EFFECT OF TEMPERATURE ON THE TENSILE STRENGTH OF A NUMBER OF GRAPHITES

Type of graphite	Density, g/cm³	Tensile strength, psi: Room temperature (∥)	Room temperature (⊥)	2500°C (∥)	2500°C (⊥)	Increase, % (∥)	Increase, % (⊥)	Ref.
AGX	1.58	2200		3900		78		111
C-18	1.60	2500		5200		108		111
CEQ	1.55	3200		5000		56		111
ECA	1.67	3500		6900		97		111
EBP	1.76	3100		6300		103		111
Speer-3499	1.57	1730		4850		181		112
942S	1.69	1780	1780	3620	2960	103	67	112
AGR	1.59	550		1560		184		112
H3LM	1.68	1420	1420	2800	2750	97	94	112
H4LM		1500	1000	2700	2200	80	120	107
CK		1500		2600		73		107

ASME BPVC.III.5-2021

FORM MDS-1 MATERIAL DATA SHEET (SI UNITS)

Grade Designation

Material Grade ______①______ Material spec. ID ______②______ ASTM spec. ______③______

Max. grain size (mm) ______④______ Designation ______⑤______

Temperature-Dependent Parameters

Property	Units	Orientation	20°C	200°C	400°C	600°C	800°C	1000°C [Note (1)]
Bulk density ⑥	$kg \cdot m^{-3}$	...	____	____	____	____	____	____
Strength – tensile ⑦	MPa	WG, AG	____	____	____	____	____	____
Strength – flexural ⑧ (4-point)	MPa	WG, AG	____	____	____	____	____	____
Strength – compressive ⑨	MPa	WG, AG	____	____	____	____	____	____
Elastic modulus ⑩ (dynamic)	GPa	WG, AG	____	____	____	____	____	____
Elastic modulus (static) ⑪	GPa	WG, AG	____	____	____	____	____	____
Coefficient of thermal ⑫ expansion	$°C^{-1}$	WG, AG	____	____	____	____	____	____
Thermal conductivity ⑬	W/m•k	WG, AG	____	____	____	____	____	____

Testing at high temperature

- ASTM has developed a guide for high temperature strength measurement.
- D8377-21

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: D8377 – 21

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

This standard is issued under the fixed designation D8377; 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.

1. Scope

1.1 This guide covers the best practice for strength measurements at elevated temperature of graphite impregnated with molten salt.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C651 Test Method for Flexural Strength of Manufactured Carbon and Graphite Articles Using Four-Point Loading at Room Temperature

C695 Test Method for Compressive Strength of Carbon and Graphite

C749 Test Method for Tensile Stress-Strain of Carbon and Graphite

D8091 Guide for Impregnation of Graphite with Molten Salt

D8289 Test Method for Tensile Strength Estimate by Disc Compression of Manufactured Graphite

E4 Practices for Force Verification of Testing Machines

3. Summary of Guide

3.1 There is currently a set of ASTM standards as stated in 2.1 that can be applied to graphite for different strength measurements (Test Methods C651, C695, C749, D8289). Each of these standards has been developed specifically to provide a method of measurement for graphite as a single material. However, in some applications such as in molten salt reactors, graphite components are submerged in a molten salt. In order to assess the effect of molten salt on graphite components, a method may be necessary for the measurement of strength for graphite specimens both impregnated with molten salt and at elevated temperatures (see Section 4). The objective of this guide is to provide advice on the application of selected standards for graphite specimens impregnated with molten salt and tested at elevated temperatures. This includes transportation of graphite specimens impregnated with molten salt, temperature measurement, equipment for measuring compressive, tensile, or flexural strength at elevated temperature, and safe handling of the molten salt.

4. Significance and Use

4.1 The Molten Salt Reactor is a nuclear reactor which uses graphite as reflector and structural material, and molten salt as coolant. The graphite components will be submerged in the molten salt during the lifetime of the reactor. The porous structure of graphite may lead to molten salt permeation, which can affect the thermal and mechanical properties of graphite. Consequently, it may be necessary to measure the various strengths of the manufactured graphite materials after impregnation with molten salt and before exposure to the reactor environment in a range of test configurations in order for designers or operators to assess their performance.

