Xe-100 Graphite Engagement: Graphite Material Model

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TBD, 2023

Department of Energy Acknowledgement and Disclaimer

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Agenda & Objectives

Agenda:

Open Portion (90 minutes):

- Background to material model
- Dimensional change
- Elastic modulus
- Strength
- Irradiation creep
- Coefficient of Thermal Expansion (CTE)
- Other properties

Closed Portion (45 minutes):

- Material selection
- Irradiation environment
- Data sources

Objectives:

- Provide an overview of the material model formulation being applied by X-energy for use in graphite stress analysis
- Provide background to subsequent presentations that will cover the implementation of these models in analysis software
- Summarize the sources of data being used and the flow of information through the design analyses

Introduction & Background

When subject to fast neutron irradiation in a reactor environment, graphite experiences dimensional change and changes to material properties. In combination with spatially varying irradiation conditions, these lead to differential strains and the generation of internal stress. If the stress exceeds a particular level, cracking results.

Computational modelling of irradiated graphite is required because:

- Reactor components are large and experience a relatively low fast neutron flux
- In pebble bed reactors, the reflector components must remain in situ for decades
- The distribution of dose and temperature, hence strain and material properties occurring in these components is complex
- It is therefore not possible to replicate the full loading scenario in testing

Instead, small samples are irradiated in high flux Materials Test Reactors (MTRs), accumulating decades worth of neutron fluence over a few years. The results from these tests are combined with a broader understanding of graphite to formulate a constitutive model for the behavior of irradiated graphite. This is used in computational models of reactor components to predict the stress and material properties, which form the basis of structural integrity assessments.

Note that unless otherwise specified, all plots in this presentation are purely illustrative and not applicable to any specific graphite grade.

Material Model Principles

- Wherever possible, models should be based on global industry best practice – modelling nuclear graphite is not a new problem
- The model form should be based on a theoretical understanding of irradiated graphite behavior. Although a prediction of irradiated graphite behavior from first principles is not possible, a semi-empirical model is preferable to a purely statistical fit.
- The same underlying model components should be used to represent the evolution of multiple linked properties
- Model fitting should take account of all relevant data rather than fitting separate models to each material property and graphite grade. RG 1.203 Element 2
- The model should allow interpolation and reasonable extrapolation beyond the available data, within limits of validity - avoid overfitting or non-physical behavior
- The limits of validity should be evaluated and clearly communicated as part of the model development and calibration. RG 1.203 Element 4
- Meaningful evaluation of variability and uncertainty in model parameters should be possible, allowing easily interpreted sensitivity studies and/or probabilistic calculations. RG 1.203 Element 4 – Step 20

Use of Material Model

This presentation focuses on material changes used in structural integrity analysis. Note that other properties also experience significant changes with irradiation, in particular the thermal conductivity. This is important for safety analysis and may be modelled using a similar approach.

Extensive irradiation testing and reactor experience was accumulated using grades of graphite that are no longer available. For modern graphite grades, data typically do not cover the full range of irradiation conditions and new MTR experiments are ongoing. With irradiation testing and component design proceeding in parallel, it is necessary to extrapolate beyond the grade-specific database.

The overall flow of information is as follows:

1. Collate relevant data from MTR experiments and unirradiated testing. This includes grade-specific data and data from historic graphite grades. RG 1.203 Element 2 – Step 7
2. Considering the full range of data and existing established methods, implement a framework of equations to relate material property changes to each other and the fast neutron dose and temperature
3. Develop a generic set of model parameters based on historic graphite grades covering a broad range of temperature and dose conditions
4. Perform grade-specific model calibration using available data
5. As new grade-specific MTR results become available, review model calibration and adjust parameters if required

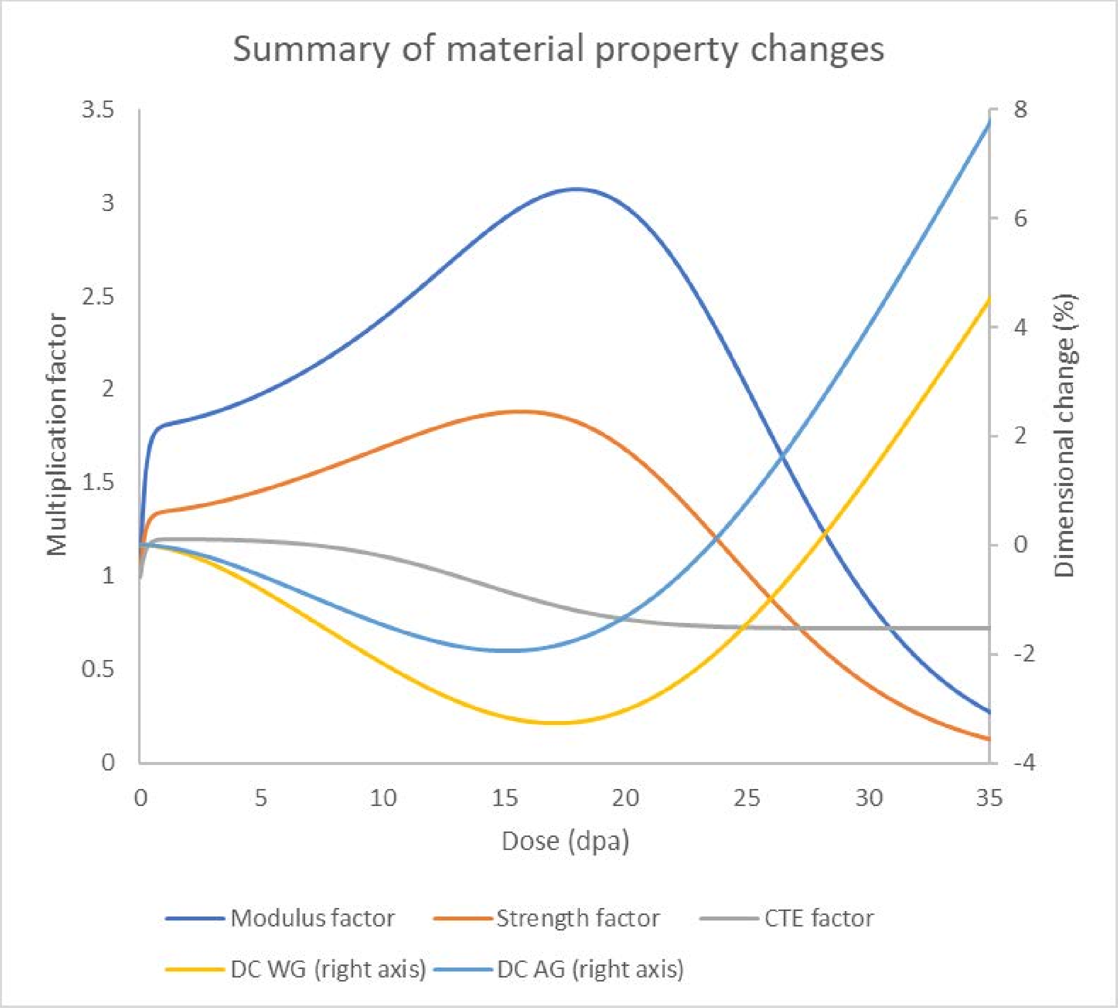
Material Properties for Structural Analysis: Summary

