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Graphite Sessions 1-3

April 2021

Changing the World's Energy Future

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Idaho National Laboratory

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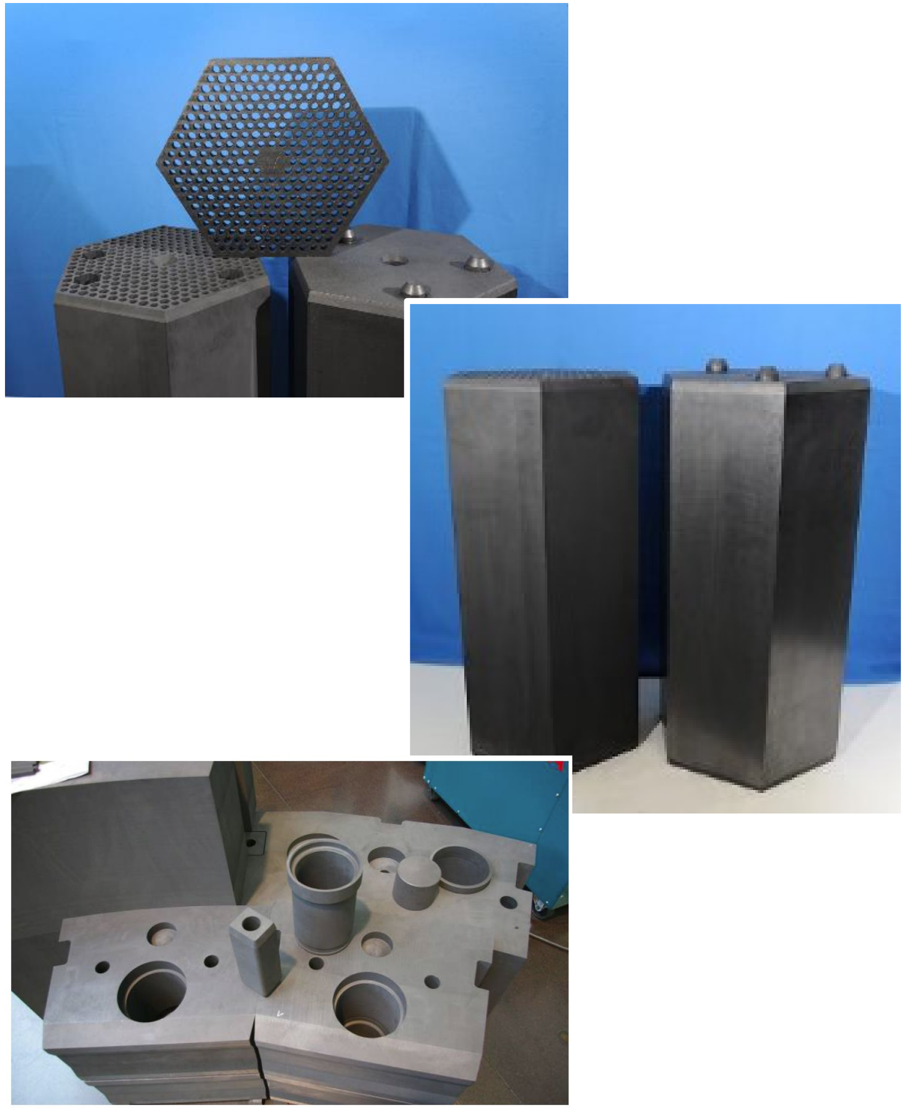
Graphite Session 1

Introduction

Idaho National Laboratory

Topics of discussion

- International Research & Development Programs
  - Who is doing what in graphite throughout the world
- Nuclear graphite components
  - Why is graphite so difficult to develop code rules?
    - *Unique features of nuclear grade graphite*
    - *No nuclear graphite standard*
    - *Brittle material in a pressure vessel code?*
- General graphite behavior and degradation
  - As-fabricated material properties
  - Irradiation behavior
  - Oxidation behavior
  - Molten salt issues



Introduction designed to familiarize you with some of the unique concepts/facts that must be considered for licensing nuclear graphite components

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International Research & Development Programs

Irradiation tests

- USA DOE (Irr & creep)
- E.U. JRC (Irr)
- U.K. EDF (Irr & creep)
- KAERI (small Irr)
- JAEA (small Irr)
- China Tsinghau (??)
- Graphite suppliers

Qualifying new graphite grades

- USA DOE
- China Tsinghau/SINAP
- Graphite suppliers

Oxidation

- JAEA (SiC)
- KAERI (B_4C)
- USA
- U.K. EDF
- Canada

Fracture

- U.K.
- China Tsinghau/SINAP
- Australia ANSTO
- USA

Molten salt

- China SINAP
- USA DOE
- Australia ANSTO

Core Component

- China Tsinghau
- U.K.

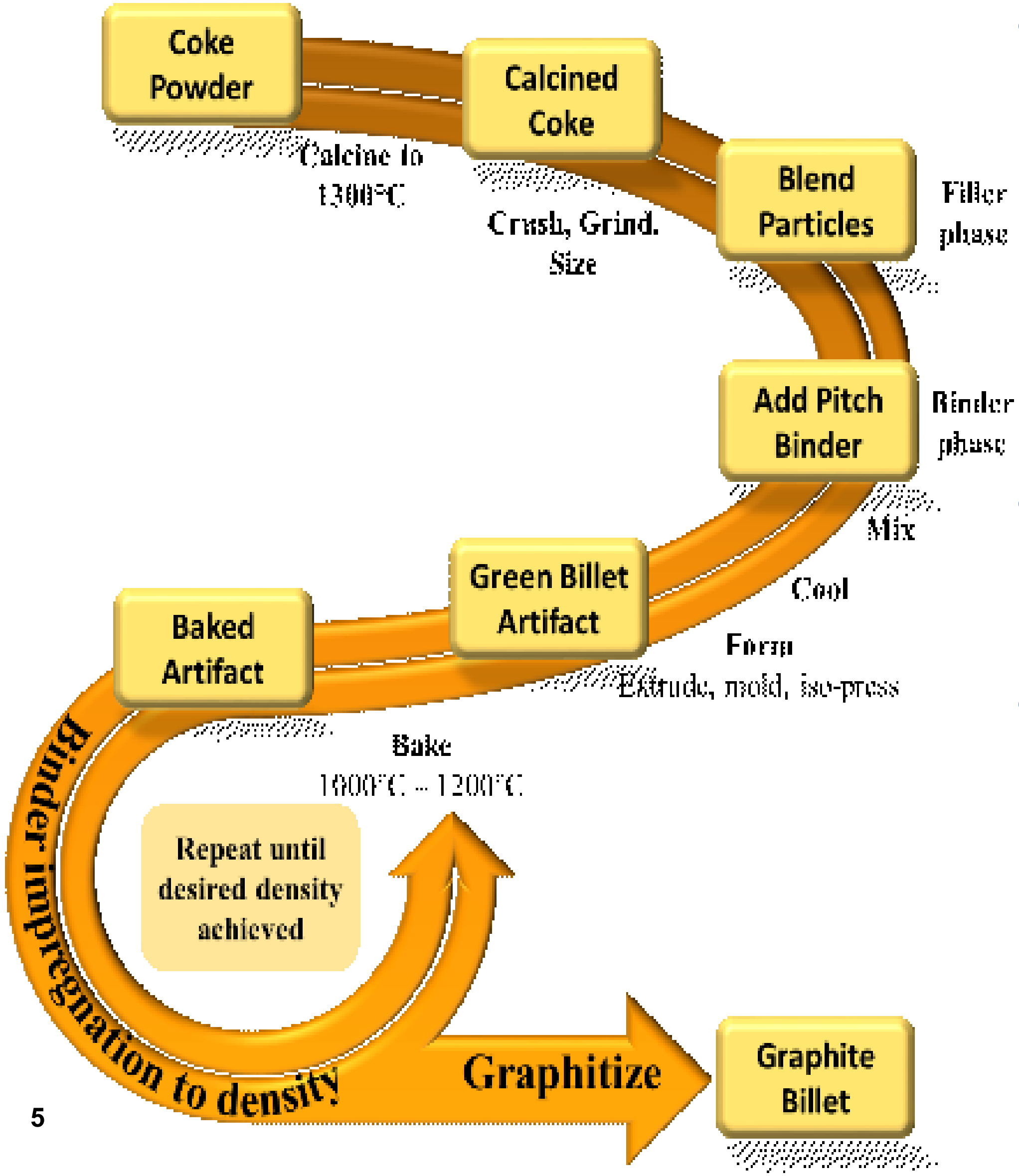
Test Standards

- USA DOE/Universities
- U.K. NNL
- KAERI
- JAEA
- China SINAP
- Australia ANSTO

Code Rules

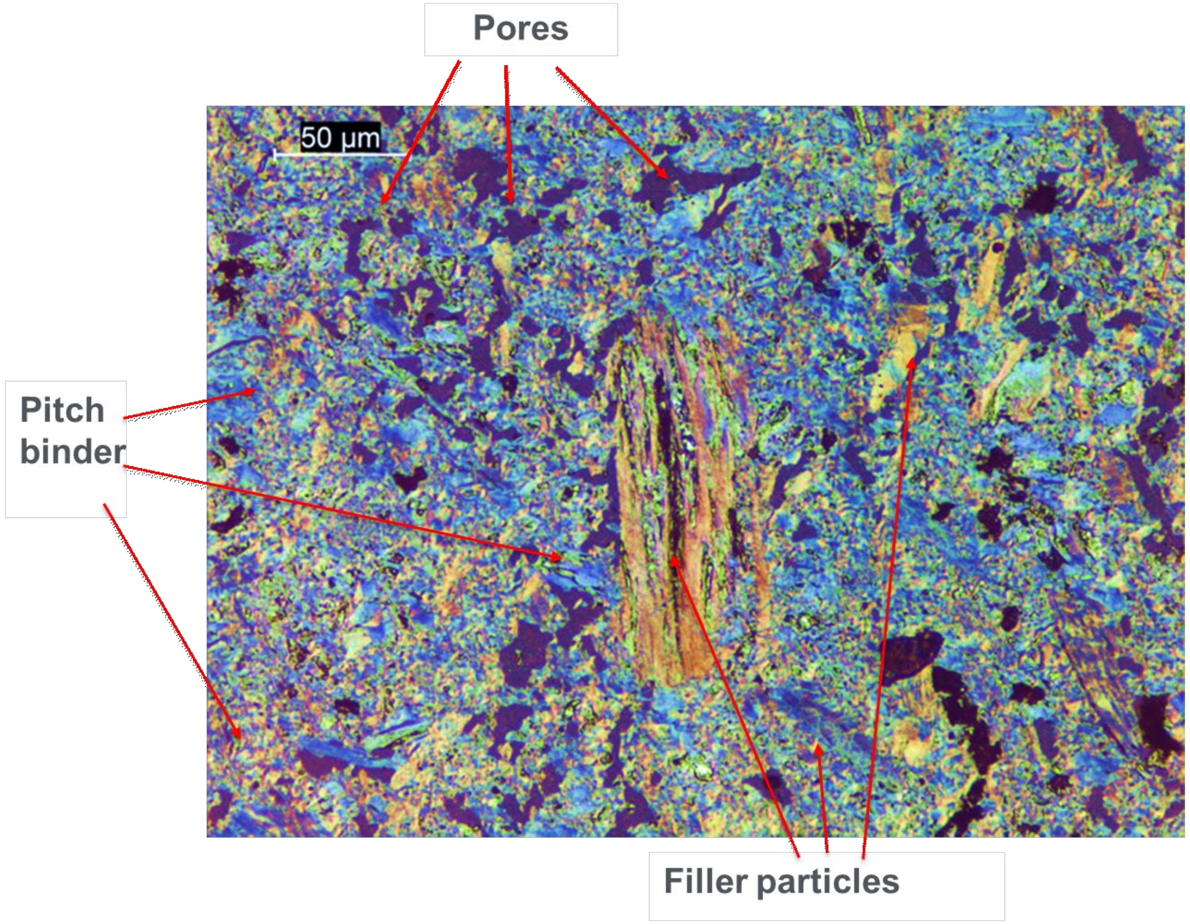
- USA DOE/Universities
- China SINAP
- U.K. NNL
- HTR designers/vendors

Graphite Manufacture and some unique properties



- To understand graphite behavior need to know the unique manufacturing process
  - Filler particles: petroleum coke/pitch coke
  - Binder phase: pitch-based liquid binder
    - *Impregnation process and density achieved*
  - Filler-binder ratio: range of particle sizes
  - Fabrication methods: extruded, vibrationally molded, isostatically molded
- Graphite is manufactured from calcined coke and a pitch binder.
  - Multiple pitch impregnations to increase density
- Graphite is anisotropic naturally.
  - How do we make isotropic material?
    - Grind filler particles to desired size
    - Mix randomly in liquid binder
    - Baked green billet is heterogenous mix of filler particles bound by carbonaceous binder phase

Graphite Manufacture and some unique properties



- Three phases in graphite microstructure
  - Filler particles, binder phase, and pores (~20%)
- Pores and pore structure define graphite behavior
  - Pore size range : nm to mm
  - Large flaws (cracks/pores) result from fabrication
    - *Filler particles bound together with carbonaceous binder*
    - *Interstitial gaps between filler provide pores and cracks*
  - **But** small (nm) pore structure gives irradiation stability also comes from
    - *Mrozowski cracks (accommodating porosity) within crystallites*
    - *Basal planes are separated during graphitization step during fabrication.*
- **Must have pores**
  - More accurate : must have accommodating porosity

Graphite Manufacture and some unique properties

Material Properties

- Near-isotropic material response
- High thermal stability > 3000°C
  - *Well above any accident temperatures*
- High heat capacity (thermal sink)
- High thermal conductivity (better than metal)
- Density: 15% - 20% porosity
- Purified graphite: Low activation (Medium waste)
- Chemically inert (Molten salt)
- Neutron moderator (thermal designs)
- Easy machinability / cheap material
- High compressive / Low tensile strength
  - *Ceramic composites for tensile*
- Ceramic like material response
  - *Low fracture toughness (~ 1-2 MPa √m)*
  - *Quasi-brittle cracking*

Component Behavior

Decent irradiation response

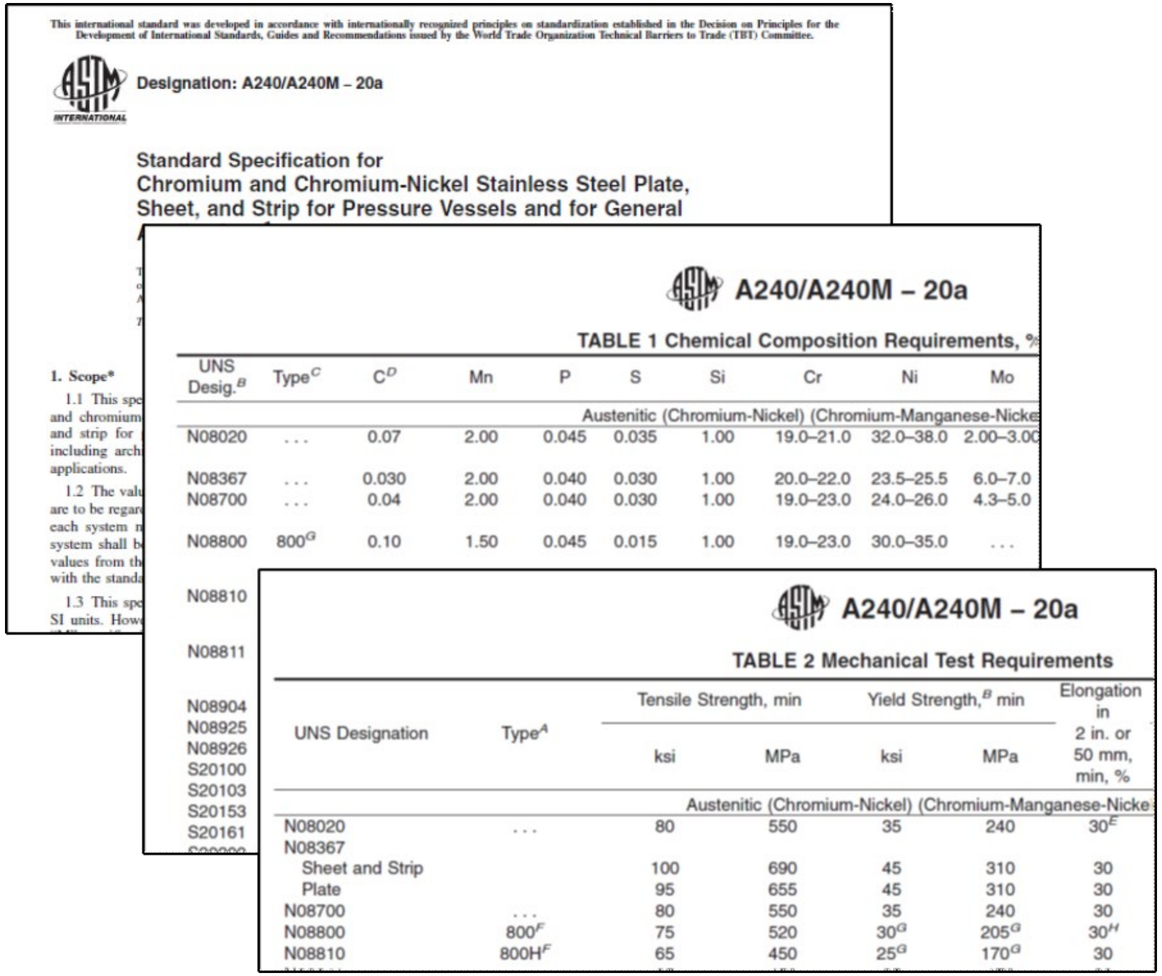
- Dimensional change (life-limiting mechanism)
  - *Multiple decades of safe operation*
  - *And* ***even longer*** *at lower temperatures*
- Generally gets stronger with irradiation
- Isotropy stays relatively constant
- Thermal stability and capacity are unaffected

Oxidation and molten salt intrusion

- Graphite does oxidize at all temperatures

  But it does not burn!
- Oxidation behavior depends on pore structure
- Molten salt can penetrate pore structure
  - Potential for erosion/abrasion

Licensing challenge: No graphite fabrication standards



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.