4.2 For gas-cooled reactors, the strength of a graphite specimen is usually measured at room temperature. However, for molten salt reactors, the operating temperature of the reactor must be higher than the melting temperature of the salt, and so the salt will be in solid state at room temperature. Consequently, room temperature measurements may not be representative of the performance of the material at its true operating conditions. It is therefore necessary to measure the strength at an elevated temperature where the salt is in liquid form. Users should also be aware that a small increase in

[1] This guide is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.F0 on Manufactured Carbon and Graphite Products.

Current edition approved Jan. 1, 2021. Published January 2021. DOI: 10.1520/D8377-21.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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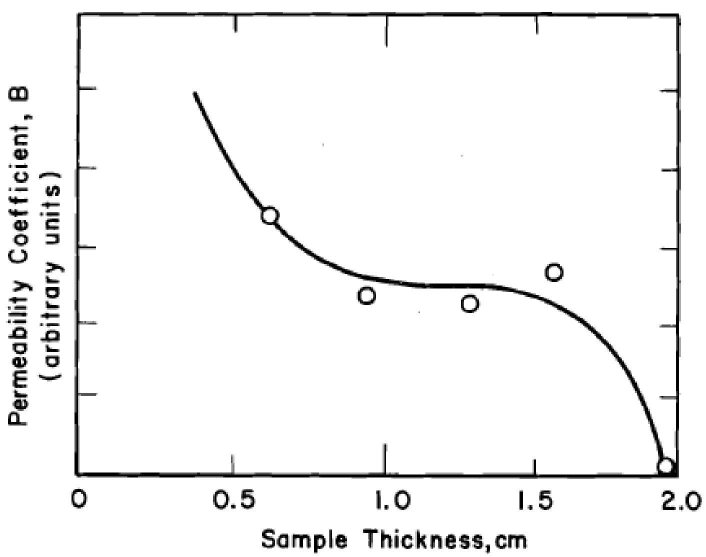
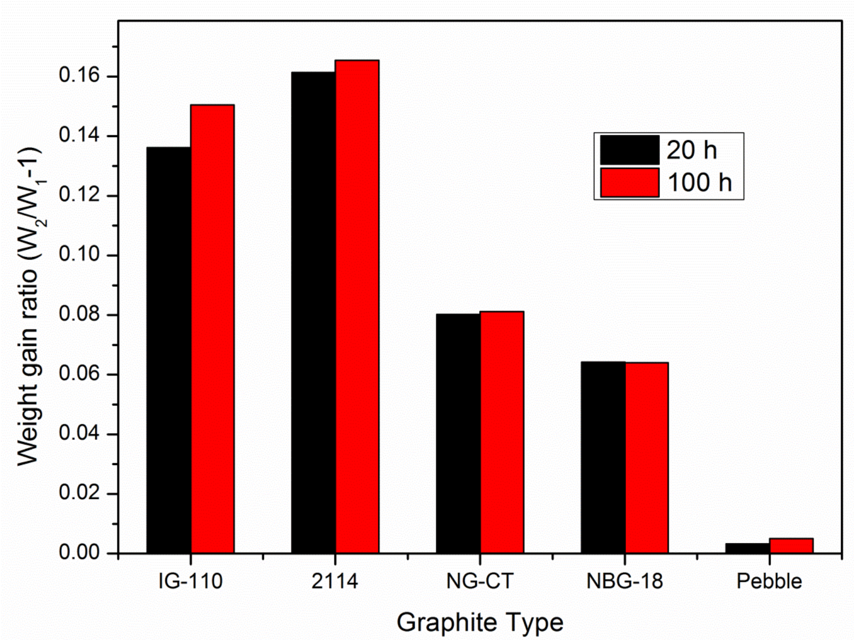
1

Molten salt permeability (ASTM)

- We still don’t fully understand the impregnation behaviour of molten salt in graphite.
- The graphite core has a lifetime much longer than impregnation test (100 hours).
- What is the MSR graphite impregnation behaviour in a longer term?
- How to do the permeability test at high temperature?
- The permeability of a liquid through graphite is varied with the sample thickness.



Water permeability of R-0025 graphite (Nightingale)



Molten salt permeability (ASTM)

- ASTM is developing a new test standard for liquid permeability of graphite.
- We are very welcome any interested party to join us to develop the standard together and make contribution.