Strain in graphite is a combination of dimensional change strain, elastic strain, irradiation creep strain and thermal strain.

For structural analysis of graphite, the following properties are required:

- Dimensional change (DC) (in with-grain (WG) and against-grain (AG) directions unless isotropic in the full range of dose and temperature)
- Elastic modulus change with irradiation
- Strength change with irradiation
- Coefficient of thermal expansion change with irradiation
- Irradiation creep model coefficients

In addition, three-dimensional distributions of fast neutron dose and temperature are required. Temperature predictions require knowledge of the irradiated thermal conductivity.

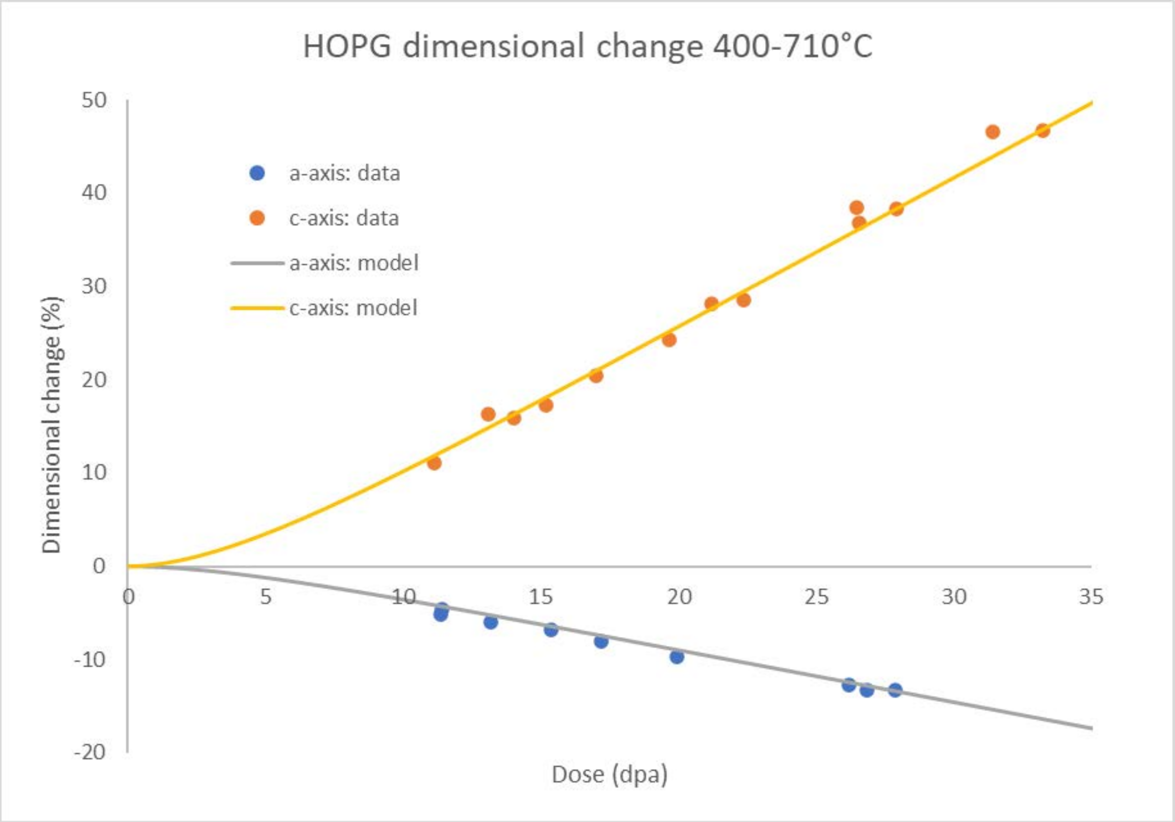


Dimensional Change: Crystal

Dimensional change drives the generation of stress and deformation in components and influences the evolution of all other material properties.