Designation: A240/A240M – 20a

Standard Specification for
Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels and for General

1. Scope*

1.1 This spe… and chromium… and strip for… including archi… applications.

1.2 The valu… are to be regard… each system m… system shall b… values from th… with the standa…

1.3 This spe… SI units. Howe…

A240/A240M – 20a

TABLE 1 Chemical Composition Requirements, %

UNS Desig.[B]	Type[C]	C[D]	Mn	P	S	Si	Cr	Ni	Mo
Austenitic (Chromium-Nickel) (Chromium-Manganese-Nicke…									
N08020	. . .	0.07	2.00	0.045	0.035	1.00	19.0–21.0	32.0–38.0	2.00–3.0…
N08367	. . .	0.030	2.00	0.040	0.030	1.00	20.0–22.0	23.5–25.5	6.0–7.0
N08700	. . .	0.04	2.00	0.040	0.030	1.00	19.0–23.0	24.0–26.0	4.3–5.0
N08800	800[G]	0.10	1.50	0.045	0.015	1.00	19.0–23.0	30.0–35.0	. . .
N08810									
N08811									
N08904									
N08925									
N08926									
S20100									
S20103									
S20153									
S20161									

A240/A240M – 20a

TABLE 2 Mechanical Test Requirements

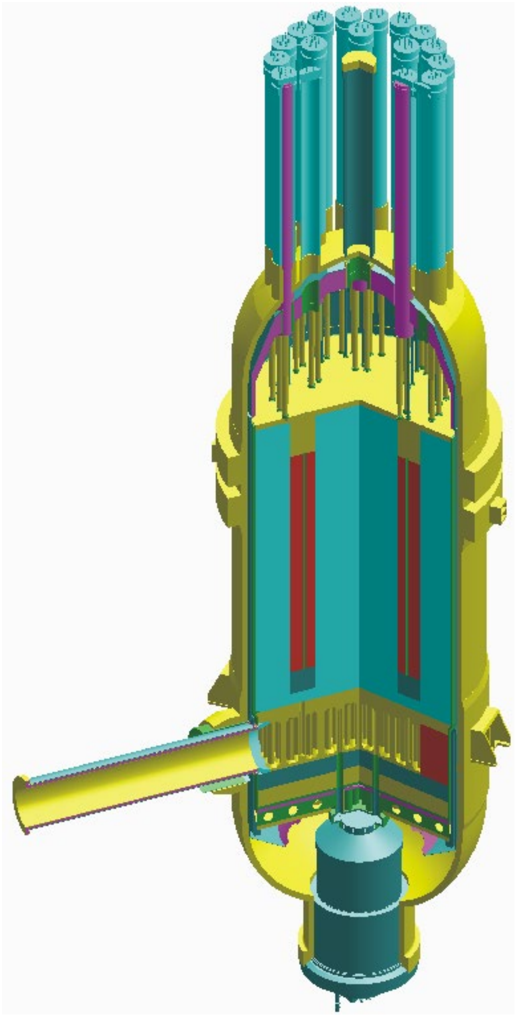
UNS Designation	Type[A]	Tensile Strength, min		Yield Strength,[B] min		Elongation in 2 in. or 50 mm, min, %
		ksi	MPa	ksi	MPa	
Austenitic (Chromium-Nickel) (Chromium-Manganese-Nicke…						
N08020	. . .	80	550	35	240	30[E]
N08367						
Sheet and Strip		100	690	45	310	30
Plate		95	655	45	310	30
N08700	. . .	80	550	35	240	30
N08800	800[F]	75	520	30[G]	205[G]	30[H]
N08810	800H[F]	65	450	25[G]	170[G]	30

- No “Standard” nuclear graphite
  - Nothing like metals have
  - ASTM D7219 provides minimum property values (not fabrication specifications)
- All graphite grades **are proprietary**. Only limited/general fabrication data is known.
  - Each grade has closely guarded, proprietary formulae owned by graphite suppliers
  - And no, graphite suppliers are not willing to give up their private recipes to the nuclear community
    - *Remember: no nuclear graphite has been ordered in decades*
- But the good news is that all grades react similarly under nuclear core conditions
  - Specific changes are dependent upon individual grade

Licensing challenge: So what do you do about lack of standards?

- You **qualify each grade** of graphite for nuclear applications
  - Designers must provide a baseline of room temperature unirradiated material properties values
    - Strength, elastic modulus, density, etc.
    - Multiple samples from 3+ billets, from 4+ different batches
  - Then you must account for material property changes
    - … across the operating temperature range
    - … for anticipated dose range
    - ... for all oxidation mass losses
    - … for molten salt interactions
    - … and combination of effects

100’s of samples



  - Then designers have to convince nuclear regulators the grade can be safely used as a core material
    - Financial risks are obvious
    - Which is why there are no “standard” graphite grades (yet)

Nuclear Components: It's actually not too difficult to prove it's safe

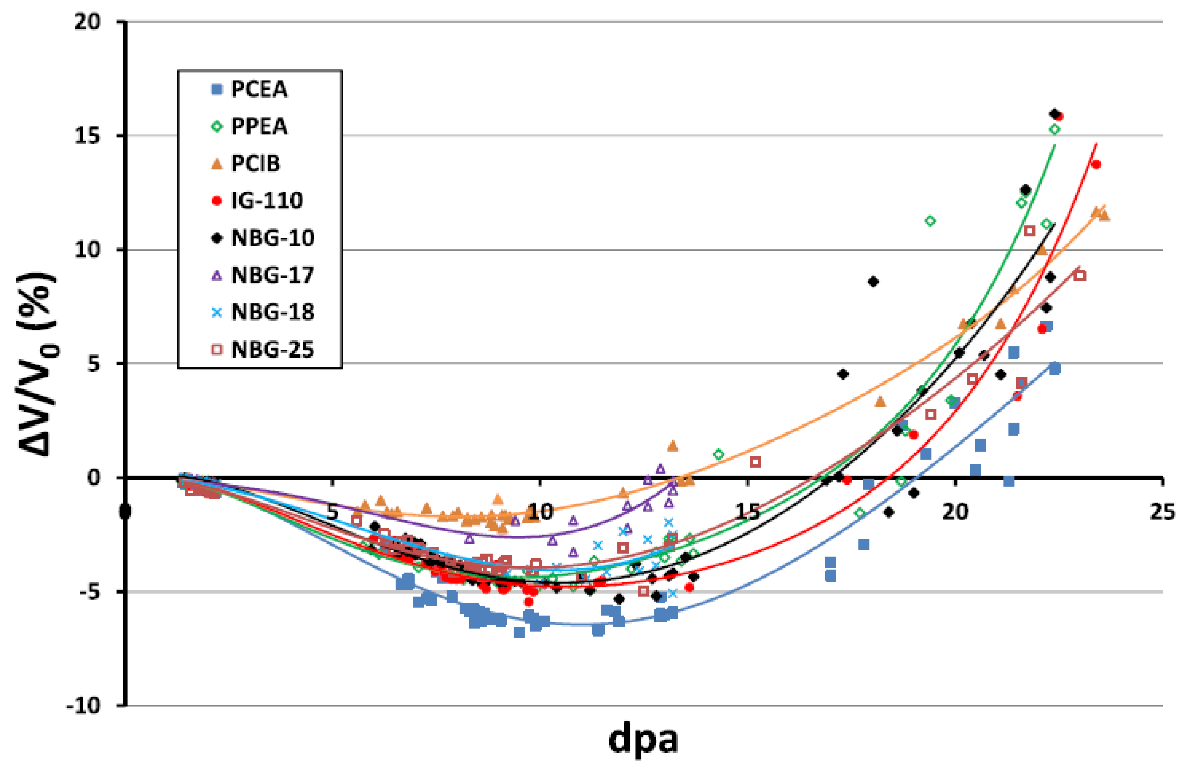


Fig. 2. Dimensional change as function of dpa at 750 °C.

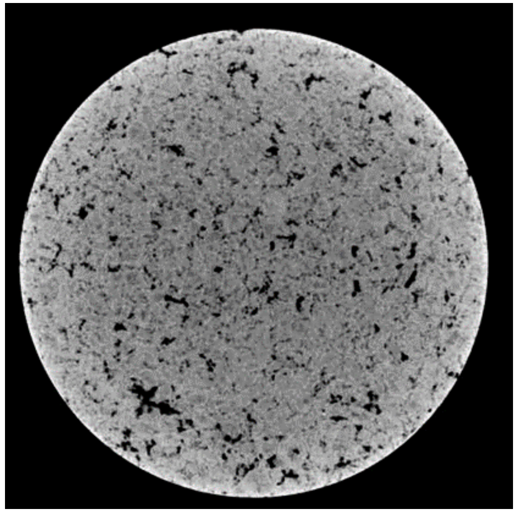
Things to keep in mind

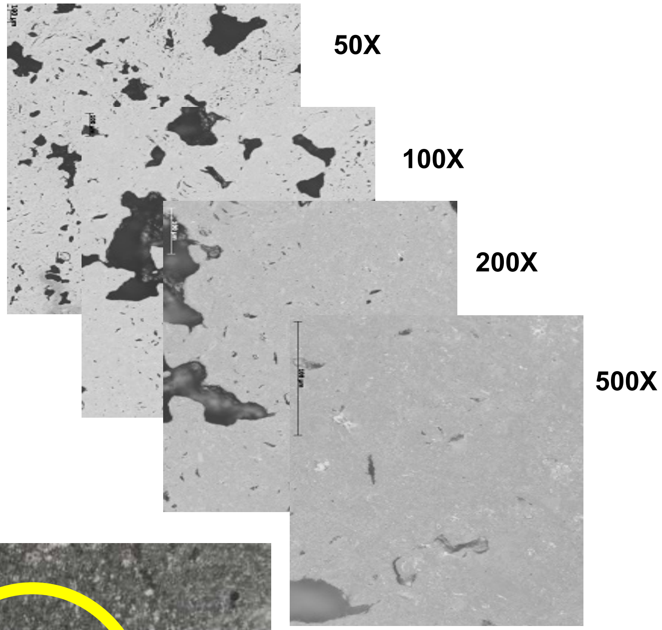
- All grades behavior similarly
  - Similar irradiation trend
  - Similar oxidation trend
  - Similar effects from temperature
- Specific amount of change is unique
  - The amount of change from degradation must be determined for selected grade
  - Temperature, oxidation, and molten salt effects must be considered as applicable
- National institutions have been working for decades gathering needed data
  - Many current grades have significant irradiation and oxidation data
  - Historical data is available and applicable
    - *IAEA Graphite Knowledgebase*

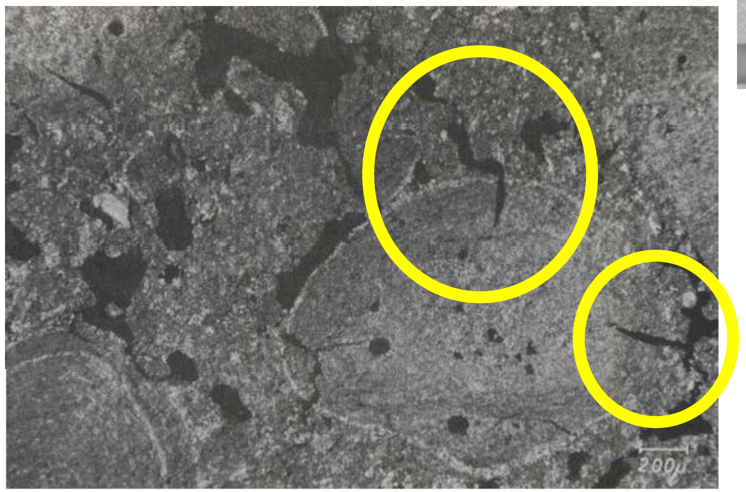
Nuclear Components: It’s actually not too difficult to prove it’s safe

More things to keep in mind

- Components already have cracks in them
  - Cracks and pores are desired
    - *Thermal & irradiation stability*
    - *Crack arresting*
- Now cracks are bad
  - *Material strength reduced (higher POF)*
  - *Air and molten salt can penetrate*
- *But nuclear core components **don’t need to hold pressure***
  - A single crack does not mean failure
    - *Cracks will not cause catastrophic failure*
    - *Retain structural integrity for fuel & control rods*
  - Graphite is thermally and chemically stable
    - *Oxidation can be managed*







Questions?

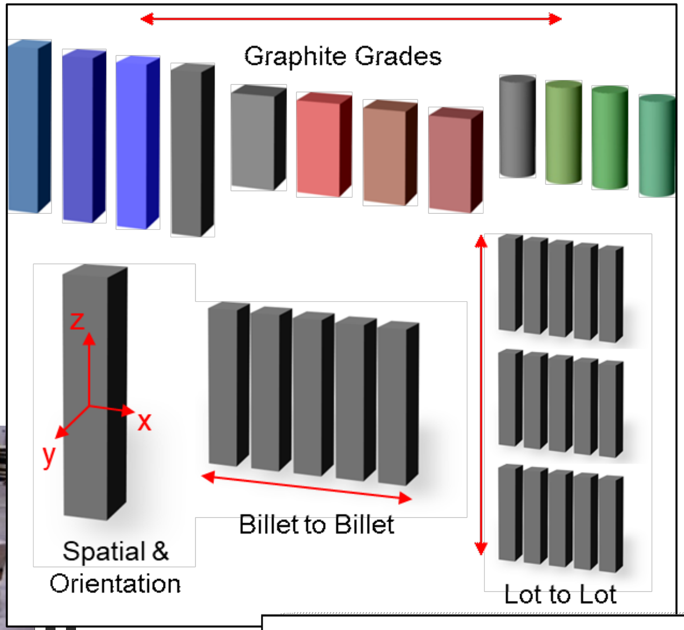
Before I move onto degradation behavior

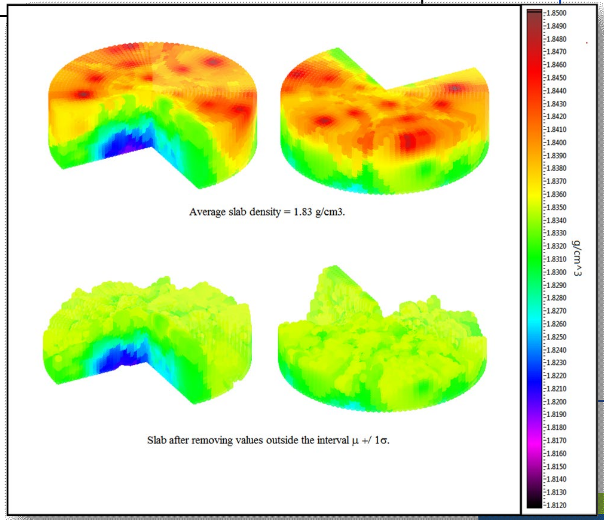
Qualifying graphite: As-fabricated properties

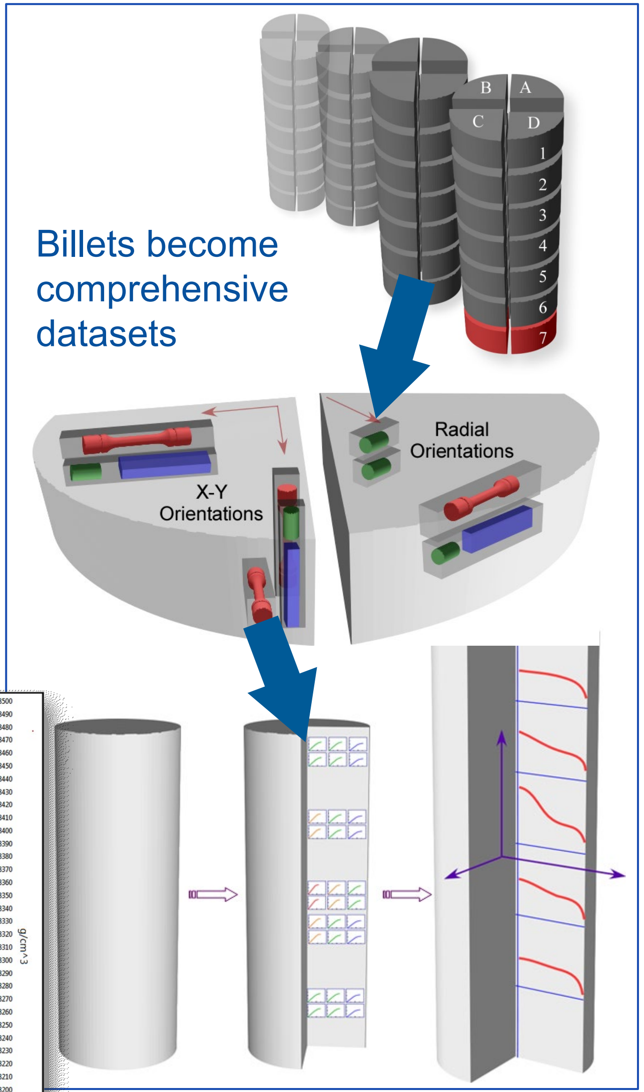
From ASTM D7219 : *Standard Specification for Isotropic and Near-isotropic Graphites*

Property	Nominal Range	Performance Attributes
Density	1.7 - 1.9 g/cm^3	Neutron efficiency, Structural integrity, Thermal efficiency
Thermal Conductivity (at Room Temperature)	> 90 W/m/K	Heat transport
Purity (Total Ash Content)	< 300 ppm	Reduced component activity levels during replacement and/or disposal Reduced graphite oxidation under normal and accident conditions.
Tensile Strength	> 15 MPa	Structural integrity
Compressive Strength	> 45 MPa	Structural integrity
Flexural Strength	> 20 MPa	Structural integrity
CTE (20°C to 500°C)	3.5 to 5.5 x 10^{-6} K^{-1}	High value is indication of isotropy = dimensional stability under irradiation Lower value potentially beneficial in terms of thermal stress
CTE Isotropy Ratio	< 1.10	Irradiation dimensional stability Structural integrity
Dynamic Elastic Modulus	8 – 15 GPa	Structural integrity Irradiation creep
Dimensional Changes with Irradiation	Minimal shrinkage Minimal differences in with-grain and against-grain directions	Structural integrity (lower internal stresses)

Qualifying graphite: Sampling

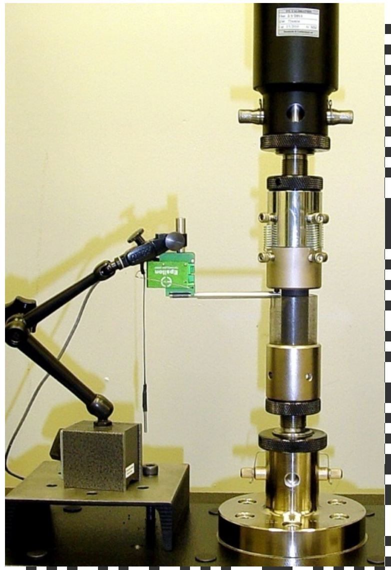






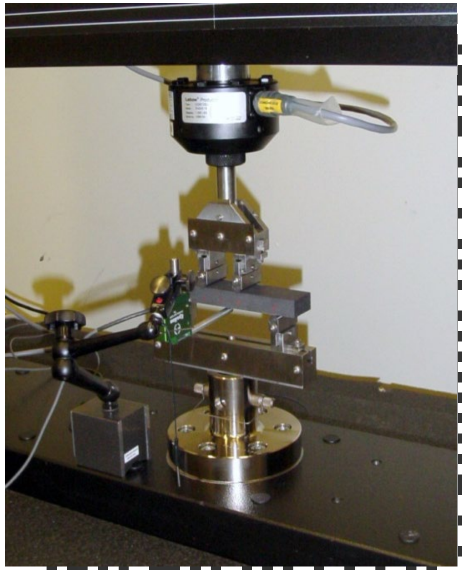
Qualifying graphite: Material Property Testing