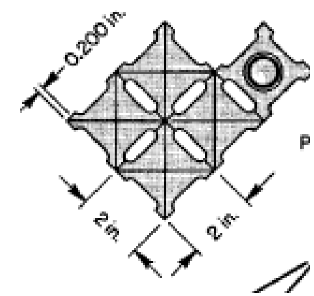
Life time of graphite core

- Usually the life of a graphite core is determined by zero strain condition.
- Ultrafine grain graphite has a considerable shorter lifetime!
- The MSR must has a replaceable graphite core and replace graphite core every 4~8 years.
- How can we improve the lifetime of graphite core?
- Can we let the molten salt pass through the graphite core instead of prevent it?
- For example NBG-18
  - longer time to reach zero strain condition
  - big pore channel for molten salt to pass through

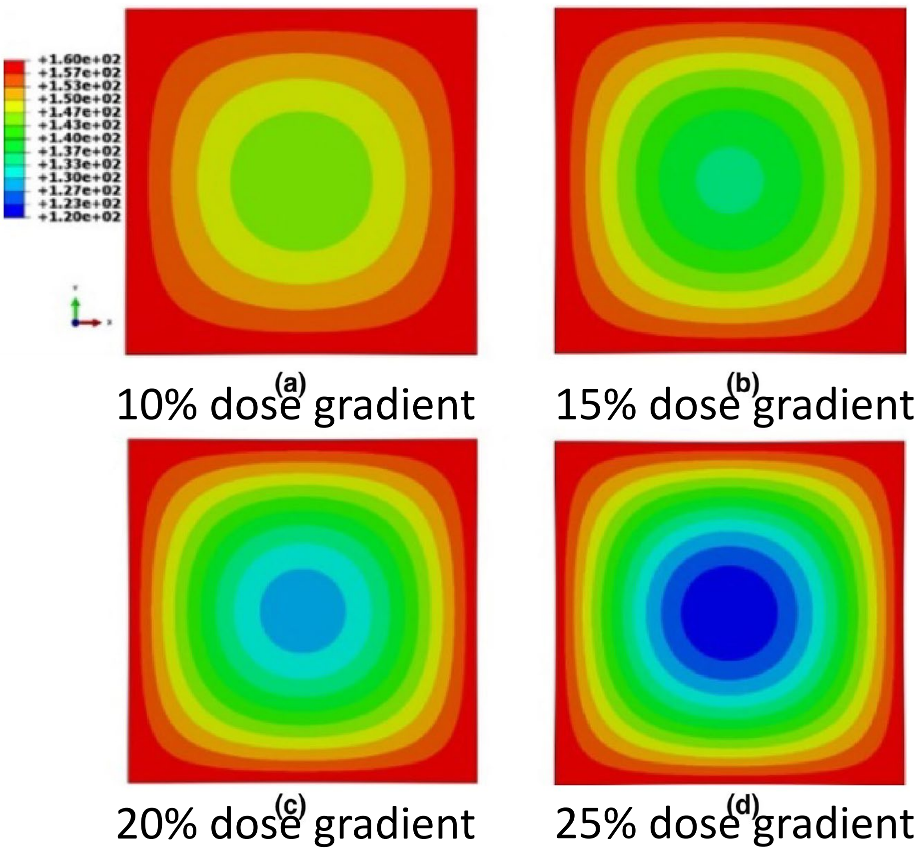
Structural Challenges

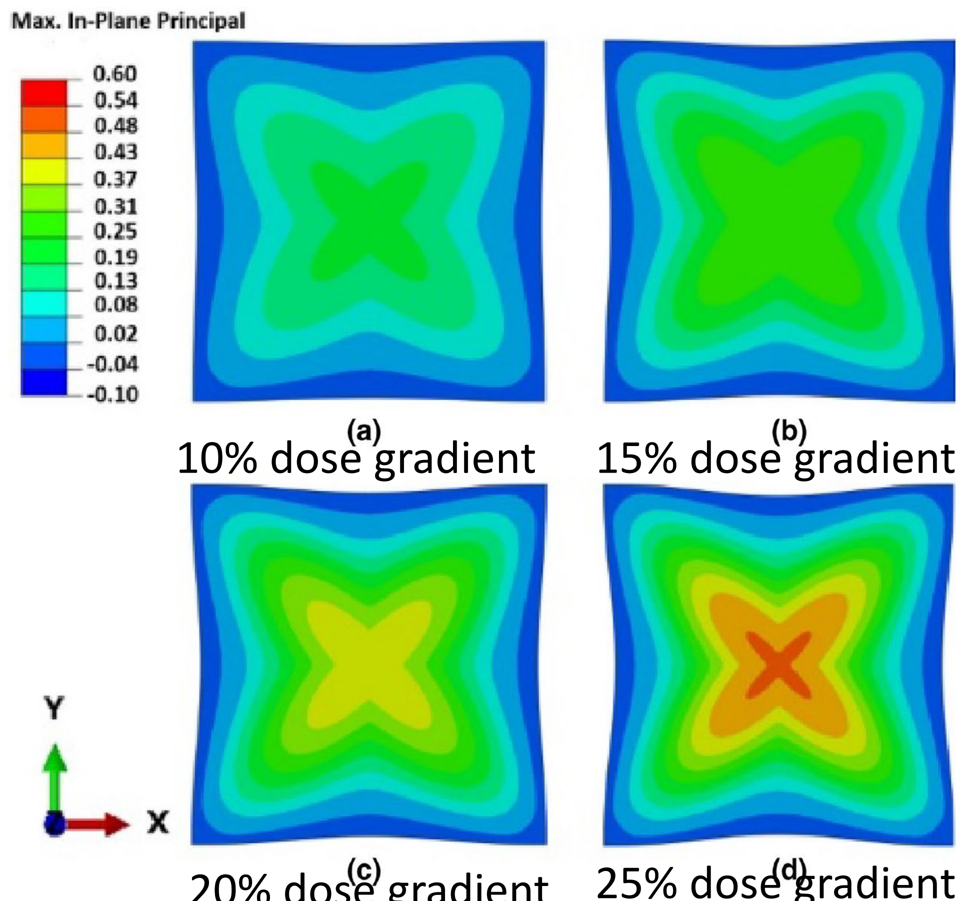
- Stress analysis
- Life prediction (ASME)
- Seismic analysis

Stress analysis



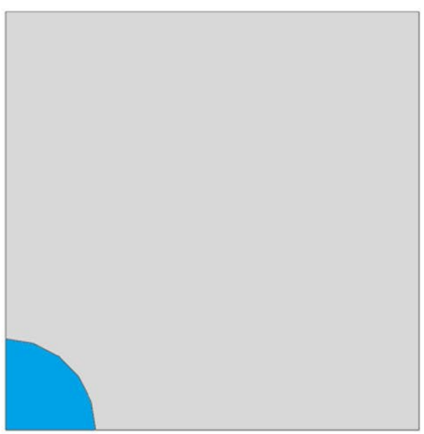
- A general study on a 50mm*50mm graphite bar with different dose profiles.