Single crystal behavior may be determined from measurements of Highly Oriented Pyrolytic Graphite (HOPG):

- After initial incubation, the rate of dimensional change is near constant with dose in a typical reactor temperature range (no turnaround)
- Graphite crystals shrink in the a-axis direction (parallel to graphene planes) and swell in the c-axis direction (perpendicular)
- Crystal dimensional change rate does not vary significantly with temperature between around 400-700°C. At higher and lower irradiation temperatures, the dimensional change rate is more rapid. Behavior below ~250°C is more complex.



Ref.: *High Dose Fast Neutron Irradiation of Highly Oriented Pyrolytic Graphite, Carbon, 1971,* B. T. Kelly and J. E. Brocklehurst

Dimensional Change Model: Polycrystalline Graphite

In polycrystalline graphite, the evolution of dimensional change depends on the crystal behavior combined with the porous microstructure of graphite (many crystals connected to each other in a material containing filler particles, binder and porosity on a very wide range of length scales from angstroms to millimeters).

- Initially, most c-axis swelling is accommodated by porosity and the bulk dimensional change is determined by the aggregate behavior of crystal shrinkage. In reactor conditions for near-isotropic graphite, the net result is shrinkage.
- Accommodation porosity is gradually closed according to some cumulative distribution with dose. As initial porosity is closed, crystal strain generates new porosity (‘pore generation’).
- When the pore generation strain rate equals the underlying shrinkage rate, dimensional change ‘turnaround’ is reached. The material then swells, eventually exceeding its initial volume.

Dimensional Change Model: Polycrystalline Graphite

Based on the model developed by Bradford and Steer*, irradiation-induced dimensional change strain ϵ_{dc} as a function of dose γ is found by integrating the following equation:

$$\frac{d\epsilon_{dc}}{d\gamma} = \frac{dG_{dc}}{d\gamma} + \frac{dF_{dc}}{d\gamma}$$

Where G_{dc} is the underlying shrinkage and F_{dc} is the pore generation term. Based on the HOPG data, the underlying shrinkage is modelled as:

$$\frac{dG_{dc}}{d\gamma} = A_{dc}(1 - e^{-k_{dc}\gamma})$$

A_{dc} depends on the irradiation temperature, graphite grade and orientation (in non-isotropic graphite grades) while k_{dc} depends on the irradiation temperature.

* Ref.: *A Structurally-based model of irradiated graphite properties, J. Nuc. Mat., 2008, M.R. Bradford and A.G. Steer*

Dimensional Change Model: Pore Generation

- Pore generation results from the closure of accommodation porosity and is depends on the underlying shrinkage rate
- The statistical distribution of size, shape and orientation of accommodation porosity leads to a distribution of closure with dose (hence microstructural connectivity), modelled as a cumulative normal distribution termed the Structural Connectivity S_c (assuming constant temperature), defined by irradiation temperature-dependent location and scale parameters μ_{Sc} and σ_{Sc} :

$$S_c' = \frac{1}{2}\left(1 + \operatorname{erf}\left(\frac{\gamma - \mu_{Sc}}{\sigma_{Sc}\sqrt{2}}\right)\right)$$

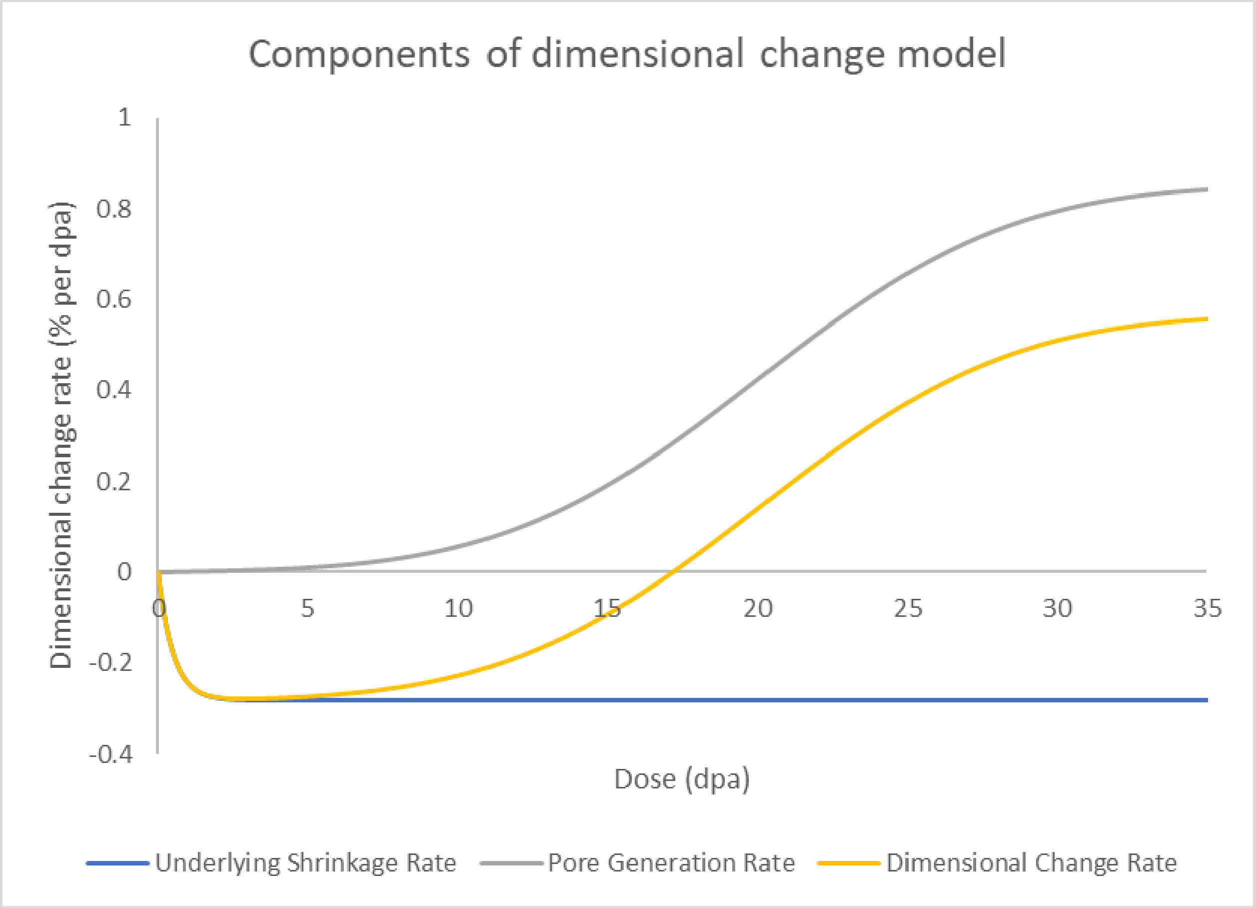
- Pore generation is modelled by the equation