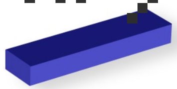
Compression Testing



ASTM C695-91

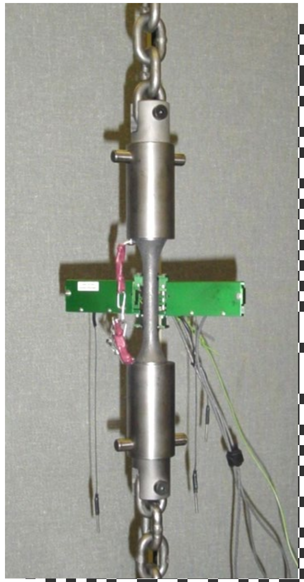
Flexural Testing





ASTM C651-11

Tensile Testing

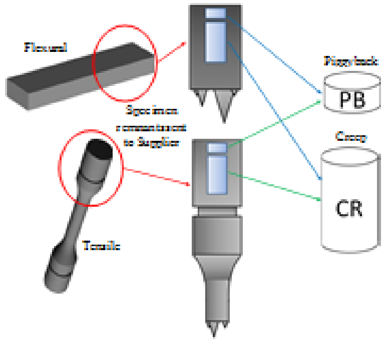


ASTM C749-08

Other Strength Techniques

Brazilian Disc

Sub-Sized 3-point Flexure

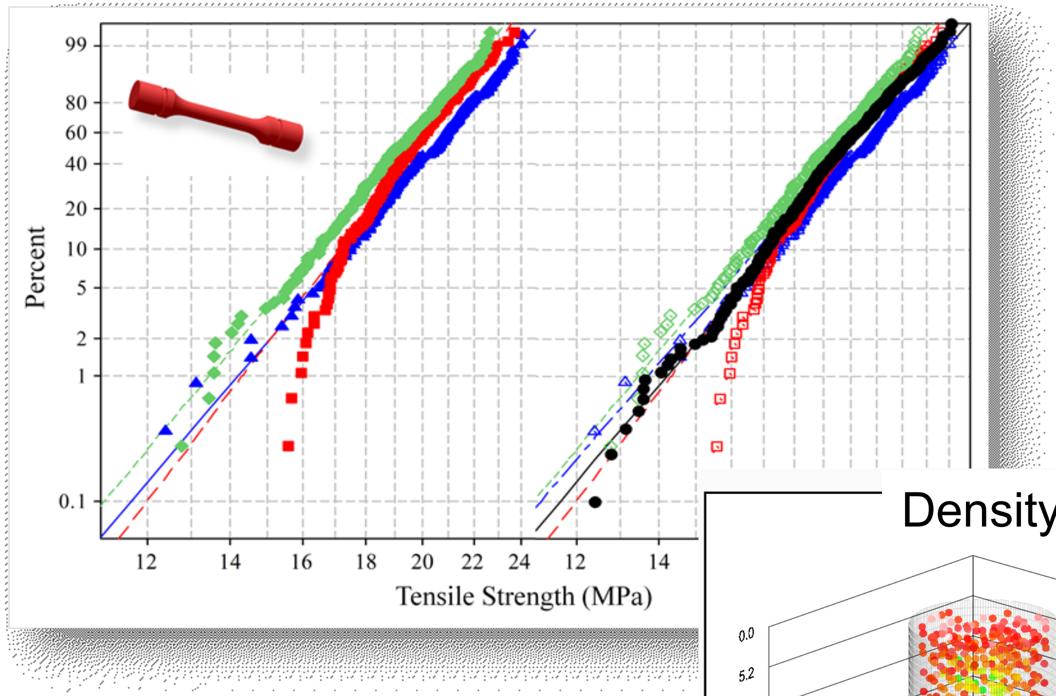


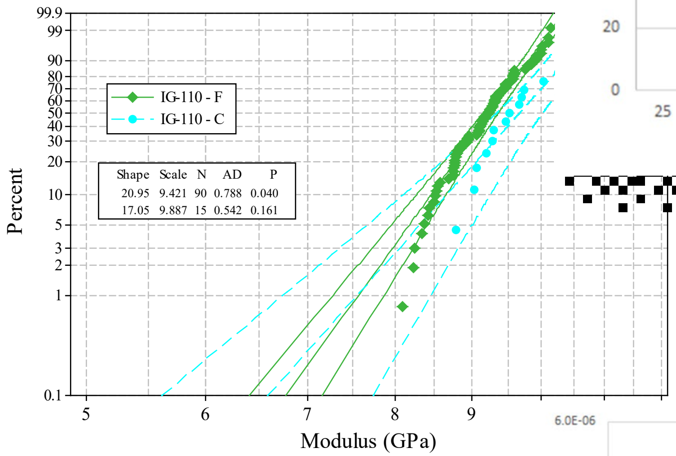
Physical & Thermal Properties Testing

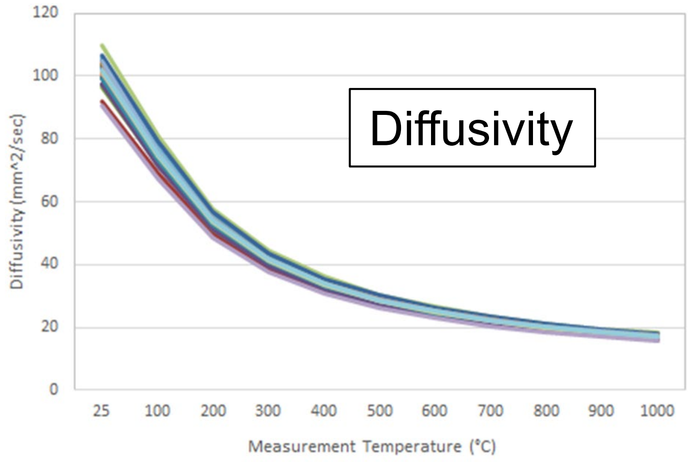
- *Density*
- *Coefficient of Thermal Expansion*
- *Thermal Conductivity*
- *Resistivity*
- *Resonant Frequency (E_{DYN})*
- *Torsional Frequency (G_{DYN})*
- *Sonic Velocity*
- *Fracture Character**

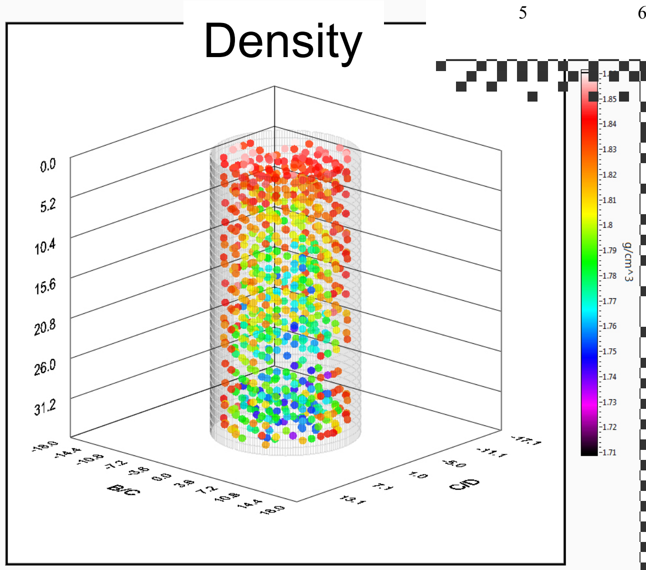
**Not a non-destructive evaluation*

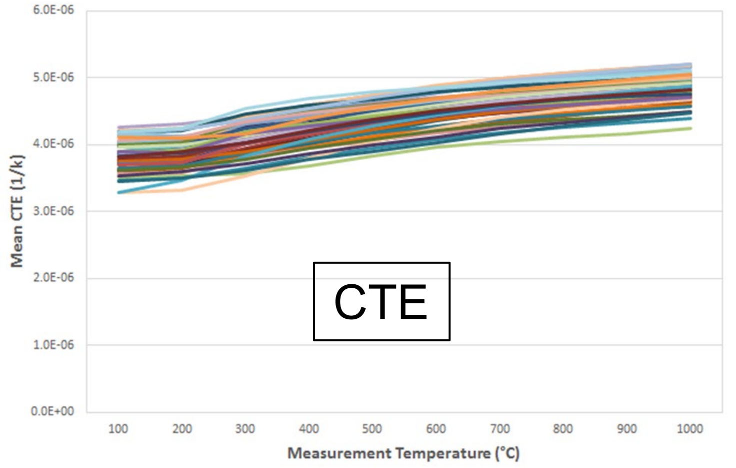
Qualifying graphite: Unirradiated Data











Qualifying graphite: Unirradiated Data Requirements

Graphite	Laboratory	Billet #	Percent Complete					Data Report	Analysis Reports
			Machining	Mass and Density	Elastic Testing	Mechanical Testing	Thermal Testing		
PCEA	ORNL	XPC01S8-11	**100%**	**100%**	**100%**	**100%**	**100%**	ORNL	ORNL
PCEA	INL	XPC02S8-7	**100%**	**100%**	**100%**	**100%**	**100%**	ECAR-3725	INL/EXT-13-30011
PCEA	INL	XPC01S8-9	**100%**	**100%**	**100%**	**100%**	70%		INL/EXT-14-33120, INL/EXT-13-30011
PCEA	INL	XPC02S8-5	**100%**	**100%**	**100%**	**100%**	60%		INL/EXT-14-33120, INL/EXT-13-30011
PCEA	INL	XPC01D3-35	Sectioned	0	0	0	0		
PCEA	INL	XPC01D3-36	**100%**	**100%**	**100%**	**100%**	**100%**	ECAR-3677	INL/EXT-16-39604
PCEA	Multiple Other Billets Available								

Statistically significant sample population
- Billets from first batch
- Billets from second batch
- Billets from third batch
- Billets from fourth batch

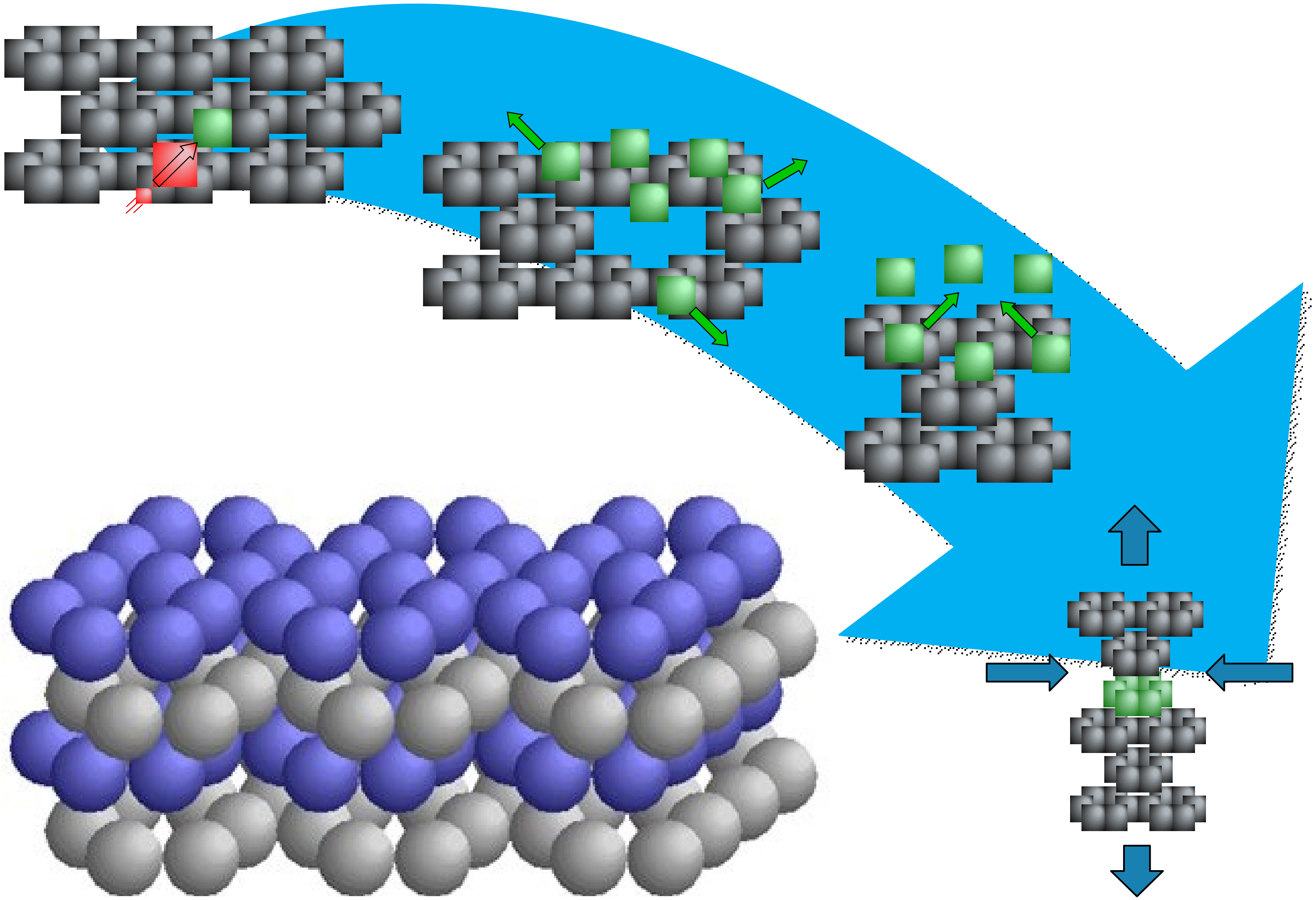
- "Volumetric" data required
  - Multiple samples from inside and near edge of billet **(intra-billet variations)**
  - Samples from multiple billets from same batch **(billet-to-billet variations)**
  - Three billets from four different batches **(batch-to-batch variations)**

Produces a "baseline" of material property values and the variability for entire grade

Graphite irradiation behavior ☢

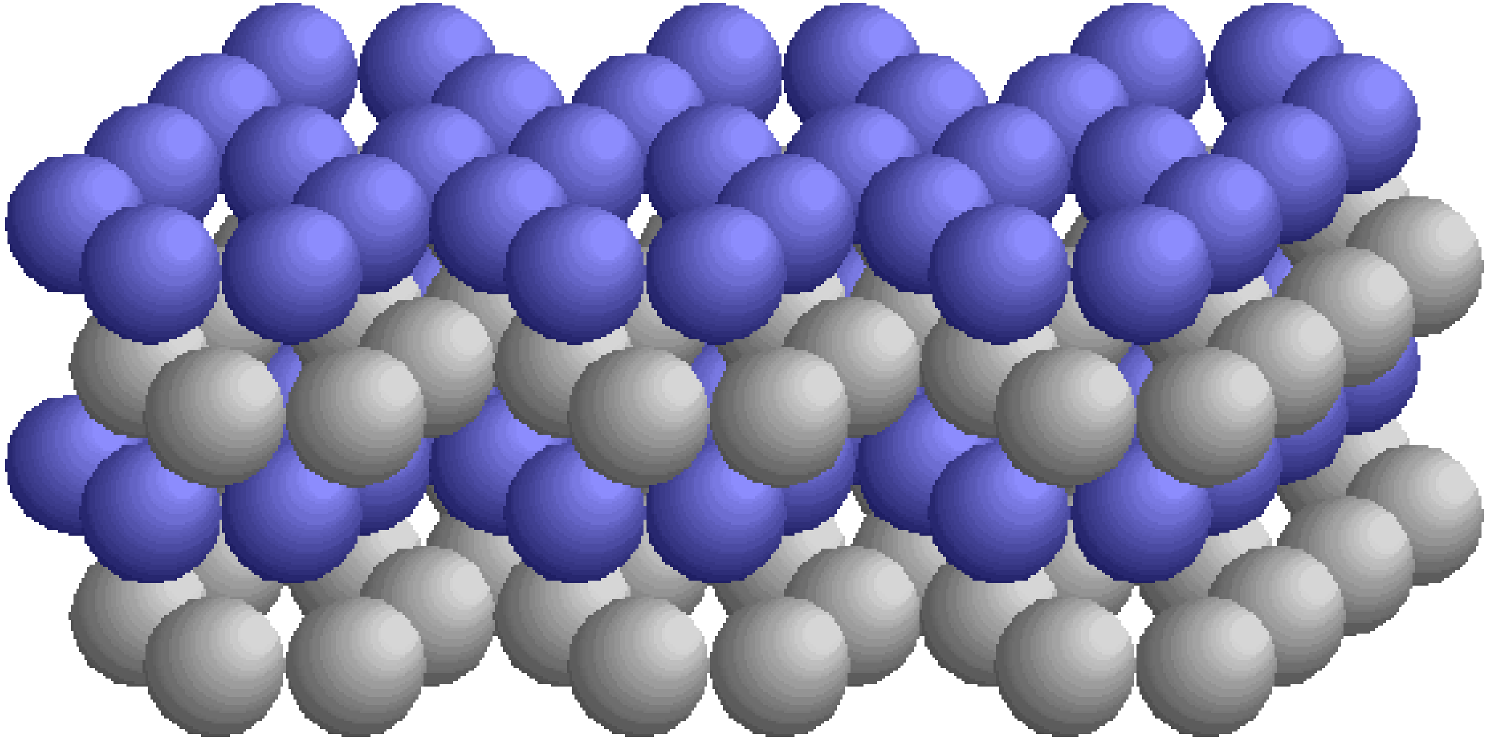
Key irradiation parameters

1. Irradiation dimensional change is life-limiting mechanism
   I. All designs **must determine** selected graphite turnaround dose
   II. Build-up of internal stresses ➔ cracks
2. Irradiation creep is good
   I. Creep relieves internal stresses
3. A basic understanding of graphite microstructure is needed
   I. To understand changes in irradiation behavior
   II. To assess whether design conclusions are accurate
4. Temperature is critical in nearly all irradiation induced property changes



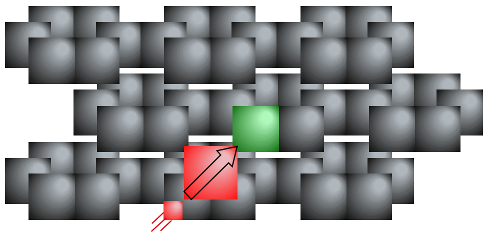
Mechanisms underlying irradiation damage

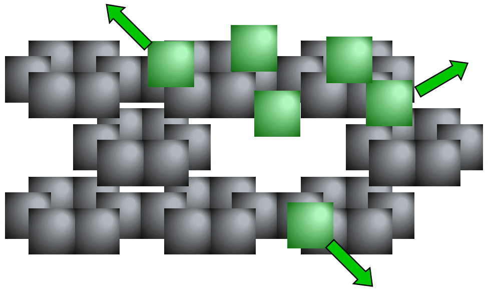
- Ballistic event physically displaces atoms for lattice position
- Sub-plane formation, vacancy clusters