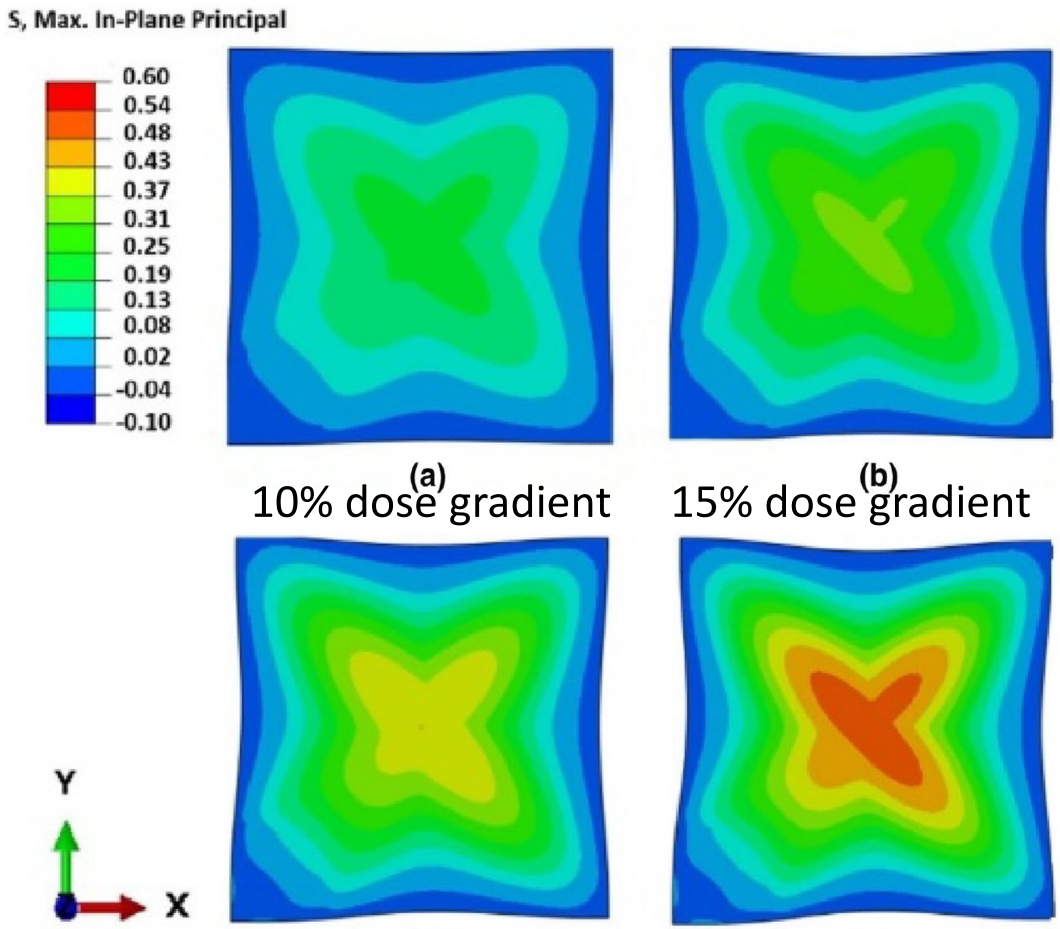


Stress analysis

- Different molten salt impregnated zone



(a)