$$\frac{dF_{dc}}{d\gamma} = B_{dc}\, S_c \frac{dG_{dc}}{d\gamma}$$

where B_{dc} depends on the irradiation temperature, graphite grade and orientation (in non-isotropic grades)

Components of Dimensional Change Model

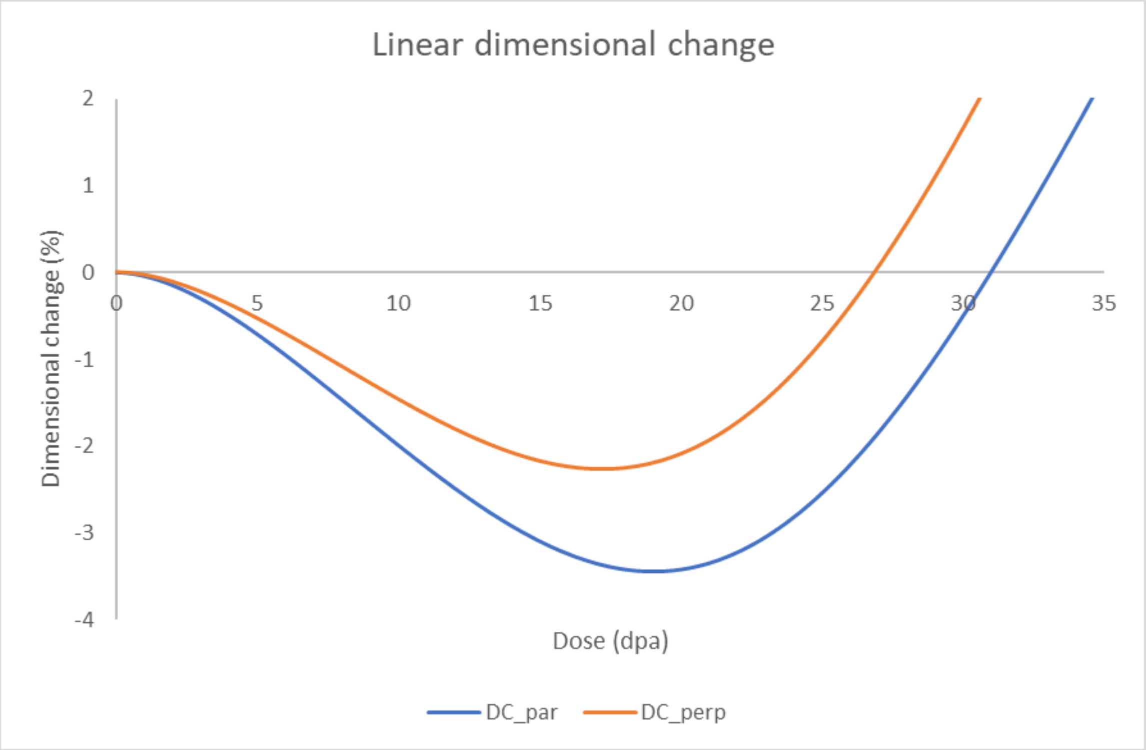
- Underlying dimensional change rate initially increases then saturates at constant value (shrinkage in typical temperature range)
- Pore generation rate has the same form as the Structural Connectivity curve in this case (begins after saturation of shrinkage rate)
- Net dimensional change rate:
  - Gradual increase in rate to period of linear shrinkage at low dose
  - Rate goes to zero (turnaround) then net swelling
  - Eventually swelling rate saturates at high dose
- Plot shows curves for one orientation, but the model allows for different rates in with-grain and against-grain directions



Dimensional Change Curves

Overall model captures:

- Initial period of slower shrinkage (incubation)
- Low-dose linear shrinkage
- Dimensional change turnaround
- High-dose swelling
- Dimensional change orthotropy
- Temperature-dependent parameters allow fit to wide range of irradiation temperatures
- Grade-dependent and orientation-dependent parameters can be tuned to grade-specific data



Material Property Changes

- There is a rapid change in material properties at low doses, before significant dimensional change has taken place. For isotropic/near-isotropic grades in the HTGR temperature range:
  - Young's modulus, strength, CTE, electrical resistivity and thermal resistivity all increase rapidly
  - Driven by within-crystal phenomena (irradiation damage) and relief of initial stress (primary creep). Conventionally termed 'pinning'.
- At higher doses, material property changes are driven by structural effects:
  - Gradual increase of Young's modulus and strength and decrease of CTE with Structural Connectivity at moderate dose (up to around turnaround)
  - High dose decrease of Young's modulus and strength and increase of thermal resistivity with Pore Generation (largely post-turnaround)
- The same Structural Connectivity curve is used for dimensional change, Young's modulus and strength
- Separate Structural Connectivity curve used for CTE (based on AGR experience and MTR data)
- Relative changes in material properties with irradiation are generally isotropic. The properties themselves may be orthotropic (determined by the initial, unirradiated values).