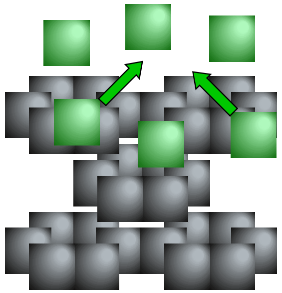
Model describing irradiation damage

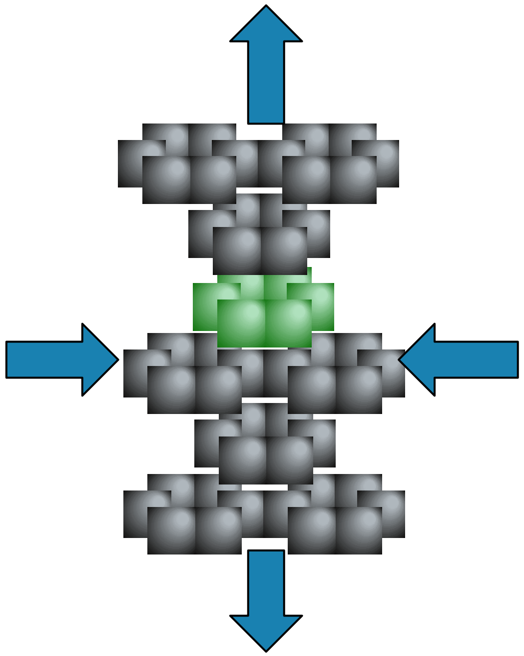
- Ballistic event physically displaces atoms for lattice position
- Sub-plane formation, vacancy clusters



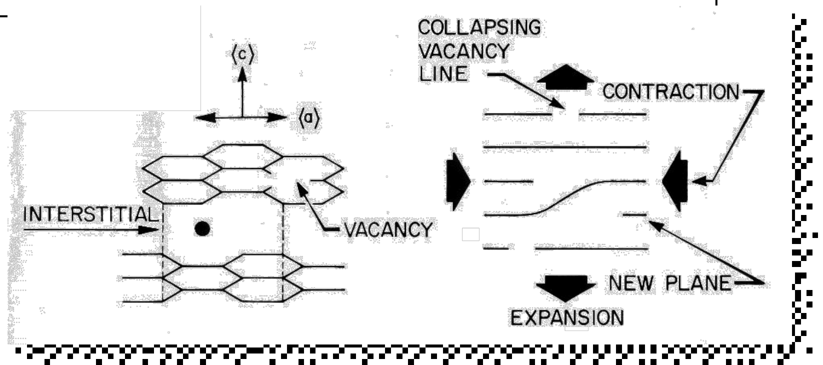


- Sub-plane formation between basal planes
- Vacancy cluster/loop collapse

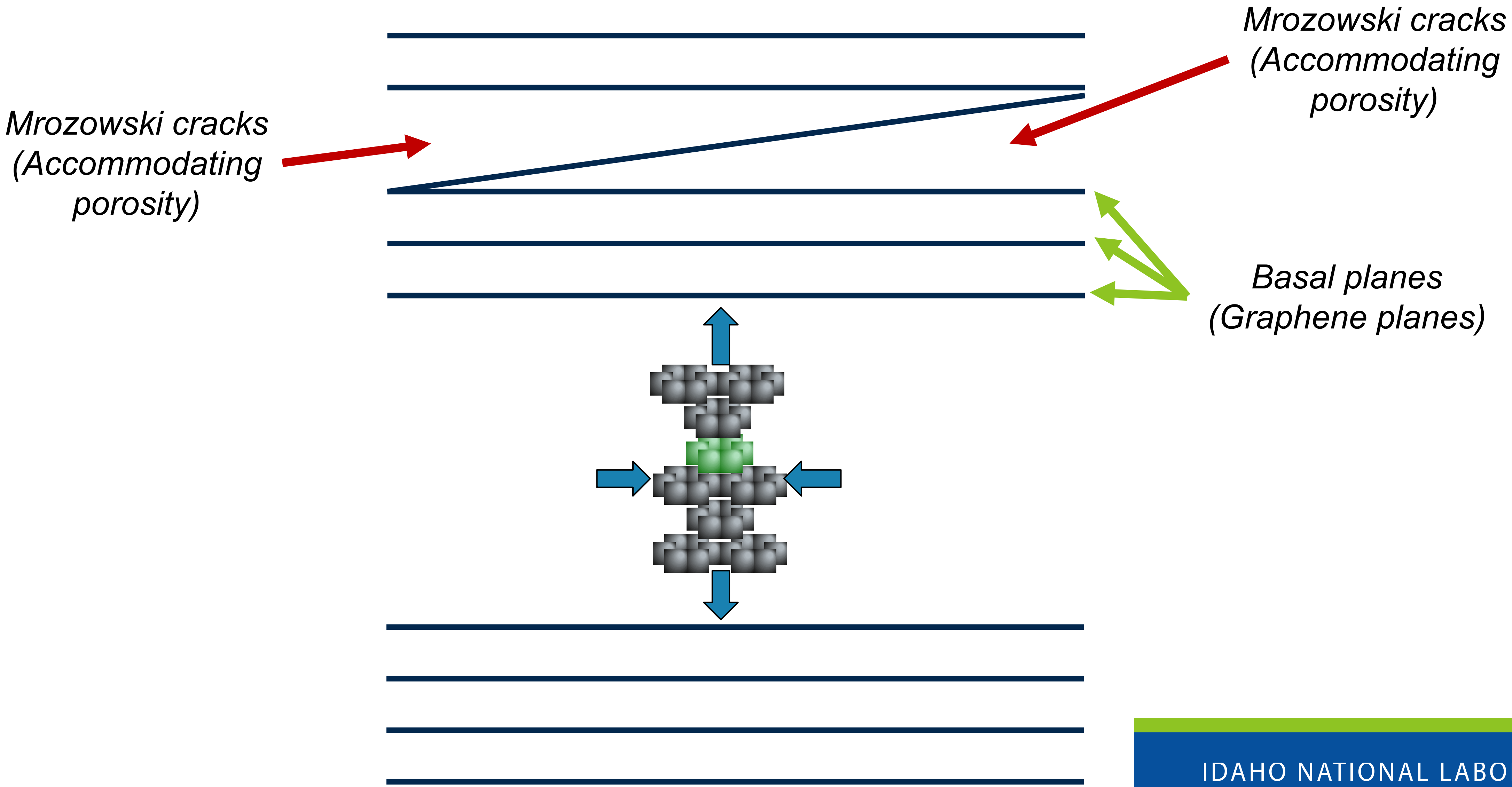




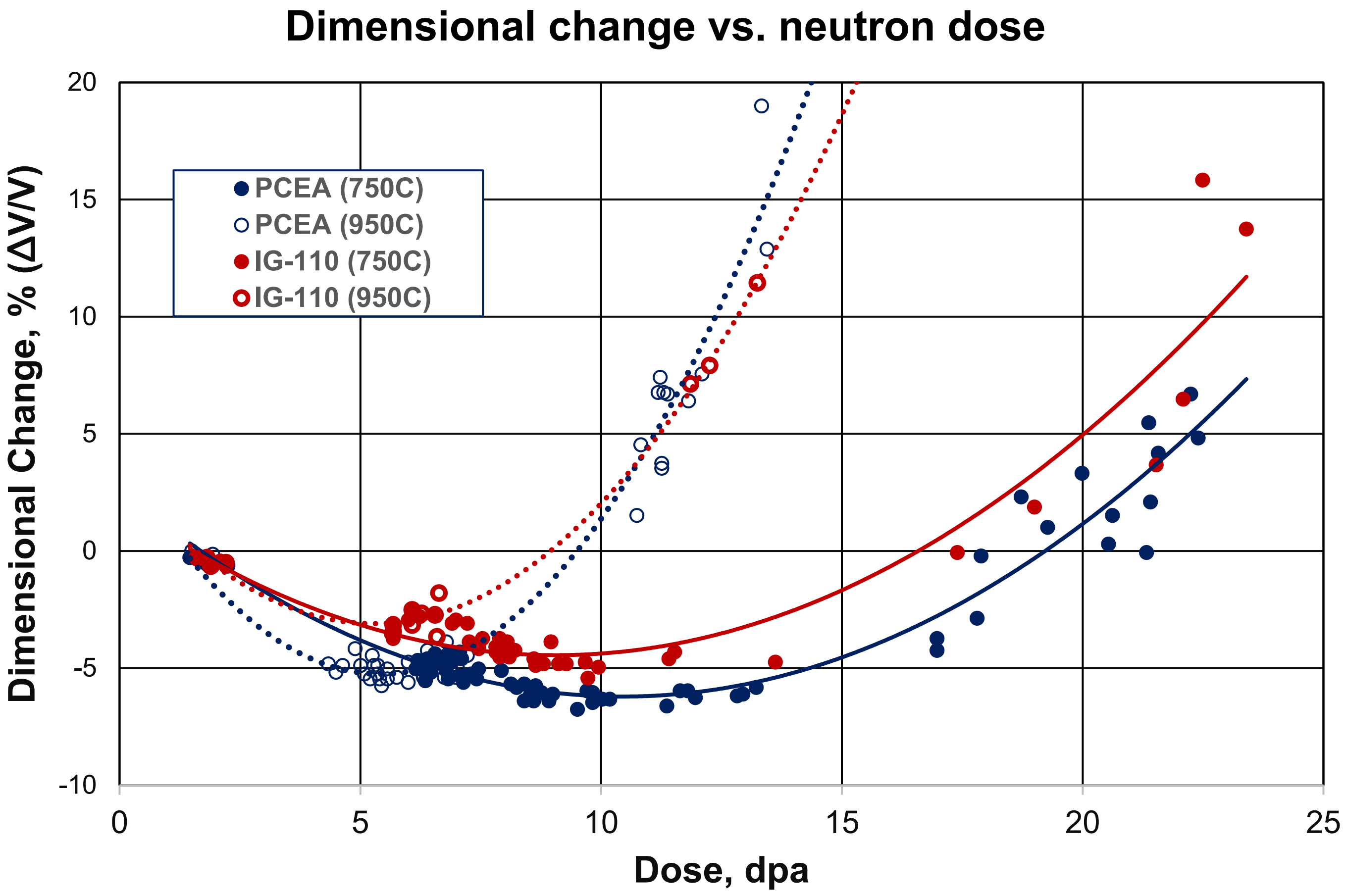
- **Crystallites shrink parallel to basal planes**
- **They grow perpendicular to planes**



Model describing irradiation damage



All vendors must establish turnaround dose for their graphite grade

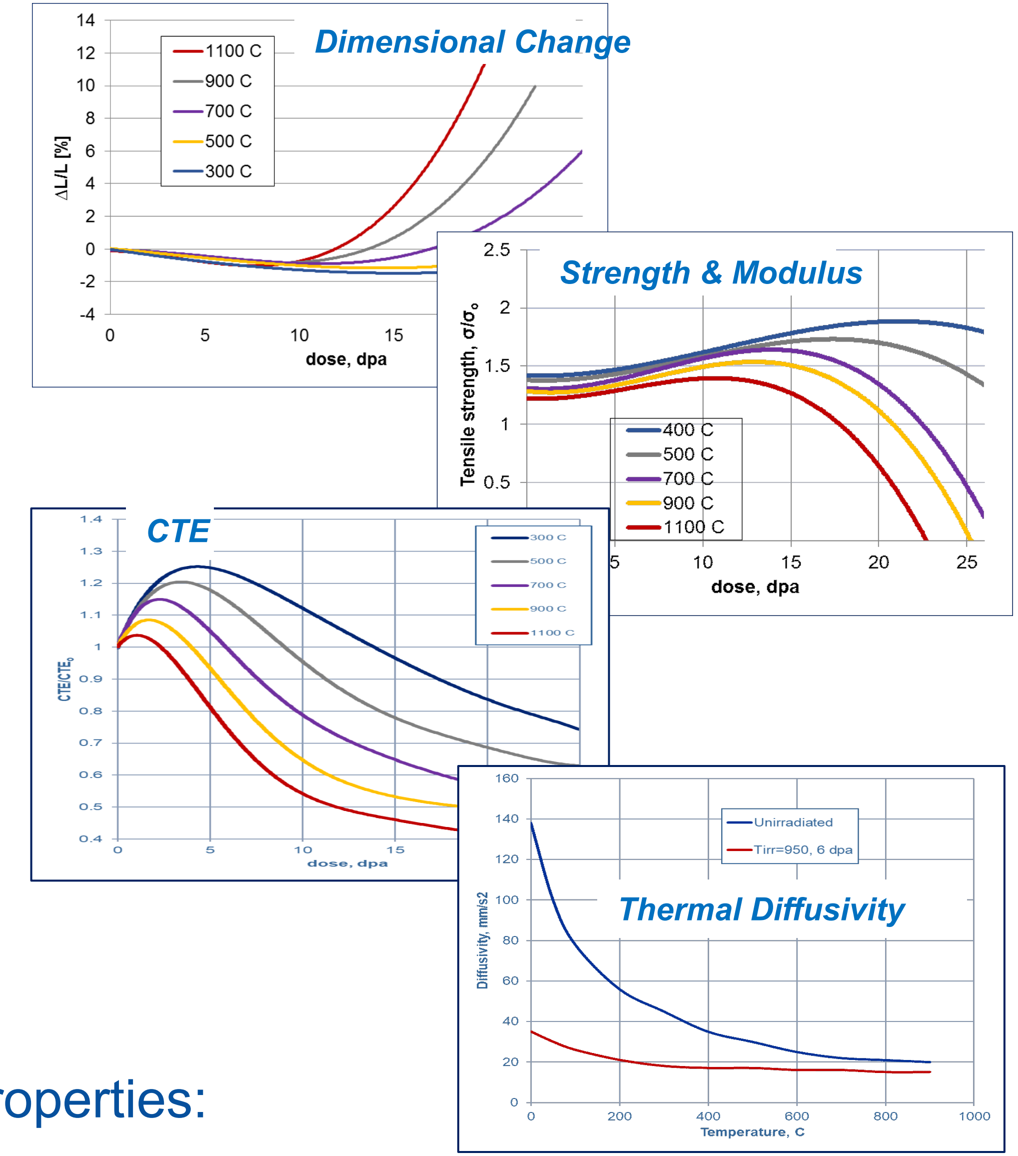


From: M.C.R. Heijna, S. de Groot, J.A. Vreeling, "Comparison of irradiation behaviour of HTR graphite grades", Journal of Nuclear Materials 492 (2017) 148e156

- Why do we care?
  - Point where irradiation induced material property changes begin to reverse.
  - Point where microstructural **densification** stops. Microcracking begins.
- Think of "before" and "after" turnaround
  - Behavior is much more predictable for all graphite grades ***before*** turnaround
    - *Much less predictable (more data scatter)* ***after*** *turnaround*
  - Crack propagation retarded in compressive stress fields.
  - Crack propagation accelerated in tensile
- Turnaround dose changes significantly with temperature
  - IG-110 (50μm) ➔ 10 dpa to 5 dpa
  - PCEA (1800μm) ➔ 11 dpa to 6 dpa

General graphite irradiation behavior

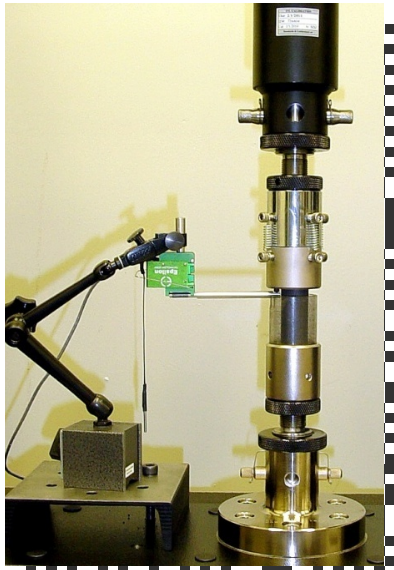
- Significant changes occur during normal operation:
  - Dimensional change
    - ***Turnaround** dose is key parameter*
    - *Highly temperature dependent*
  - Density
    - *Graphite gets denser with irradiation until **Turnaround** dose*
    - *After **Turnaround** density decreases (volumetric expansion)*
    - *Formation of microcracks (molten salt consideration)*
  - Strength and modulus
    - *Graphite gets stronger with irradiation …*
    - *Until **Turnaround** dose is achieved. It then decreases*
  - Coefficient of thermal expansion
    - *Initial increase but then reduces before **Turnaround***
    - *CTE is why properties are so temperature dependent*
  - Thermal conductivity
    - *Decreases almost immediately to ~30% of unirradiated values*
    - *At temperatures it is same as unirradiated conductivity*



- Significant changes **do not** typically occur in the following properties:
  - Neutron moderation, specific heat capacity, or emissivity

Irradiated Material Property Testing

Compression Testing

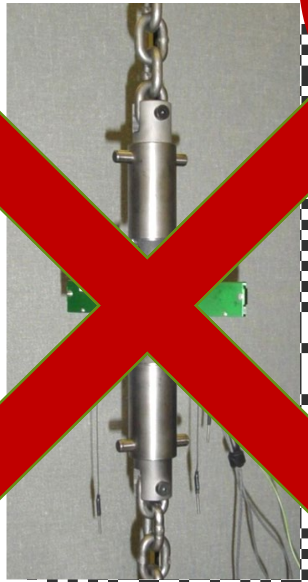


ASTM C695-91

Flexural Testing

ASTM C651-11

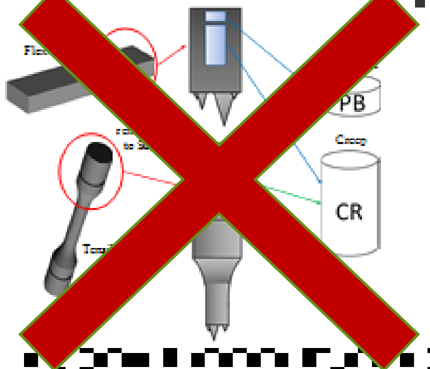
Tensile Testing



ASTM C749-08

Split-disk test

Sub-Sized 3-point Flexure



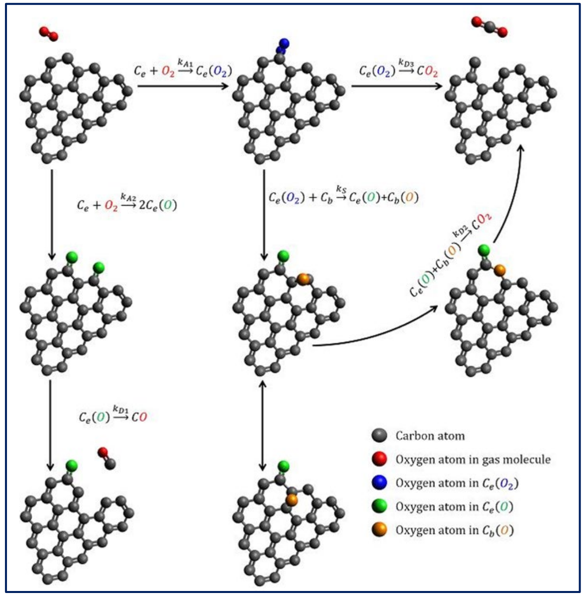
Physical & Thermal Properties Testing

- *Density*
- *Coefficient of Thermal Expansion*
- *Thermal Conductivity*
- *Resistivity*
- *Resonant Frequency (E_{DYN})*
- *Torsional Frequency (G_{DYN})*
- *Sonic Velocity*
- *Fracture Character**