10% dose gradient

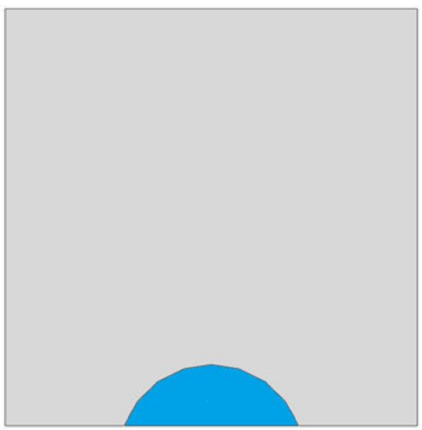
15% dose gradient

20% dose gradient

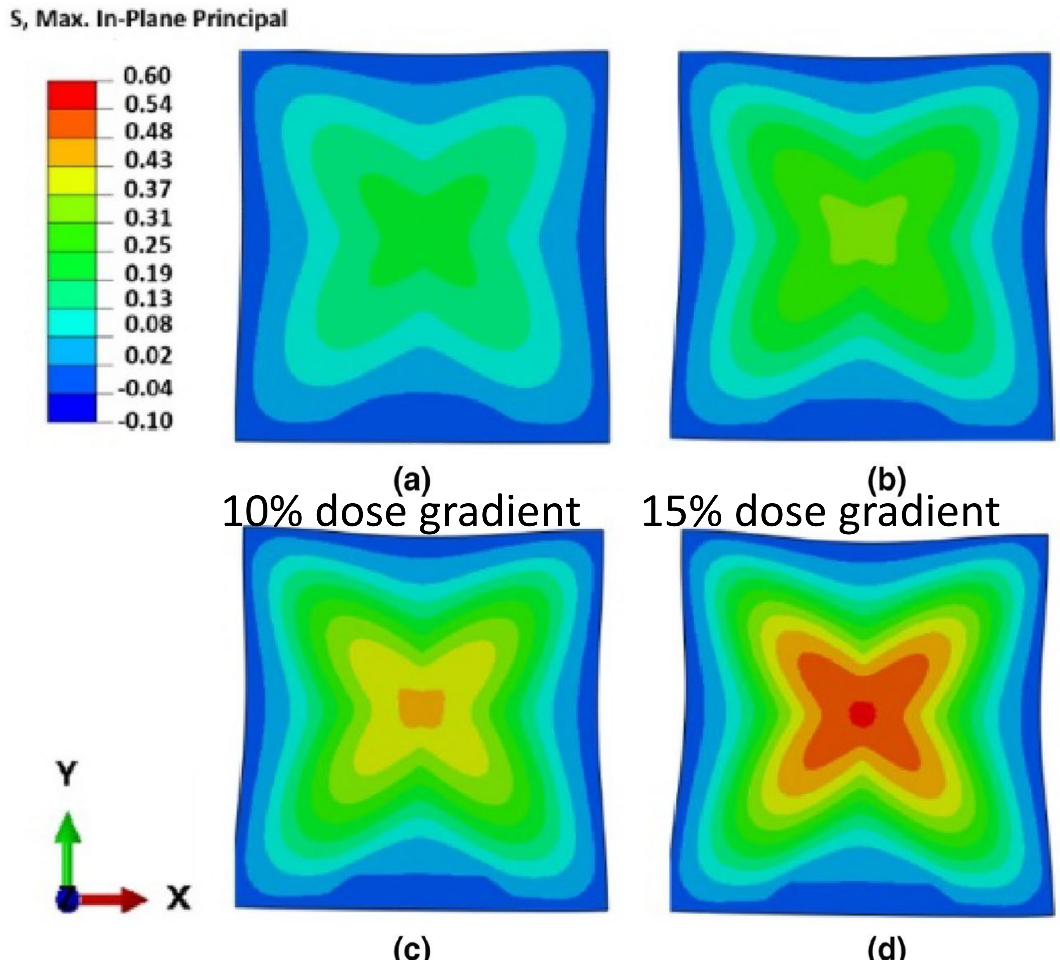
25% dose gradient

Stress analysis

- Different molten salt impregnated zone



(b)