Young’s Modulus

- In common with historical United Kingdom Atomic Energy Authority (UKAEA) methods, the Young’s modulus is decomposed into several terms:
  - E_0: unirradiated Young’s modulus
  - ‘Pinning’ (P’) – rapid, low-dose increase (saturates on short dose scale, ~1dpa). Note that P’ here denotes a function of dose that starts at 1 and asymptotes to some value P. At high doses, P and P’ may be treated as equivalent.
  - ‘Structure’ term (S’) – slower pre-turnaround increase and high dose decrease
- In the model developed by Bradford and Steer, the Structure term has three components:
  - Structural connectivity
  - Densification (effect of underlying shrinkage)
  - Pore generation
- The irradiated Young’s modulus is as follows:

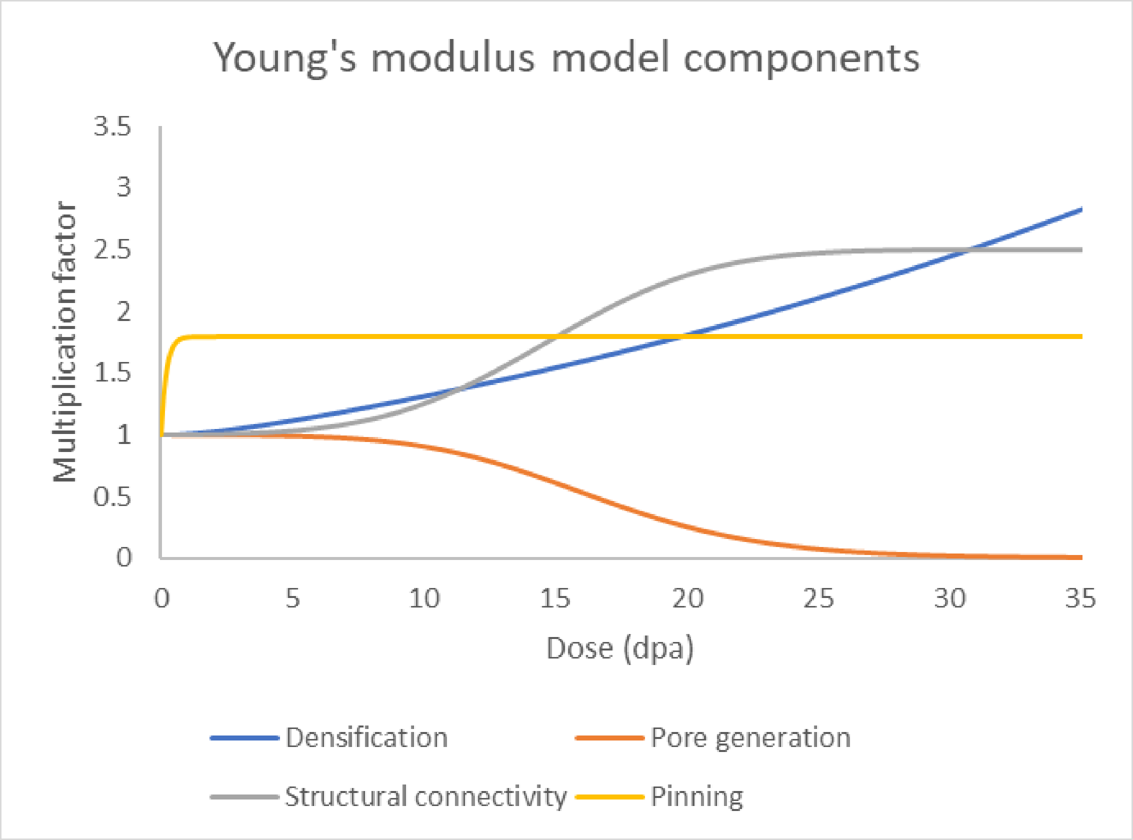
$$E = E_0 P'\left(1 + C \times S_c(\gamma)\right) e^{-\beta_d \Delta v_d} e^{-\beta_{pg} \Delta v_{pg}}$$

Where the Δv_d and Δv_{pg} terms represent the volume change due to shrinkage and pore generation respectively with corresponding coefficients β_d and β_{pg}.

  - S_c is the same structural connectivity term used in the dimensional change equation
  - P’ and C may vary with irradiation temperature
  - Changes to the shear modulus are assumed to follow the same pattern. The elastic Poisson’s ratio is assumed not to vary with irradiation.