**Not a non-destructive evaluation*

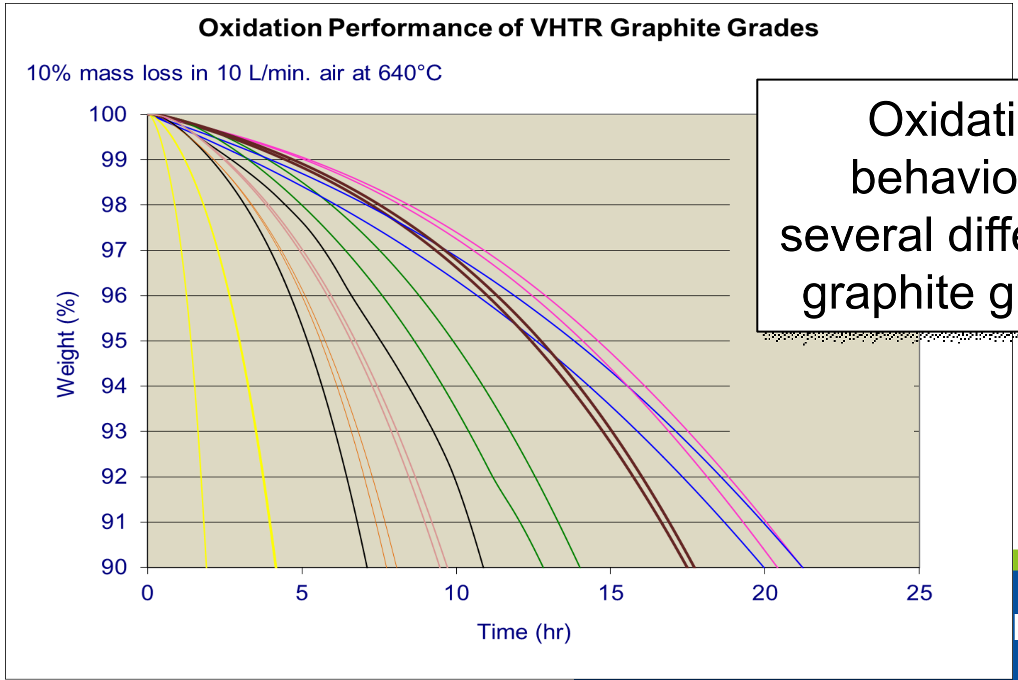
24

Graphite Oxidation



- Graphite **can** and **does** oxidize – rapidly at high temperatures
- Needs continuous oxygen and temperatures above ~ 200°C.
  - *Temperatures > 400°C is rapid acute oxidation (accidents)*
  - *Temperatures < 400°C slow chronic oxidation (normal op)*
- **How** oxidation occurs is more important than strict mass loss
  - *Low temperature kinetic-controlled oxidation*
  - *High temperature diffusion-controlled oxidation*

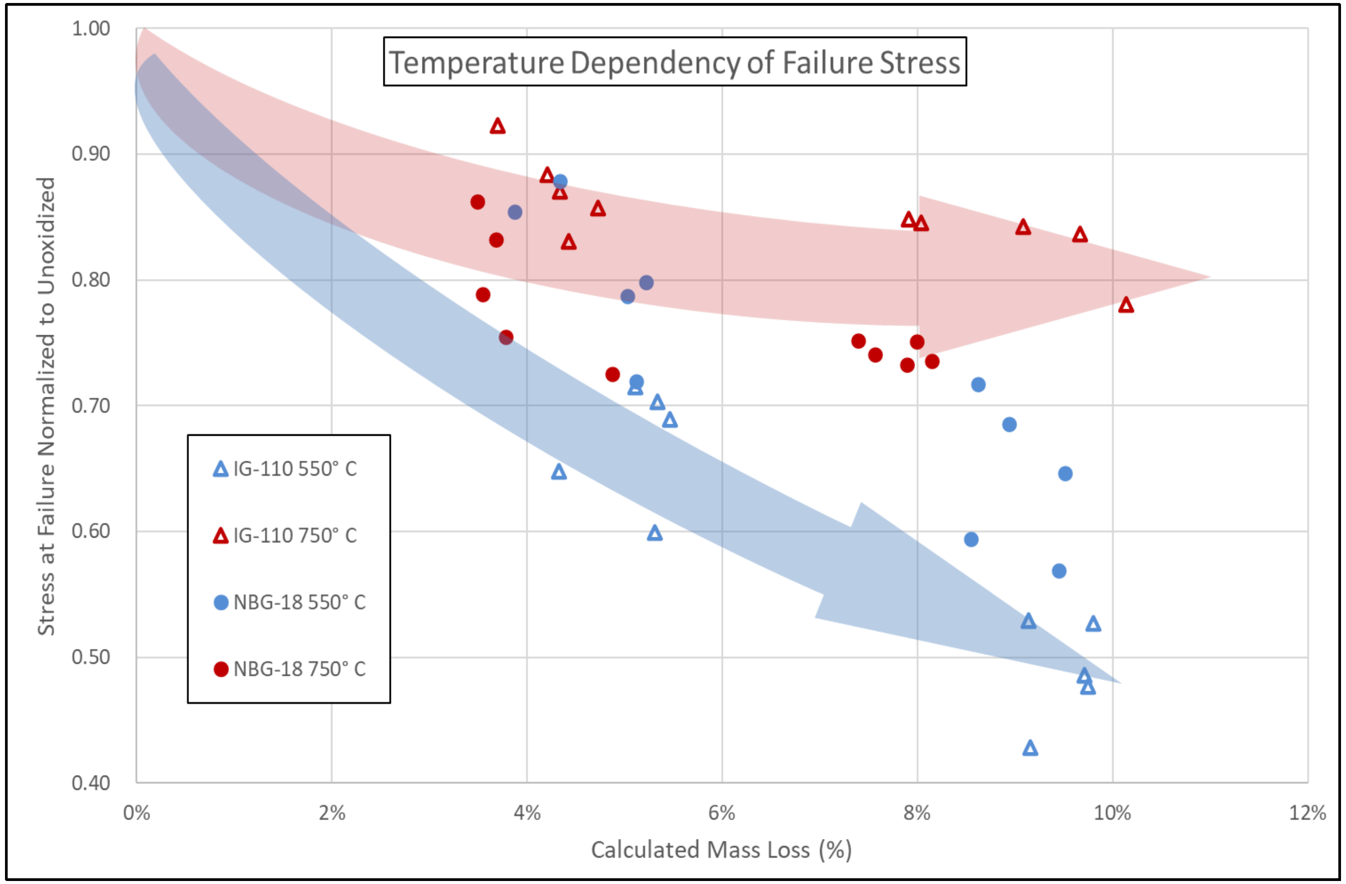
- Oxidation behavior of different grades can be compared using ASTM D7542 standard
  - Small grain grades >> than large grain size
  - Microstructure influences more kinetic- or diffusion-controlled oxidation behavior
- D7542 can (should) be used to determine when diffusion-controlled oxidation occurs in specific grade



Oxidation behavior of several difference graphite grades

Residual strength after oxidation

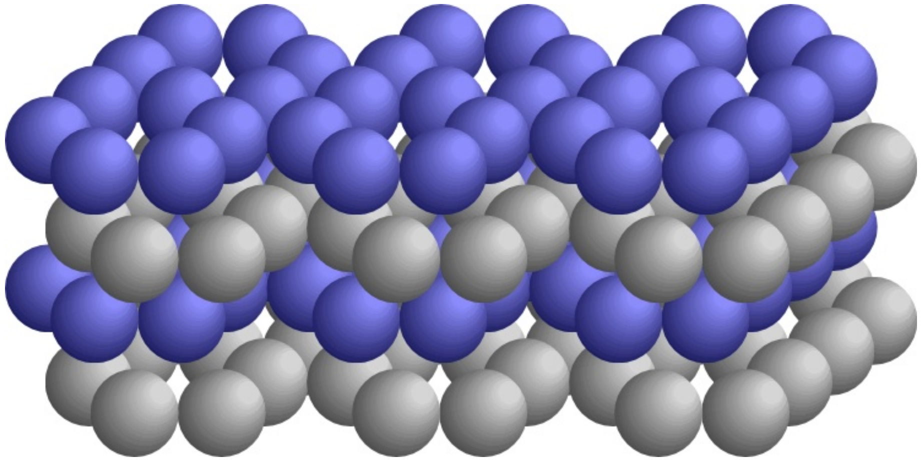
- What's important are the effects from oxidation:
  - Strength remaining after oxidation
- Depends upon **how** graphite oxidizes
  - Diffusion-controlled (HT) oxidation = less interior oxidation
  - Kinetic-controlled (LT) oxidation = more interior oxidation

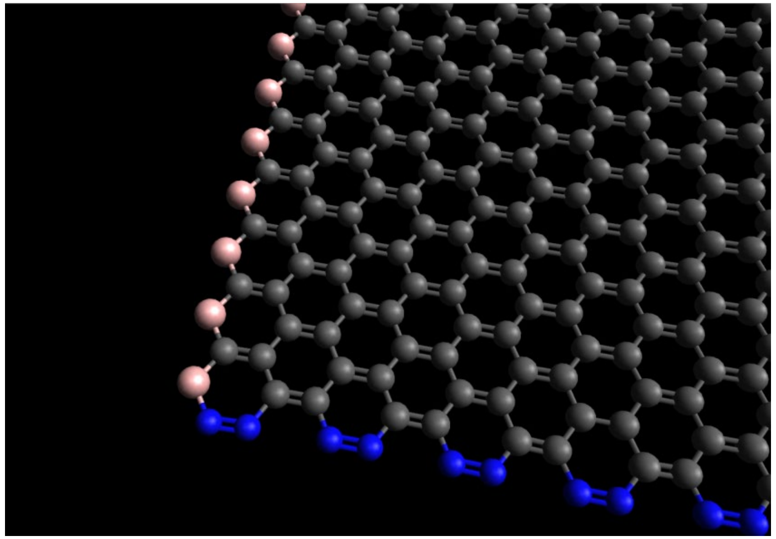


Need to understand how the graphite oxidizes before you can determine the effects

Graphite “Burning” and dust “Explosions”

- Graphite **can not** burn – just physically can not sustain self oxidation
  - Fire needs ➡ Heat, fuel, and oxygen
  - Self-sustained oxidation (better definition than simple burning) can not be sustained.
  - Fuel (carbon) is restricted to only the edges. Oxygen is restricted by the crystallography.





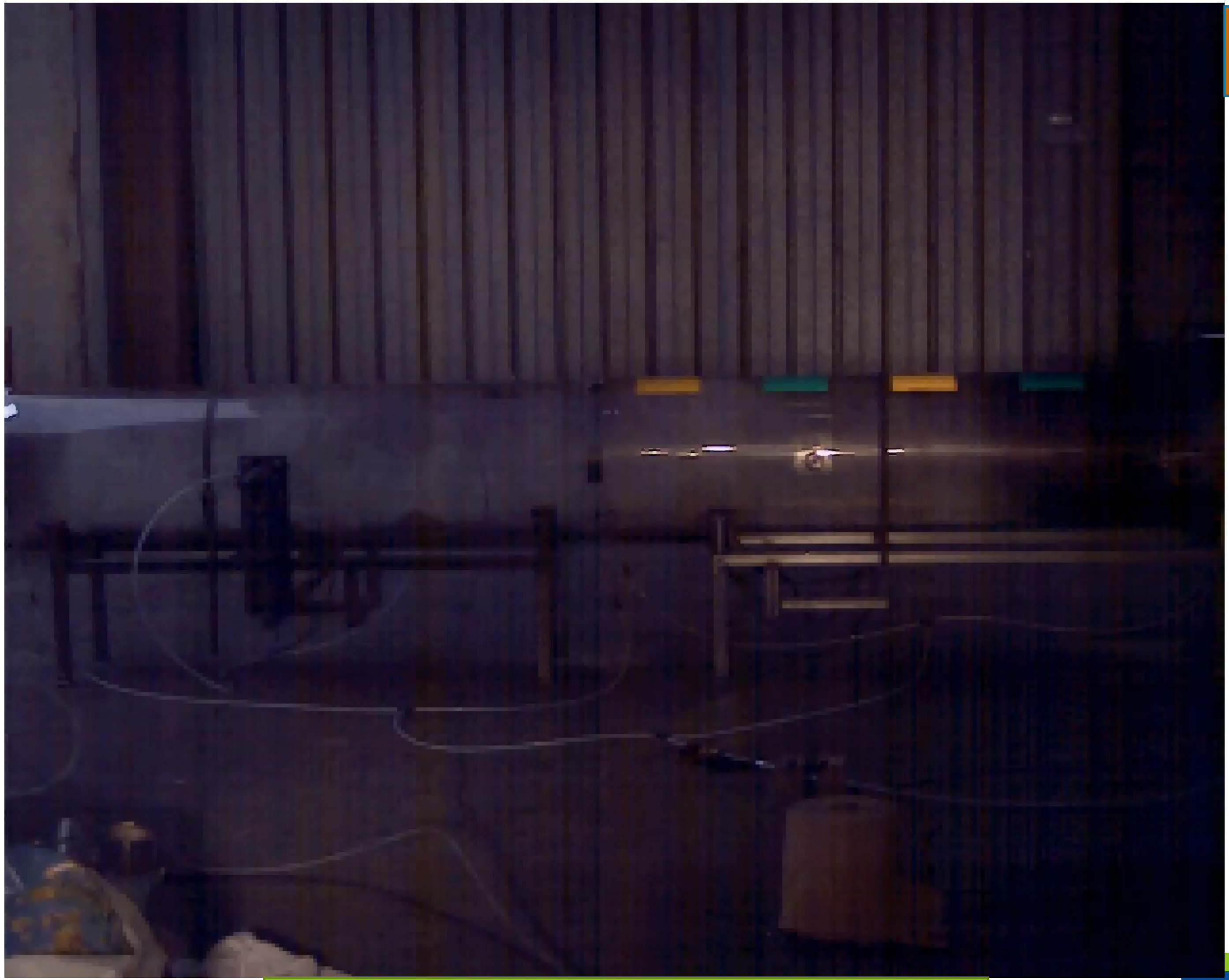
- Graphite dust **can not** explode
  - It does react and rapidly but it self-suppresses. Similar to “burning”
  - Initial flare up of surface layer on dust particles – but then nothing.
    - *No chain reaction*

Graphite "Burning"

Acheson

White hot graphite from furnace

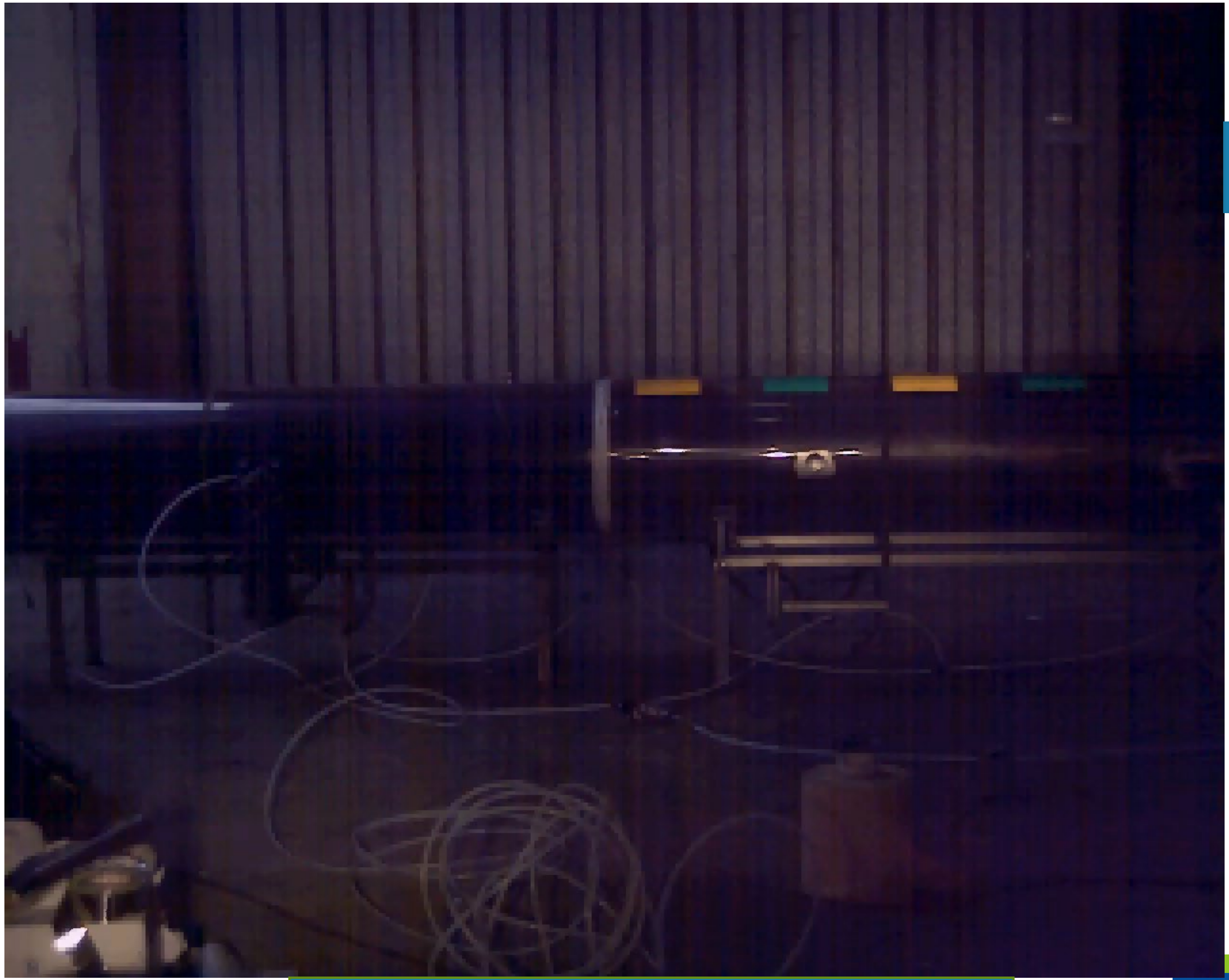
Graphite dust "explosions"



Corn

Corn Maize Dust

Graphite dust "explosions"