10% dose gradient

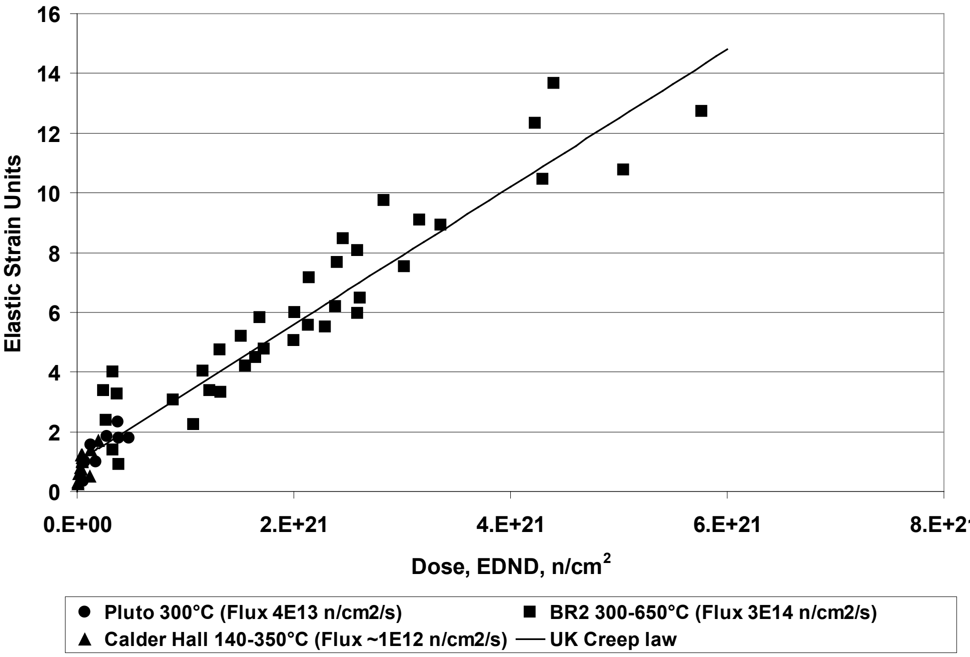
15% dose gradient

20% dose gradient

25% dose gradient

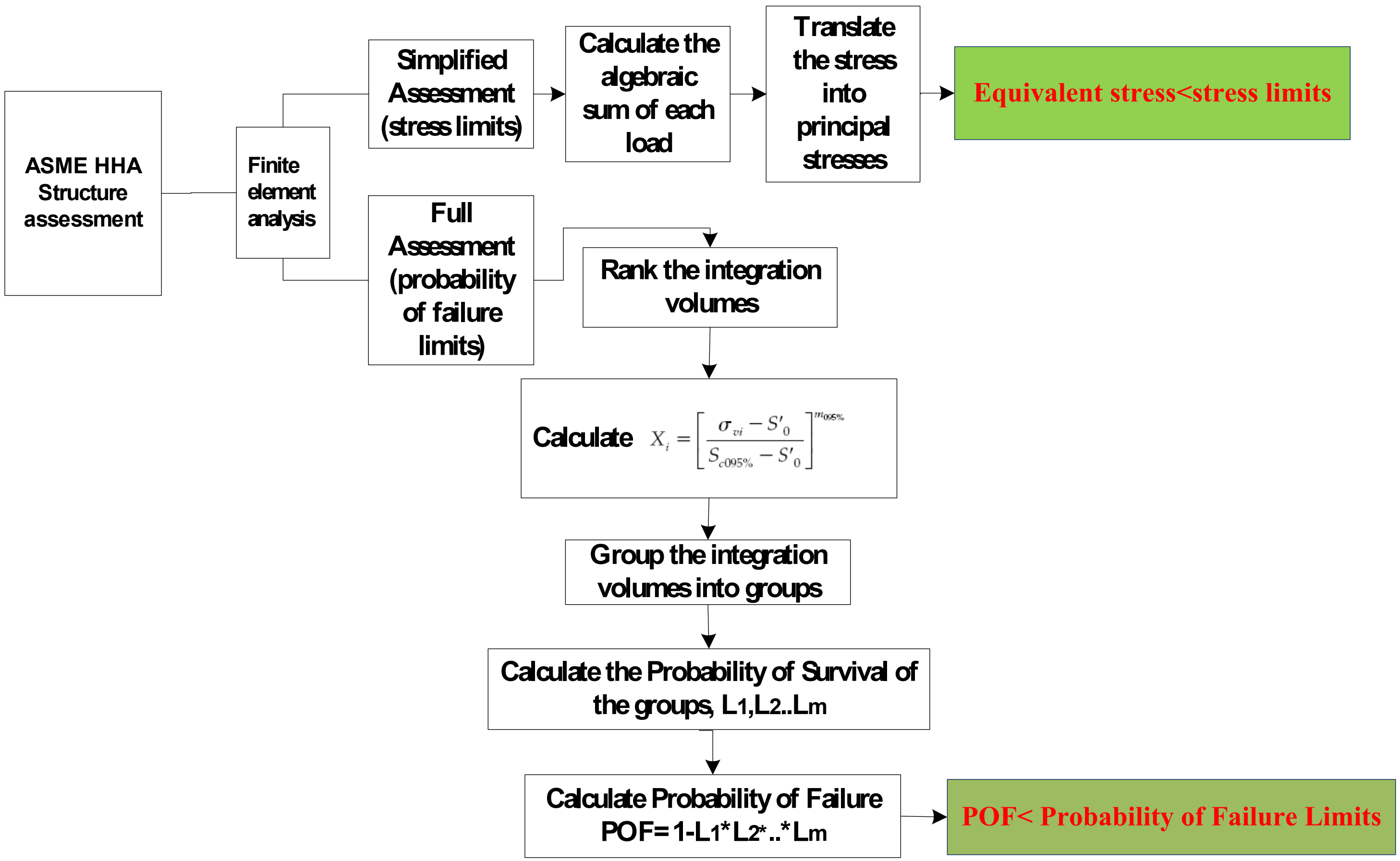
Stress analysis

- In all cases, stress values are moderate.
- It is well known that stress results are very