Young’s Modulus Model Factors: Illustrative Example

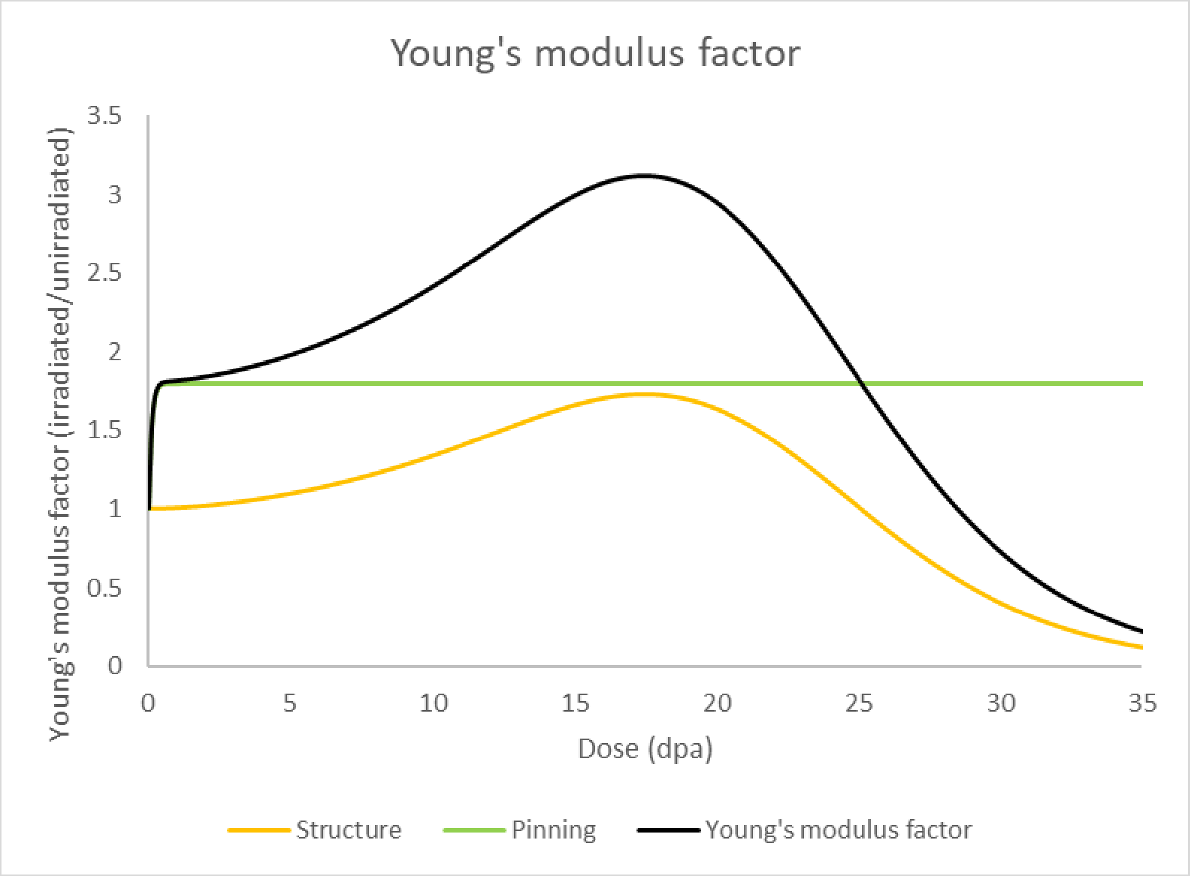
- Net effect of dimensional change on elastic modulus (densification and pore generation) is a slight increase at moderate dose and significant decrease at high dose
- Structural connectivity leads to an increase in elastic modulus that saturates at high dose
- Pinning saturates rapidly at low dose



Young's Modulus Model: Overall

The combination of structure and pinning terms leads to:

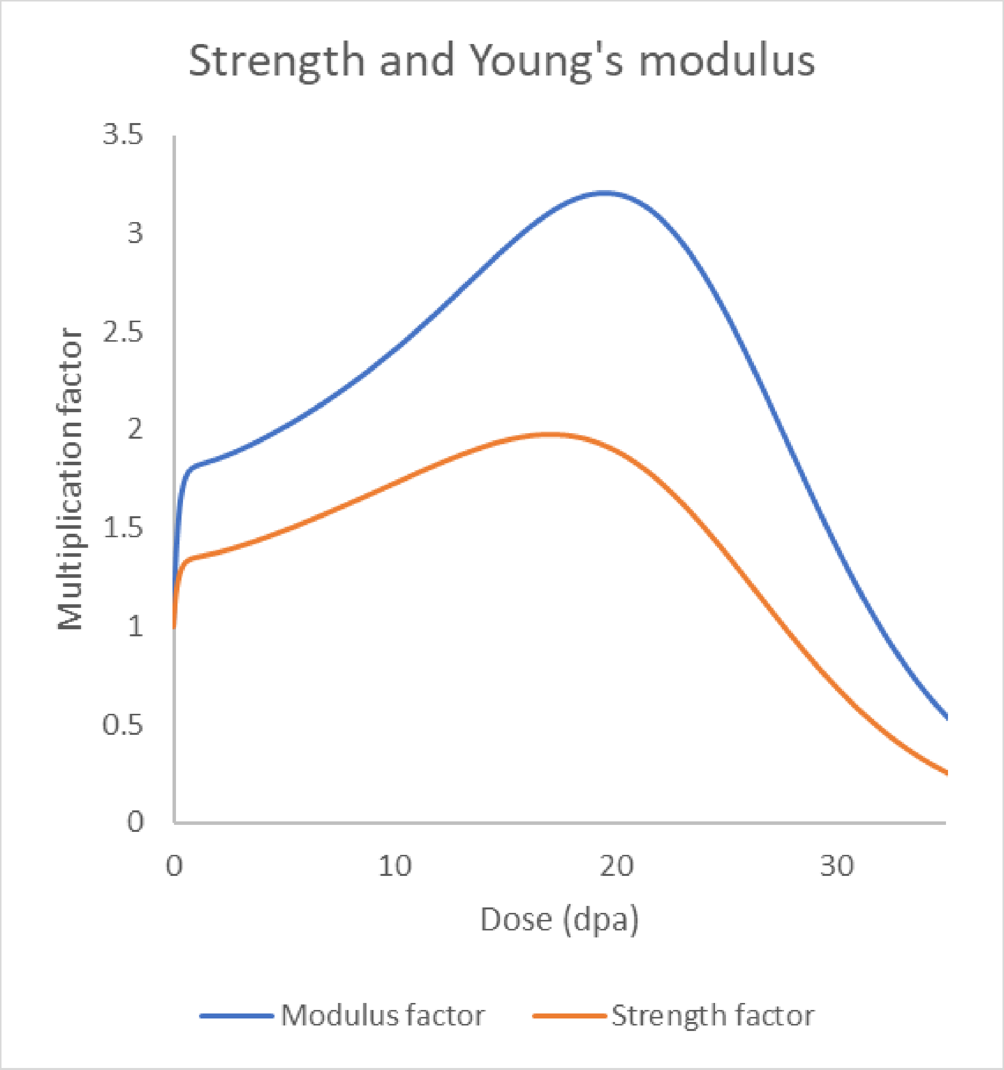
- Rapid initial rise (pinning),
- Gradual, approximately linear increase (densification),
- Faster increase up to peak (structural connectivity); then
- Decrease beyond the peak (pore generation)