Graphite

Graphite Dust

Molten Salt Issues

Large molten salt tests are just being initiated

- Salt impregnation into graphite pores
  - Physical damage/cracks
  - “Hot spots” from fueled molten salt
- Wear/abrasion/erosion
  - Molten salt has higher density than graphite
  - Liquid flow over soft graphite has potential
- Chemical coupling with metallic systems
  - Graphite – MS is inert
  - There are questions when a metallic component is added

Salt residue

After immersion in FLiNaK

Before immersion in FLiNaK

Molten Salt: Salt impregnation in pores

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

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

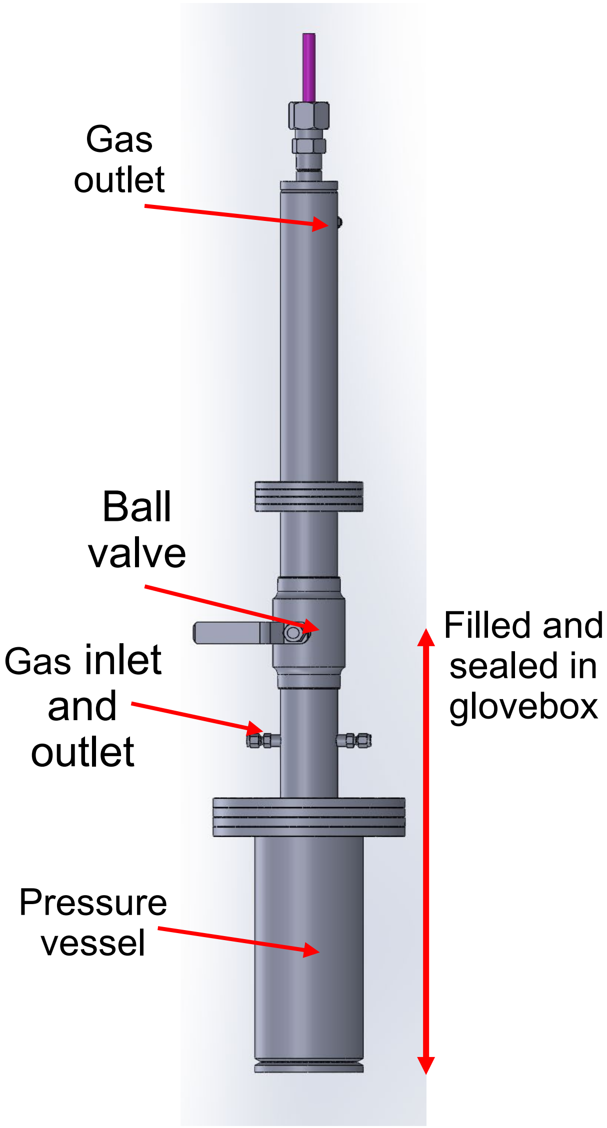
$$D_1 = \frac{w_2 - w_1}{\rho V_{total}}$$

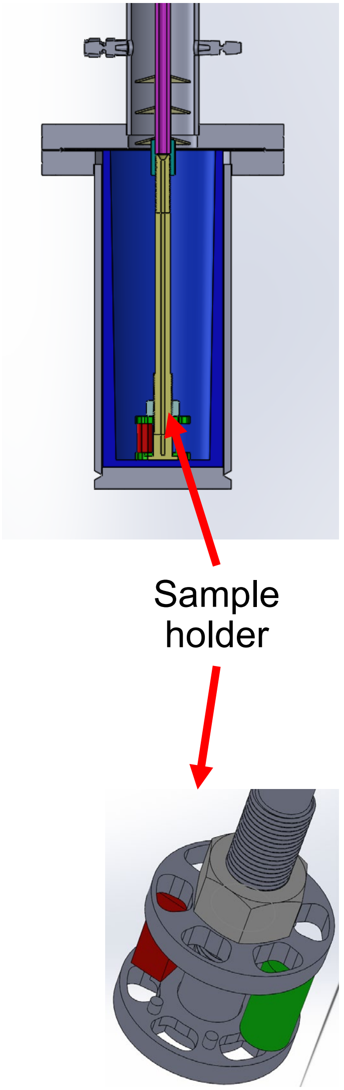
w_1 = initial weight
w_2 = weight after impregnation
V_{open} = open pore volume
V_{total} = total pore volume
ρ = salt density at impregnation temperature

INTERNATIONAL

https://www.astm.org/

Molten Salt: Erosion/abrasion





Current molten salt testing

- The initial tests have been conducted with FLiNaK salt
- No metallic materials contact the salt during the test – only graphite
- Design and build FLiBe-dedicated system for flowing salt
- Characterization of salt-exposed samples to understand chemical interaction and structural changes in graphites

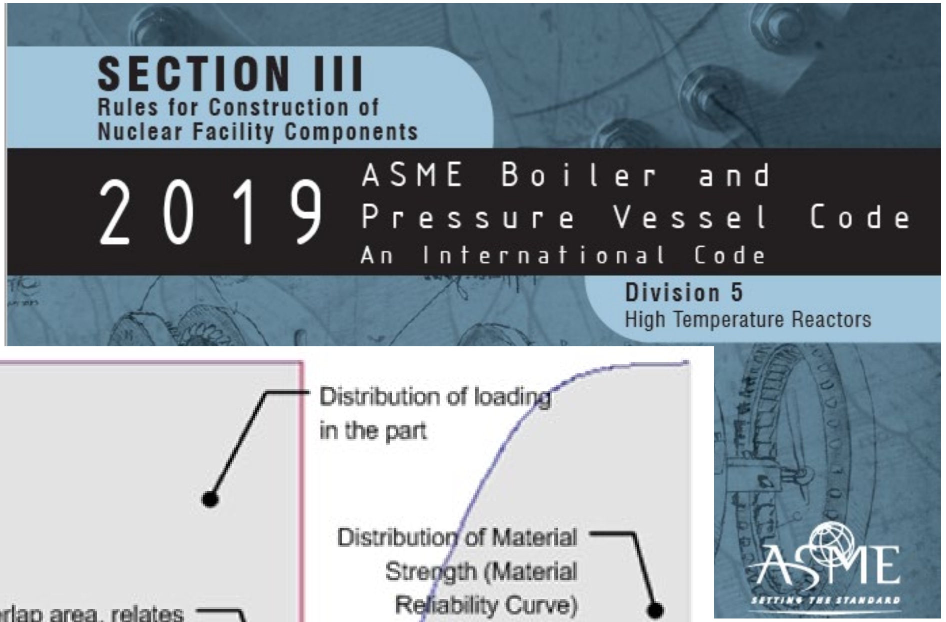
Graphite Session 2

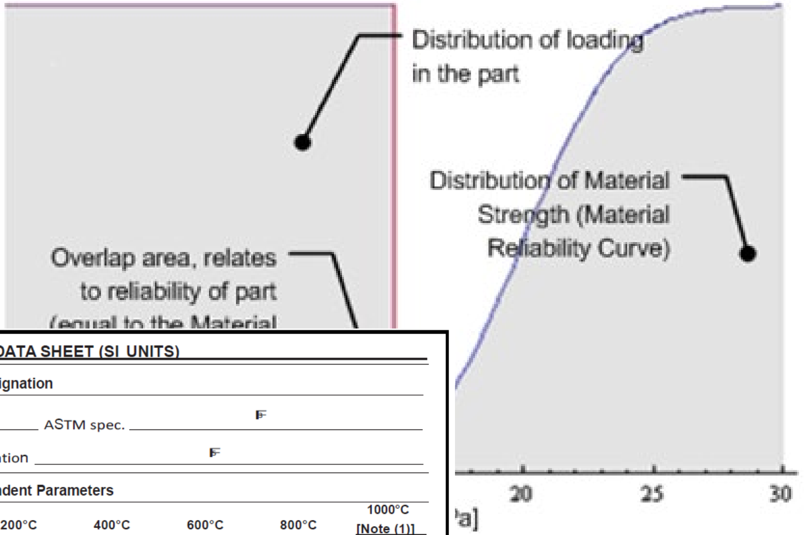
ASME Code Rules

Idaho National Laboratory

ASME Code : Topics of discussion

- ASME code rules development
  - Probabilistic design
    - *How it works practically*
  - Material Data Sheets
    - *Required material properties*
  - How to apply degradation
    - *Irradiation*
    - *Oxidation*
    - *Molten salt*
  - Design Specifications
    - *How design can affect rules*





FORM MDS-1 MATERIAL DATA SHEET (SI UNITS)

Grade Designation

Material Grade ______ Material spec. ID ______ ASTM spec. ______

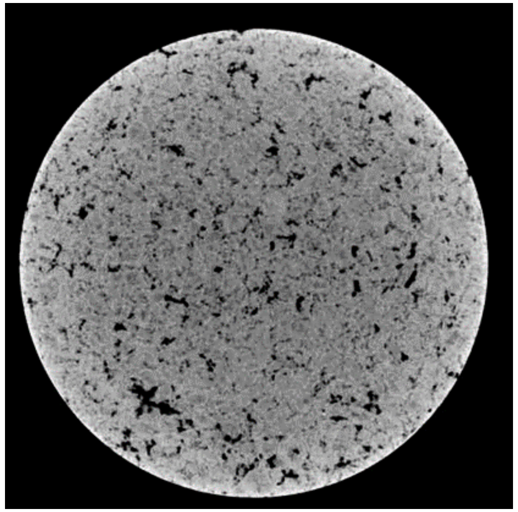
Max. grain size (mm) ______ Designation ______

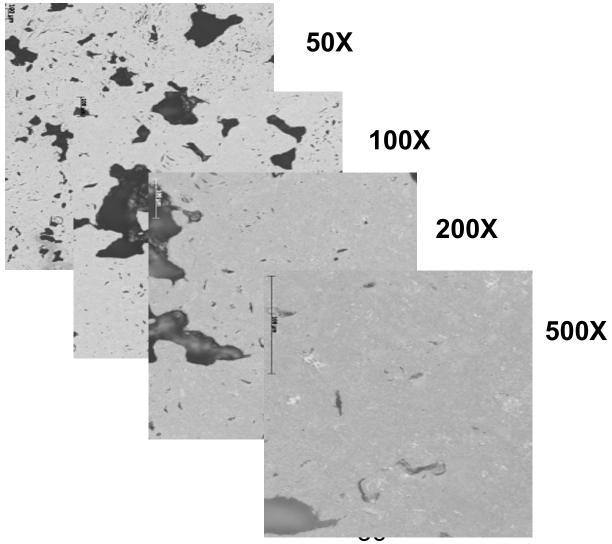
Temperature-Dependent Parameters

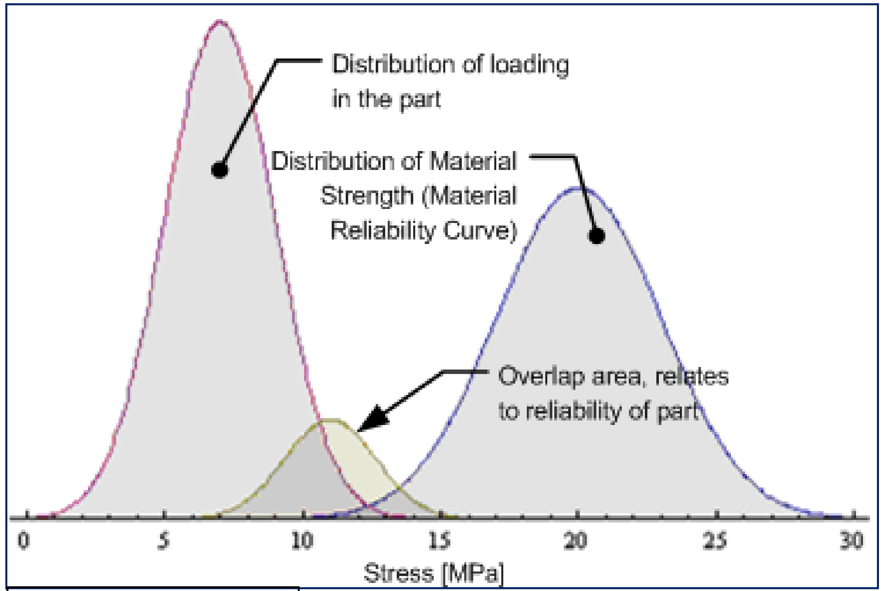
Property	Units	Orientation	20°C	200°C	400°C	600°C	800°C	1000°C [Note (1)]
Bulk density	kg•m⁻³	...						
Strength – tensile	MPa	WG, AG						
Strength – flexural (4-point)	MPa	WG, AG						
Strength – compressive	MPa	WG, AG						
Elastic modulus (dynamic)	GPa	WG, AG						
Elastic modulus (static)	GPa	WG, AG						
Coefficient of thermal expansion	°C⁻¹	WG, AG						
Thermal conductivity	W/m•k	WG, AG						

Probabilistic Design

- We know nuclear graphite has significant flaws
  - *Some amount of failure (i.e., a crack) is certain*
- Therefore, core components need to be designed to accept some amount of failure.
  - *Probability of failure approach is taken*
  - *Based upon overlap of applied stresses and inherent strength of the nuclear grade used*







From Dr. Mark Mitchell – PBMR Inc.

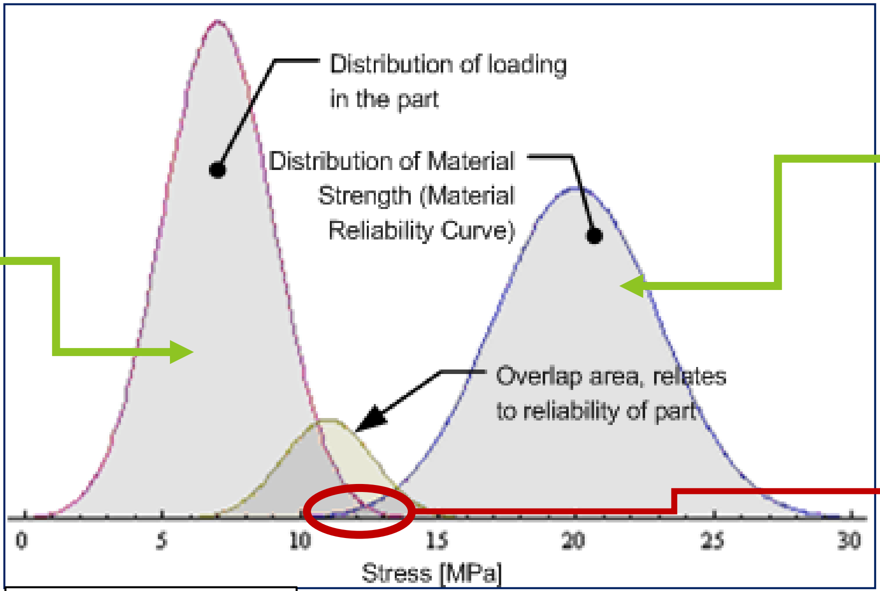
Probablistic verses **deterministic** design approach

- Deterministic is generally too limiting for a brittle material
- A distribution of possible strengths in a material is needed for quasi-brittle materials (i.e., flaw size for graphite).
- Probability of failure in component based upon inherent strength of graphite grade ***and*** applied stresses during operation.

Probabilistic Approach

Design

- *Values calculated from the reactor design.*
- *Received dose and temperature for all core components.*
- *FEM volume elements of core components*
  - *Normal and off-normal conditions*



From Dr. Mark Mitchell – PBMR Inc.

Material Property

- *Inherent material properties of selected graphite.*
- *Strength and thermal conductivity.*
  - ***Not** just average strength.*
- *Approach = Weibull str. analysis*

Reliability of Part

Probability of failure (POF)

Overlap of ***design stress*** and inherent ***material strength***

Where is component "loading" coming from?

- Thermal gradients
- Physical loads (extremely small)
- **Irradiation effects**
  - Dimensional change imposes huge internal stress
  - These stresses *will* lead to cracks
    - *U.K. bricks as example*
  - Stress buildup = Dependent upon component dose and temperature

Strength distribution comes from "baseline" testing

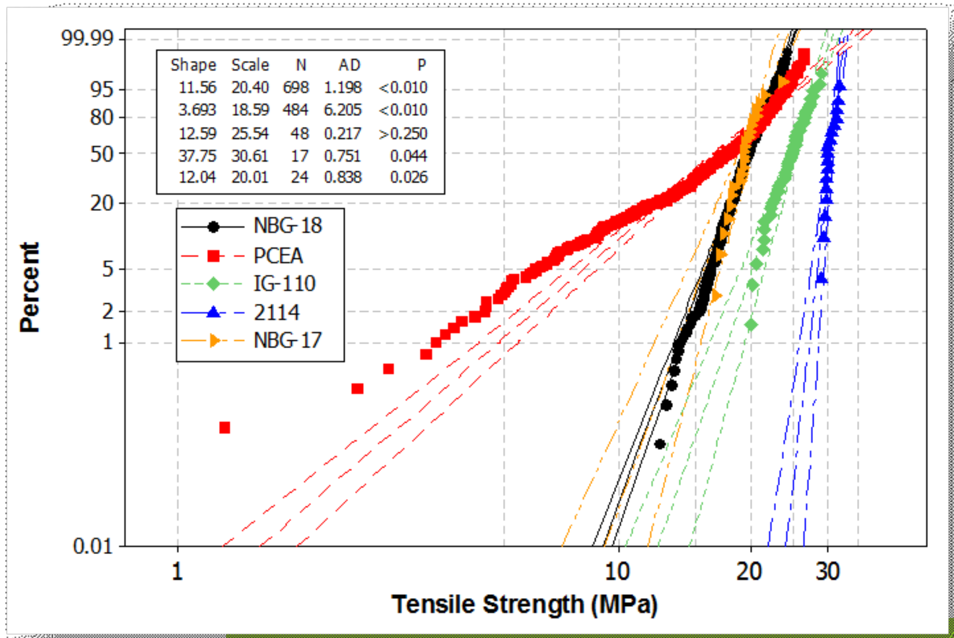
- Brittle strength dependent upon flaw sizes.
  - *Due to large flaw size range it can theoretically break at any stress*
- Must determine range of strength values
  - *Determine failure over entire stress range*
  - *Can't use average strength*
- Variations of the Weibull distribution best describe the graphite reliability curve.