sensitive to irradiation creep equation used. UK creep law was used in the analysis.
- However, we don't know the irradiation creep behaviour of ultrafine grain graphite.
- Does UK creep law apply?



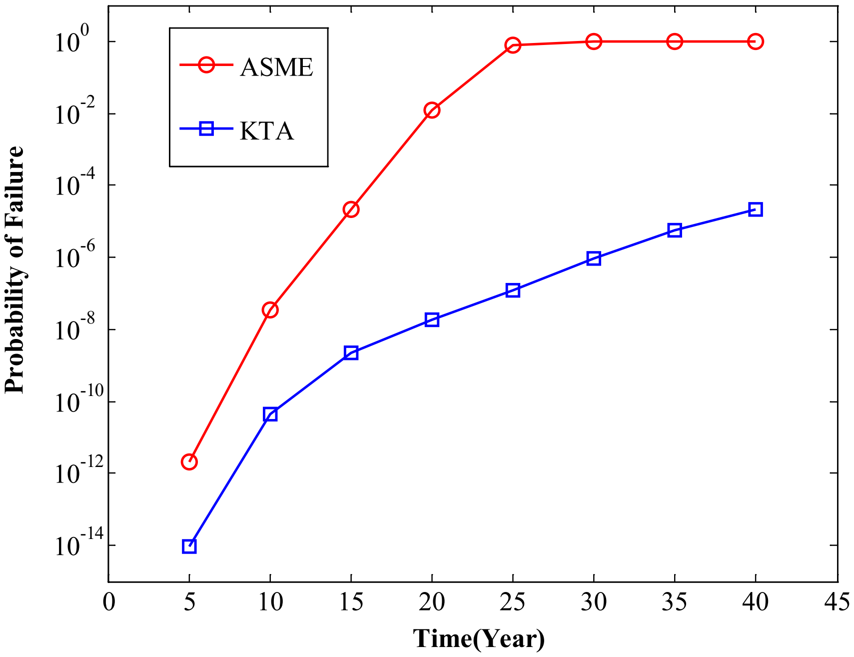
Life prediction (ASME)