Strength

- Strength changes are caused by the same physical processes as Young's modulus changes. The same model form is used, but the pinning and structure terms are raised to an exponent k, typically 0.5 (based on fracture mechanics)
- Densification and pore generation components of strength model apply equally to Young's modulus and strength
- All strength values are assumed to vary equally with irradiation (tensile, compressive etc.)
- In ASME code, strength change with irradiation can be omitted where this is conservative. Strength typically falls to initial value somewhere around dimensional change crossover

$$S = S_0[P'(1 + C \times S_c(\gamma))]^k e^{-\beta_d \Delta v_d} e^{-\beta_{pg} \Delta v_{pg}}$$



Coefficient of Thermal Expansion (Effect of Irradiation, Unstressed)

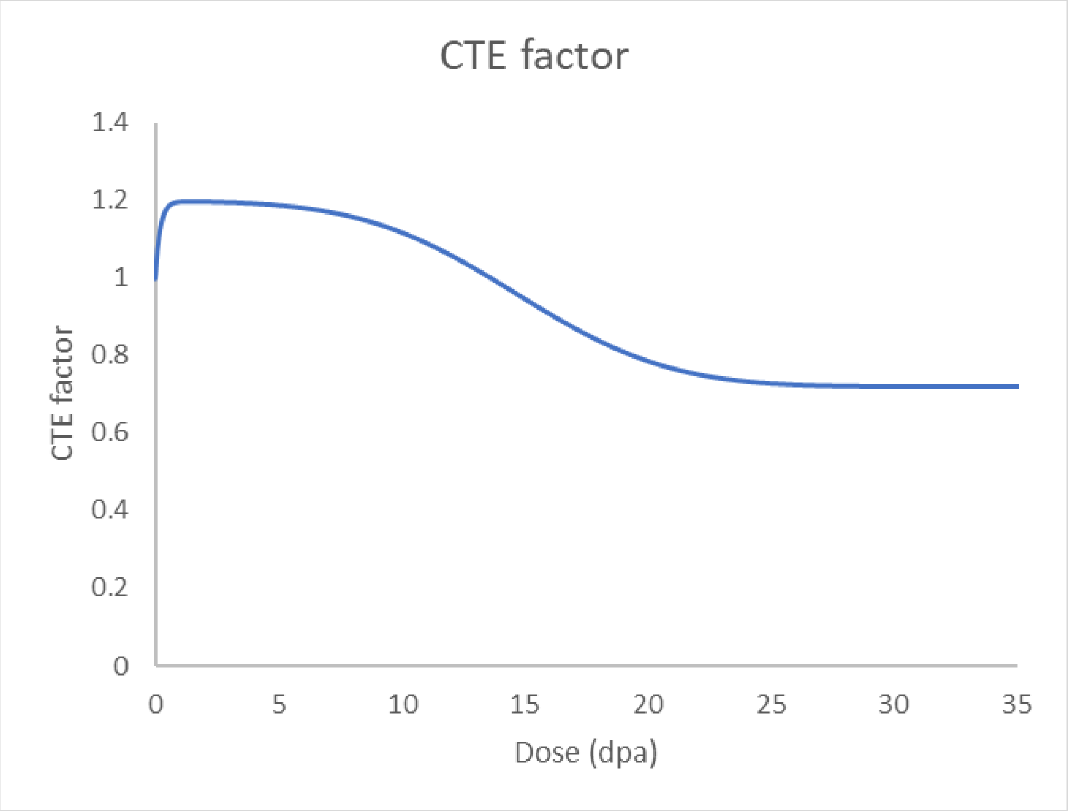
In isotropic and near-isotropic graphite grades in the relevant temperature range, the CTE generally increases slightly at low dose before decreasing to a high-dose saturated value.

The high dose behavior is modelled using a structural connectivity curve. It is understood that different parts of the microstructure control CTE and other mechanical properties.

$$\frac{CTE}{CTE_0} = P'_{CTE}(1 - D \times S_{c_{CTE}})$$

S_{c_CTE} has the same form as S_c in the dimensional change and Young's modulus model but different parameters (μ and σ are not the same as those used in the dimensional change model).