How the graphite (and composite) ASME Code works

Three methods are provided for assessing structural integrity

1. Deterministic
   - *Simplified conservative method based on ultimate strength derived from Weibull statistics.*
   - *Irradiation changes well contained within the operational envelope*
2. Full Analysis Method
   - *Detailed structural analysis taking into account stresses, temperatures, irradiation history, and chronic oxidation effects.*
   - *Weibull statistics used to predict failure probability*
   - *Maximum allowable probability of failure defined for three Structural Reliability Classes (**SRCs**), which relate to safety function*
3. Qualification by Testing
   - *Full-scale testing to demonstrate that failure probabilities meet criteria of full-analysis method.*

Structural Reliability Class	Maximum Probability of Failure
SRC-1	1.00E-04
SRC-2	1.00E-02
SRC-3	1.00E-01



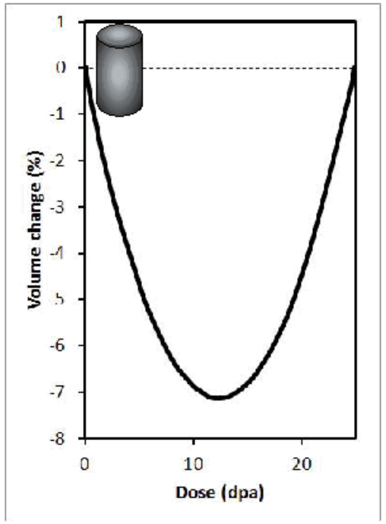
The graphite code is a "**process**". Not just picking a preapproved material

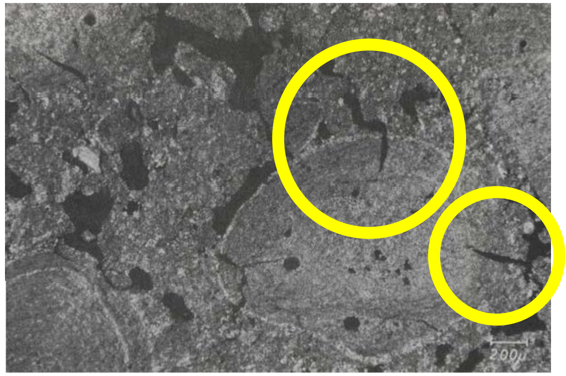
- *The applicant must demonstrate the graphite grade selected will consistently meet the component requirements.*

Getting the material property "proof" is responsibility of the applicant

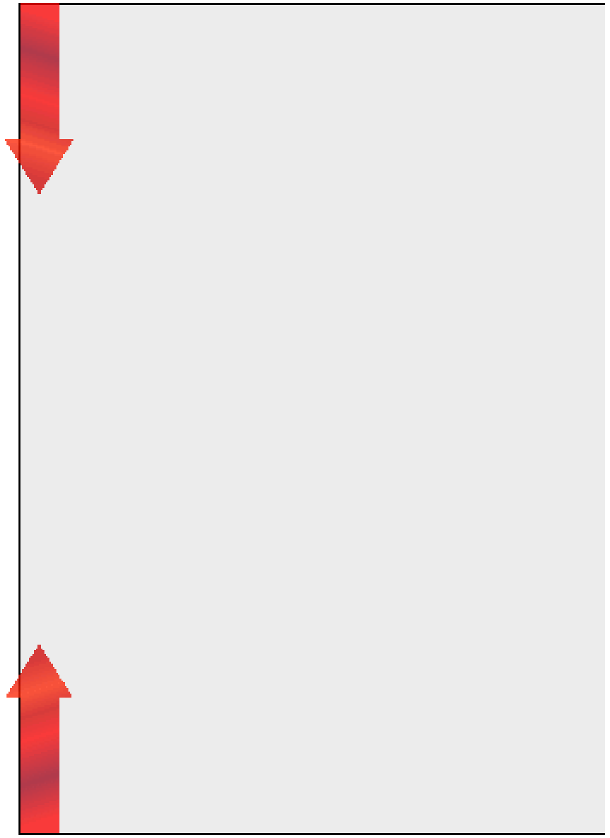
And then … the hard part

- Fundamental material properties change with irradiation/oxidation/MS must be addressed
  - Applicant must assess changes to design of component due to Irradiation effects
    - *New cracks formed after Turnaround*
    - *Internal stresses from dimensional change. Need creep response, too*
    - *Changes to density, strength, CTE, thermal conductivity*





G. Haag," ***Properties of ATR-2E Graphite and Property Changes due to Fast Neutron Irradiation", Juel-4183, 2005***



  - Applicant must also assess changes to design due to oxidation and molten salt degradation
    - *Changes in density, strength, elastic modulus, CTE, erosion/wear, and thermal conductivity.*

Graphite Degradation (ASME Material Data Sheets)

FORM MDS-1 MATERIAL DATA SHEET (SI UNITS)

Grade Designation

Material Grade ______ Material spec. ID ______ ASTM spec. ______

Max. grain size (mm) ______ Designation ______

Temperature-Dependent Parameters

Property	Units	Orientation	20°C	200°C	400°C	600°C	800°C	1000°C [Note (1)]
Bulk density	kg•m⁻³	...						
Strength – tensile	MPa	WG, AG						
Strength – flexural (4-point)	MPa	WG, AG						
Strength – compressive	MPa	WG, AG						
Elastic modulus (dynamic)	GPa	WG, AG						
Elastic modulus (static)	GPa	WG, AG						
Coefficient of thermal expansion	°C⁻¹	WG, AG						
Thermal conductivity	W/m•k	WG, AG						

Graphite Oxidation – Effect

Property	Units	2%	4%	6%	8%	10%
Strength [.]						
Elastic modulus (dynamic) [.]						
Thermal conductivity [.]						

Irradiated Graphite

Property	Units	WG	AG
Dimensional change [.]			
Creep coefficient [.]			
Coefficient of thermal expansion [.]			
Strength [.]			

ASME Data sheets capture most of the graphite degradation issues:

- Material properties of interest
  - Strength
  - Elastic modulus
  - CTE
  - Conductivity
- Irradiation effects
- Temperature dependence
  - Temperature affects everything
- Oxidation effects
- Molten salt issues are not (yet) in ASME code:

Graphite Degradation (ASME Material Data Sheets)

FORM MDS-1 MATERIAL DATA SHEET (SI UNITS)

Grade Designation

Material Grade ________ Material spec. ID ________ ASTM spec. ________

Max. grain size (mm) ________ Designation ________

Temperature-Dependent Parameters

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Bulk density	kg•m⁻³	...	___	___	___	___	___	___
Strength – tensile	MPa	WG, AG	___	___	___	___	___	___
Strength – flexural (4-point)	MPa	WG, AG	___	___	___	___	___	___
Strength – compressive	MPa	WG, AG	___	___	___	___	___	___
Elastic modulus (dynamic)	GPa	WG, AG	___	___	___	___	___	___
Elastic modulus (static)	GPa	WG, AG	___	___	___	___	___	___
Coefficient of thermal expansion	°C⁻¹	WG, AG	___	___	___	___	___	___
Thermal conductivity	W/m•k	WG, AG	___	___	___	___	___	___

Graphite Degradation (ASME Material Data Sheets)

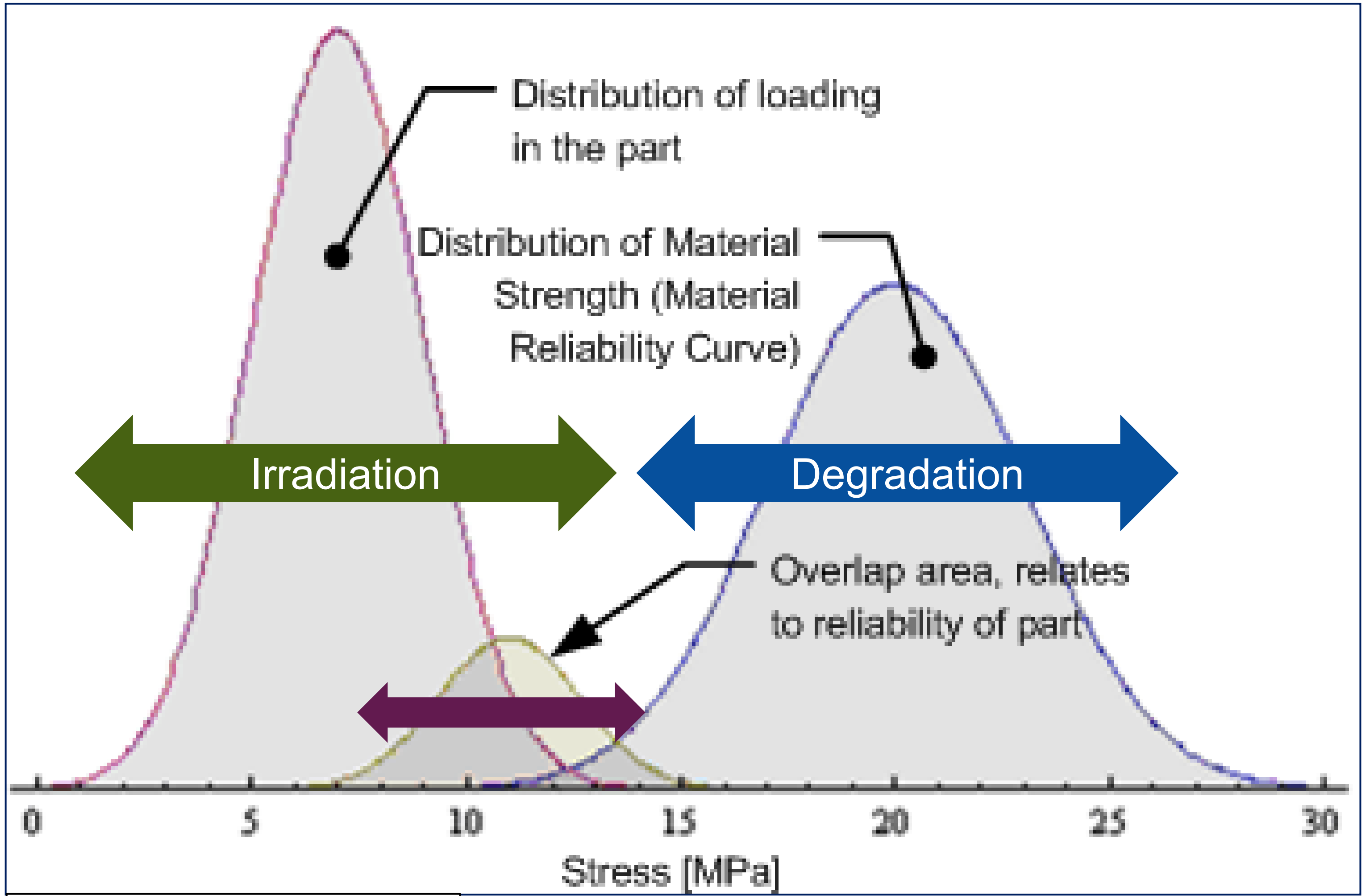
Graphite Oxidation – Effect

Property	Units	2%	4%	6%	8%	10%
Strength [.]						
Elastic modulus (dynamic) [.]						
Thermal conductivity [.]						

Irradiated Graphite

Property	Units	WG	AG
Dimensional change [.]			
Creep coefficient [.]			
Coefficient of thermal expansion [.]			
Strength [.]			

How to apply degradation to POF

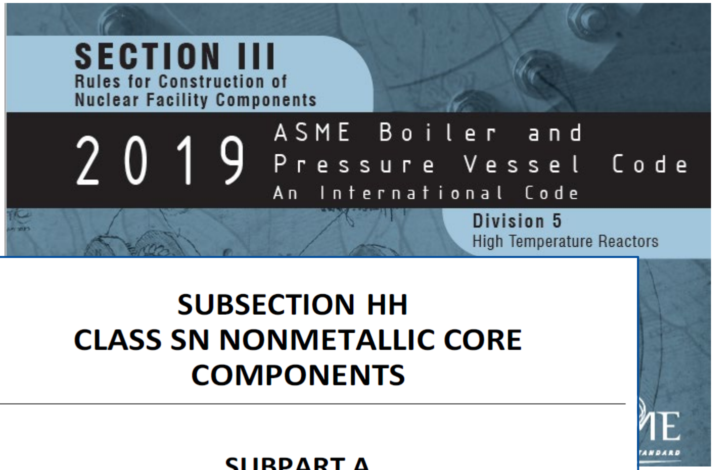


From Dr. Mark Mitchell – PBMR Inc.

- Degradation changes the material properties
  - Irradiation strength increases
  - High temperature increases strength
  - Oxidation strength decreases
  - Molten salt strength (maybe) decreases
- Irradiation changes stress loading of the part
  - Dimensional change increases stress
  - Irradiation creep relieves stress
- Overlap will change.
  - POF will change

Design Specifications: Impact on design rules

- ASME Nonmetallic Core Component code rules have been difficult to write
  - BPVC has focused primarily on metals
  - Very little operational experience with Nonmetallics
  - Data is not generally suitable for Pressure Vessel criteria
- Then there is the problem with graphite non-standards
  - Basically anything that works and is safe, is OK
- Up to the Designer/User to qualify the components
  - Designer must show that graphite is safe to use within the core design specifications
  - ASME nonmetallic code is more ***method*** than ***rules***
  - So what's "safe" is left up to the Users more than metallic code
- Puts a huge burden on regulators
  - They have to truly understand ***how*** graphite behaves in order to assess licensee's data and interpretations



SUBSECTION HH
CLASS SN NONMETALLIC CORE COMPONENTS

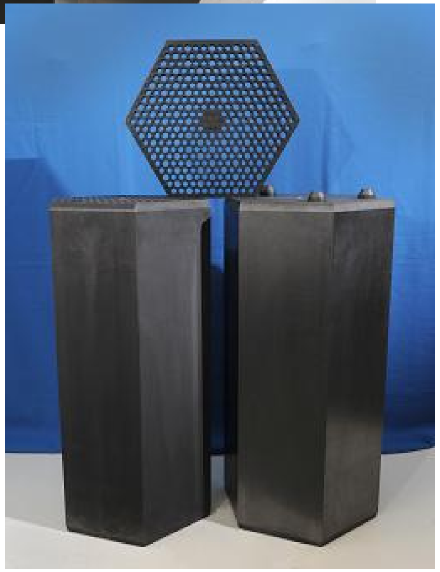
SUBPART A
GRAPHITE MATERIALS

SUBPART B
COMPOSITE MATERIALS

ARTICLE HHB-1000
INTRODUCTION

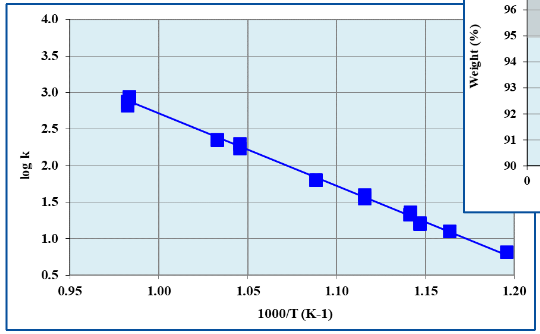
Design Specifications: Impact on design rules

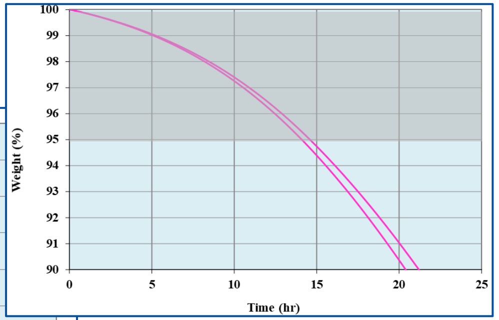
- Depending upon design, the “same” core component can either be safe or not safe
  - Lower or higher energy density (low/high dose per year):
    - *Internal stress development, component operational life-time*
  - Lower or higher operating temperature
    - *Component operational life-time (yrs), oxidation behavior, material property change rate*
  - Helium or Molten-salt cooled:
    - Oxidation potential, molten salt interactions, erosion
- The designers and regulators must understand what happens within all design options
  - What happens at higher dose rates and what happens at low?
  - What happens at higher and low temperatures?
- Implies a certain level of expertise in graphite behavior to really assess what is going on
  - These scenarios are not covered within the design code



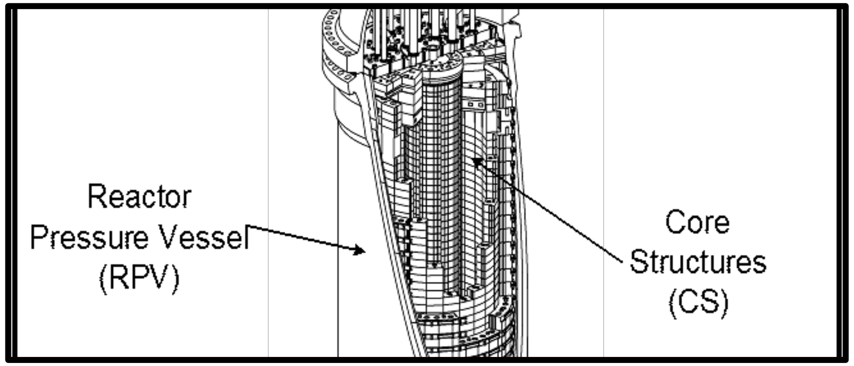
Design specifications example: HTGR oxidation degradation

1)
- Use D7542 to determine temperatures where grade switches from kinetic to diffusion-controlled oxidation
  - Regardless of operation temperatures



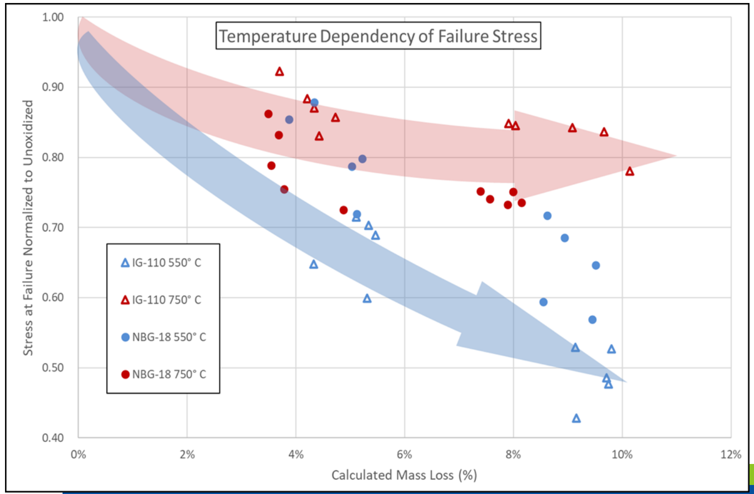


2)



- **From design**: Entire possible temperature range
  - Normal and Off-normal operations

3)
- Then determine strength loss *for appropriate temperatures*
  - Need to perform oxidation strength loss tests on selected graphite grade.



4) ***Oxidation residual strength is then used in POF calculations***
- ***Strength loss will be specific to core design***

Graphite Session 3

Questions & Issues

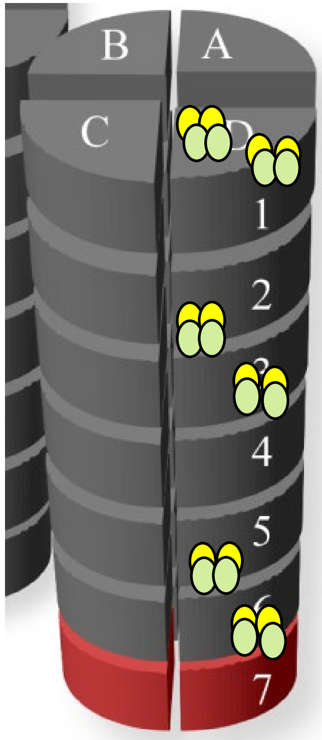
Questions & Issues : Topics of Discussion

- How much data is needed?
  - Unirradiated, irradiated, oxidation, molten salt, combinations
- Lack of standard tests
  - How do you measure material properties without test standards?
- What is failure?
  - What constitutes failure when you already have a cracked component?
- Significance of turnaround dose
  - A lesson in risk management
- Irradiation creep
  - Creep in graphite is desired
- Behavior Models
  - Some material properties can only be determined by models

Licensing: How much data is needed?