HHA 3230 Probability of failure limits for graphite core components –full assessment



Life prediction (ASME)

- KTA-3232 is a German standard and has been applied in HTR 10.
- ASME is an American standard
- Main difference in POF calculation
  - KTA-3232: do not group the integration volume
  - ASME: group the integration volume by maximum grain size (ultrafine grain graphite has a very small grain size)
- POF calculated from ASME is more conservative than that of KTA.



Life prediction (ASME)

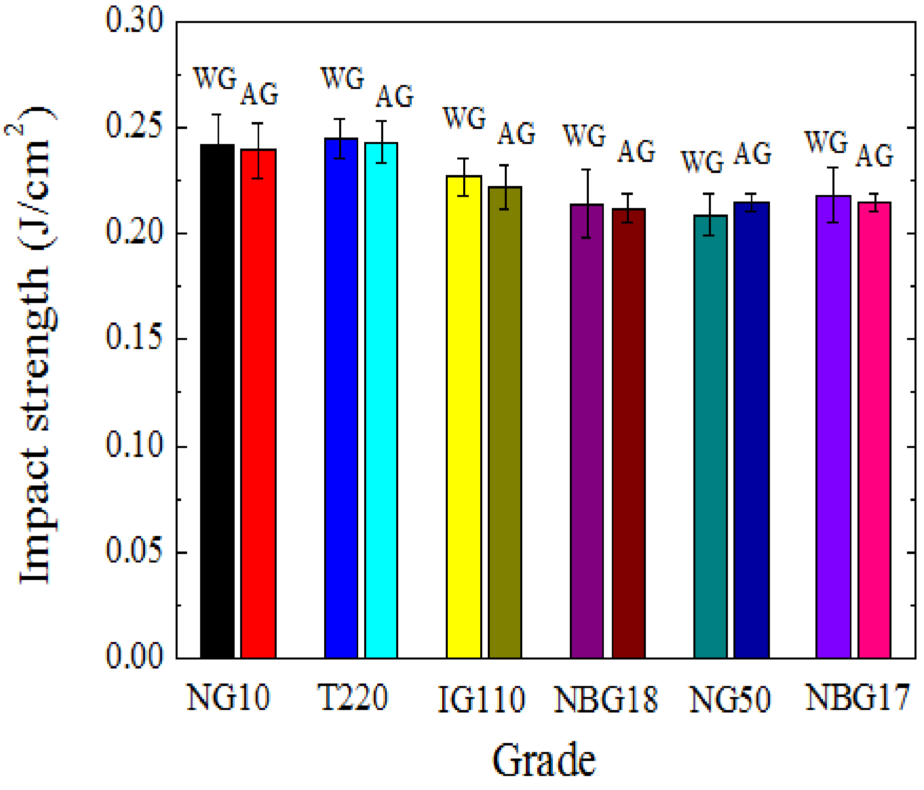
- Recently, ASME proposed group the integration volume by fracture toughness.

$$\textit{Process Zone Size,} \qquad r_c = \frac{1}{2\pi}\left[\frac{K_{Ic}}{\sigma_t}\right]^2$$

- Fracture toughness is a parameter for crack propagation.
- However, we want to assess POF of a graphite component without any cracks!
- Fracture toughness maybe not a best parameter for POF assessment.
- Also, the POF assessment method needs verification by experiment.

Seismic analysis

- The graphite components occupy about ~85% volume of the MSR reactor core and the rest is molten salt.
- It is important to assess the dynamical behaviour of a reactor core under seismic loading.
- Molten salt can provide some damping effect and hence protect graphite components from damage during earthquake.
- We need to develop a method which can model the interaction between graphite components and molten salt without to much computational power.



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Thank you for your attention

The opinions expressed in this talk are those of the author and not necessarily of those of SINAP.