ASME requires minimum of 288 (total) specimens

- So how much data is needed to qualify a graphite component?
  - How much is needed to qualify the graphite grade?
  - Are 288 specimens (144/orientation) sufficient?
    - *Are 24 specimens enough to determine location variation within volume of an entire billet?*
    - *Are 96 specimens enough to determine billet to billet variations?*
    - *Are 144 specimens enough to determine total variation across batch and billet?*
- Can you perform Weibull analysis on only 144 specimens (per orientation)
  - Does the sample population affect the Weibull analysis in code?



4 specimens in center

2 with-grain

2 against-grain

4 specimens exterior

2 with-grain

2 against-grain

Top, middle, bottom locations of billet

24 specimens per billet

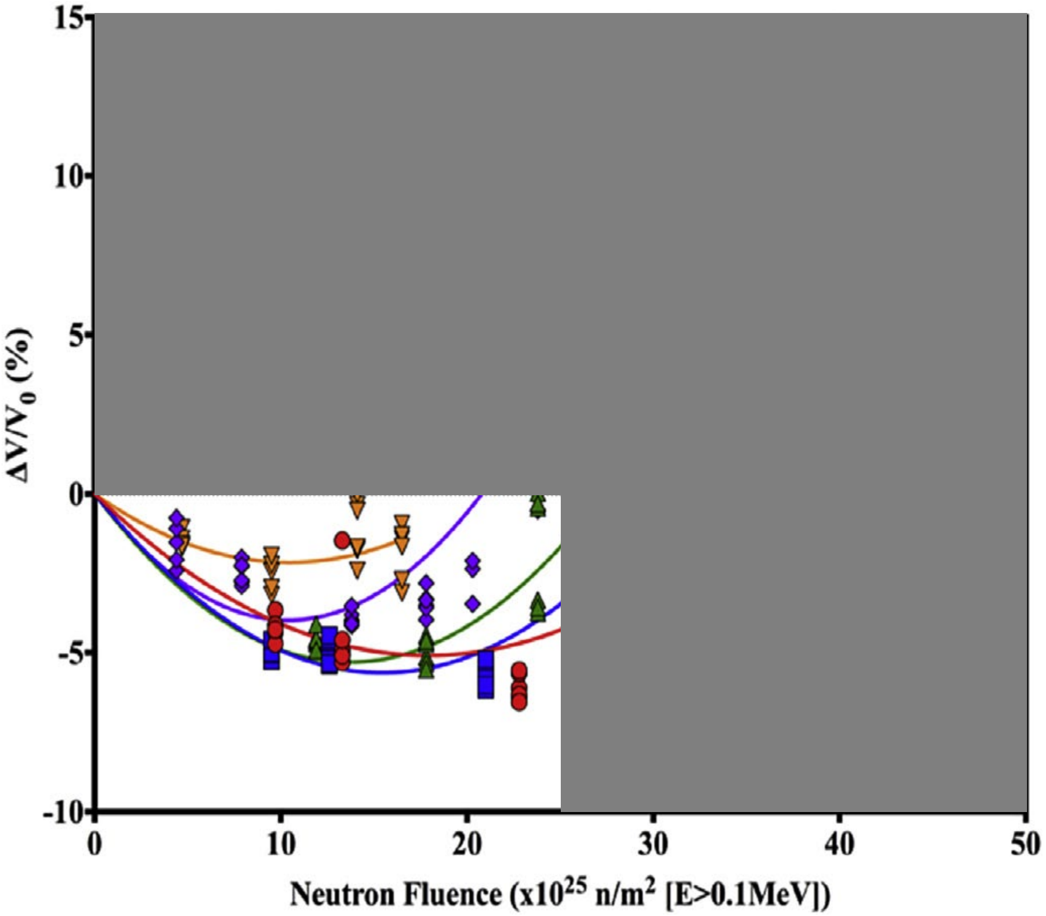
4 billets per batch

3 batches

<u>Total samples = 288</u>

How much irradiation data is needed to qualify?

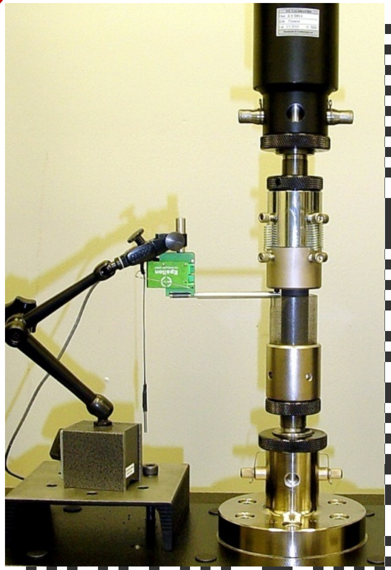
- At first, this looks like a lot of data
- But a lot of this data isn't applicable
  - Nobody has ever designed beyond cross-over (return to 0%)
  - Structural integrity risks increase substantially further from turnaround
    - *Nobody has operated close to cross-over*
  - Design consideration: Cracks begin to appear after turnaround
    - *Molten salt designs may not be able to go past turnaround*
  - What is designed operating temperature
    - *Behavior at temperatures higher or lower may have limited applicability*



From: Anne A. Campbell, Yutai Katoh, Mary A. Snead, Kentaro Takizawa, "Property changes of G347A graphite due to neutron irradiation", Carbon 109 (2016) 860-873

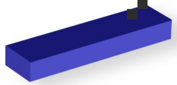
Lack of testing standards

Compression Testing



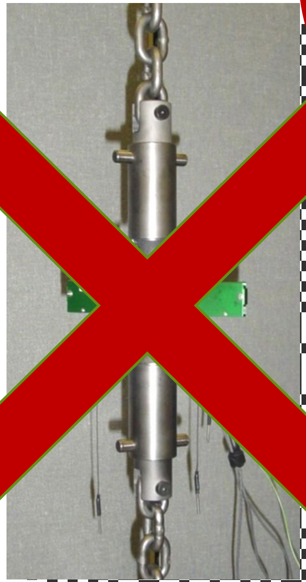
ASTM C695-91

Flexural Testing



ASTM C651-11

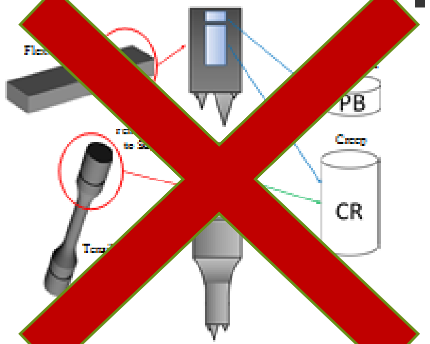
Tensile Testing



ASTM C749-08

Split-disk test

Sub-Sized 3-point Flexure



Physical & Thermal Properties Testing

- *Density*
- *Coefficient of Thermal Expansion*
- *Thermal Conductivity*
- *Resistivity*
- *Resonant Frequency (E_{DYN})*
- *Torsional Frequency (G_{DYN})*
- *Sonic Velocity*
- *Fracture Character**

**Not a non-destructive evaluation*

Lack of testing standards

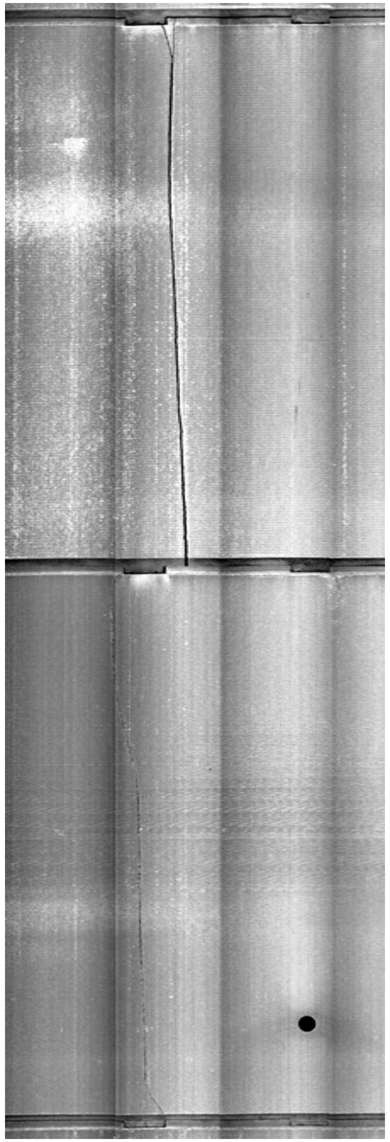
- If designer uses room temperature standards they must demonstrate they produce accurate results
  - Most times they do not
- Designer will need to prove their testing procedure is accurate and precise.
  - This will require significant time and an increase in samples tested
- This is a problem for nearly all degradation conditions
  - irradiation testing, elevated temperature testing, oxidation, and molten salt interactions

Sub-Sized testing

What is failure?

- If components are already cracked and they are not pressure boundaries (needing only 1 through crack) what is a failed component?
- Must go to U.K. for the answer:
  - All AGC cores have multiple cracked bricks (See Hunterston B)
  - First crack detected ~ year 2000. Yet they have operated safely for decades now.
  - So what defines a failed component
- Only the designer can define what/how a component fails
  - Depending upon design, a single crack may constitute a failed component.
  - Or multiple cracks
  - Or cracks with a specific orientation or surrounding a specific critical design feature (control rod opening).

Cracked AGR core brick at Hunterston B power station



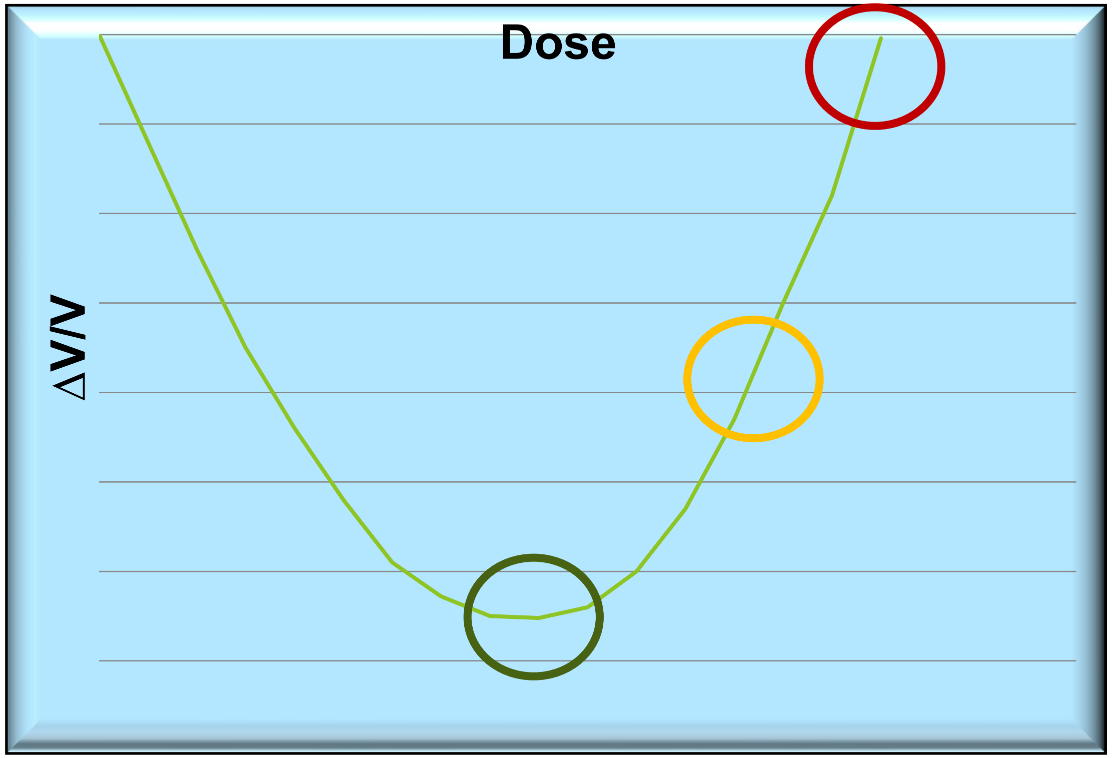
Significance of turnaround dose: A lesson in risk management

When do you replace the graphite?

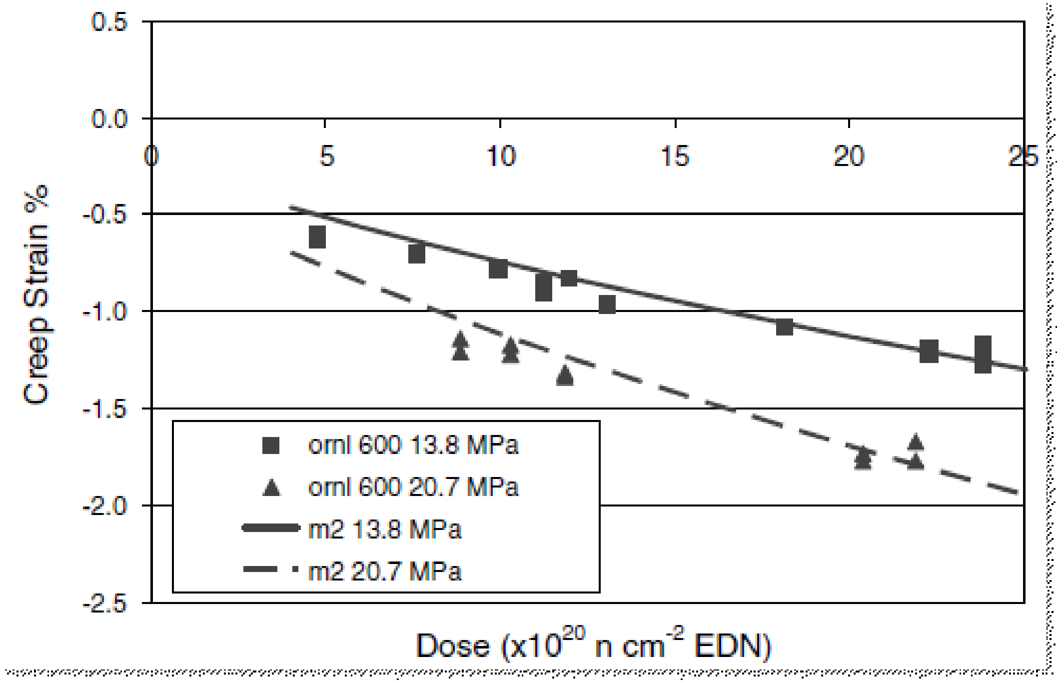
Most conservative dose level

More risk but Rx do operate here

Highest risk



Irradiation creep

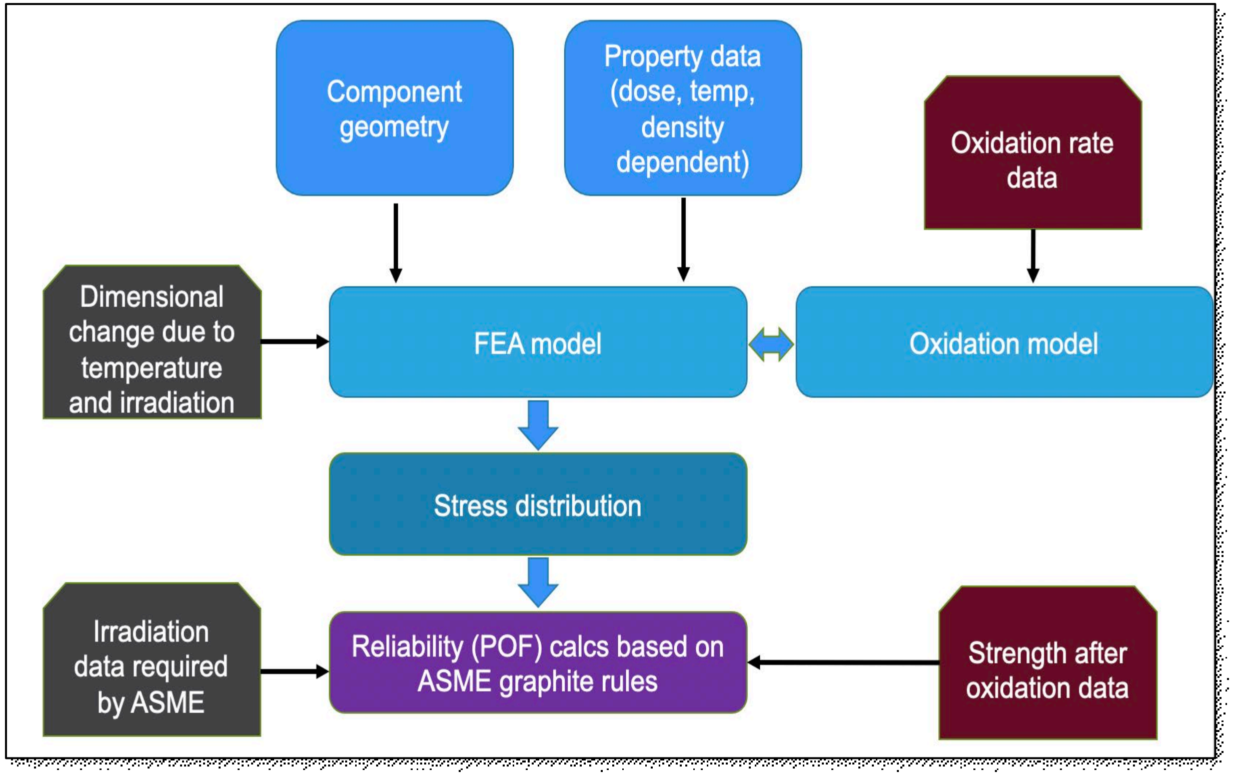


Mark A. Davies and Mark Bradford, "A revised description of graphite irradiation induced creep", Journal of Nuclear Materials 381 (2008) 39–45

- Irradiation creep in graphite relieves stress
  - Stresses from irr dimensional change
  - Thermal stresses
- Creep rate is being determined for a number of current grades
  - How creep should be used is the question?
  - Generally, you reduce internal stresses using measured/predicted creep strain
  - Creep behavior (strain) is considered linear from 0 dpa to turnaround dose
    - Linear Creep Law
- U.K. (EDF, U.K.) has the most sophisticated creep models
  - M^2 model

Behavior Models

- Graphite behaviors usually empirically measured through testing
  - As discussed previously, some test requirements are not compatible to each other
    - *Simply no way to **test** oxidized, irradiated graphite*
    - *The U.K. has made progress but procedure is not standardized*
  - We can't do oxidation testing on large core components
- The only way to determine some behavior is through modeling
  - Empirically based models have been initiated
  - Adding behavior from different conditions will be the most challenging



Questions?
Discussion?

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