- Model parameters are irradiation temperature dependent
- CTE also depends on the measurement temperature
- CTE is affected by creep strain



Irradiation Creep

- If graphite is subjected to a load while simultaneously being irradiated, an additional strain is observed. Irradiation creep is defined as the difference in strain between graphite under load and non-loaded graphite in the same irradiation conditions.
- Irradiation creep includes a small, rapid initial creep strain (‘primary creep’), which is fully recoverable with further irradiation if the load is removed
- Higher dose irradiation under load leads to a larger strain, generally treated as being permanent. This is referred to as ‘secondary creep’.
- There is evidence for recovery of irradiation creep significantly in excess of the primary creep strain, on longer dose scales. Therefore, an additional ‘recoverable creep’ component is included in the model.
- Irradiation creep remains subject to significant conceptual uncertainty, therefore alternative creep model formulations may be applied to explore sensitivity to assumptions
- The model described here was developed by Davies and Bradford*, based on historic UK creep models

**A revised description of graphite irradiation induced creep, J. Nuc. Mat, 2008, M. A. Davies and M. R. Bradford*

Irradiation Creep Model

The creep strain, ε_c is calculated as $\varepsilon_c = \varepsilon_{c,p} + \epsilon_{c,s} + \varepsilon_{c,r}$ where the three terms represent the primary, secondary and recoverable creep, respectively. These are determined by integrating the following equations with respect to dose γ:

$$\frac{d\varepsilon_{c,p}}{d\gamma} = k_{c,p}\frac{\alpha}{E_0 S'}\sigma e^{-k_{c,p}\gamma}$$

$$\frac{d\varepsilon_{c,s}}{d\gamma} = \frac{\beta}{E_0 S'}\sigma$$

$$\frac{d\varepsilon_{c,r}}{d\gamma} = k_{c,r}\frac{\omega}{E_0 S'}\sigma e^{-k_{c,r}\gamma}$$

The primary and recoverable creep dose scales values $k_{c,p}$ and $k_{c,r}$ depend on the irradiation temperature, with primary creep occurring over a shorter dose scale than recoverable creep. S' is the Young's modulus structure factor as previously defined, equal to $\frac{E}{E_0 P\prime}$. There are three creep coefficients, α, β and ω. The secondary creep coefficient β is known to vary with irradiation temperature.

Effect of Irradiation Creep on Other Properties

There is extensive evidence for a large effect of irradiation creep strain on the Coefficient of Thermal Expansion and inconsistent evidence for a small effect of creep on the elastic modulus. In the current model formulation, the effect of creep on the CTE is as follows:

$$\frac{CTE_s}{CTE_u} = 1 + a_{cte,p}\epsilon_{c,p} + a_{cte,r}\epsilon_{c,r}$$

- The CTE is allowed to vary with primary creep and recoverable creep but not secondary creep
- The elastic modulus is assumed not to vary as a function of creep strain
- The evolution of stress and strain in three dimensions in combination with spatially varying dose, irradiation temperature and instantaneous temperature together lead to a complex distribution of thermal expansion with significant implications for stress in nuclear graphite components, in particular at shutdown

Summary of Model Framework

A semi-empirical model for the irradiation response of graphite has been presented with the following characteristics:

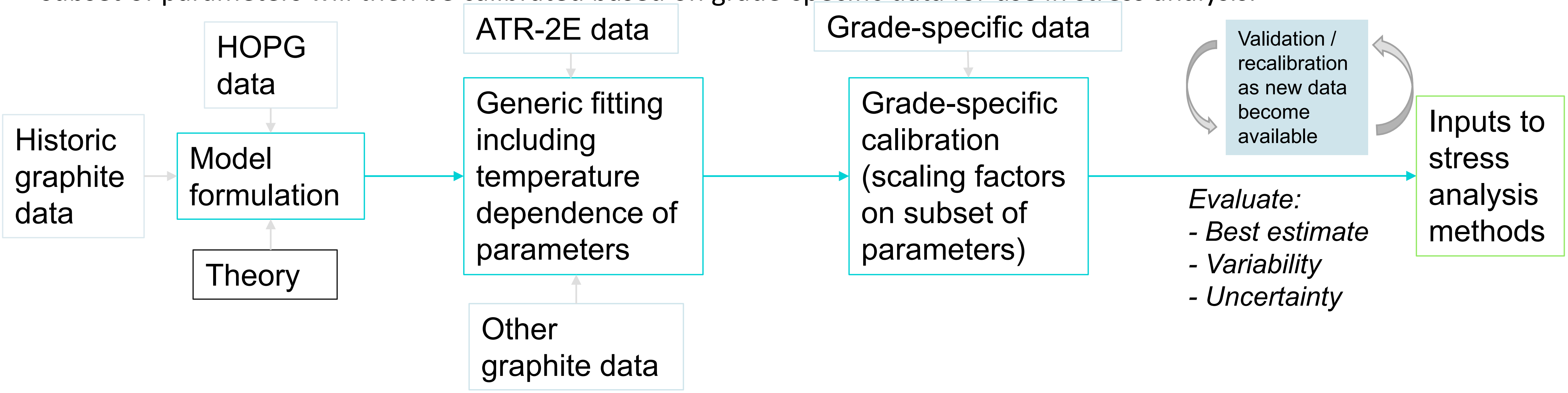
- Underlying dimensional change curve based on HOPG-derived single-crystal behavior
- Closure of accommodation porosity represented by cumulative normal distribution
- Dimensional change modelled as the sum of:
  - Underlying shrinkage
  - Pore generation following from closure of accommodation porosity
- Young's modulus depends on:
  - Low-dose irradiation 'pinning'
  - Structural connectivity (closure of accommodation porosity)
  - Exponential functions of volume changes due to underlying shrinkage and pore generation
- Strength has the same model form as Young's modulus, but depends on the square root of the pinning and structural connectivity terms
- CTE has a similar form: rapid initial rise, high dose reduction following structural connectivity curve (assumed to be different to Young's modulus, Strength and DC)
- Creep model includes primary and secondary creep, plus an additional slow recoverable creep term. Creep rate is modified by the Young's modulus structure term.
- The CTE is modified by the creep strain (primary and recoverable components)

Model Fitting and Grade-Specific Calibration

The model framework was originally developed for the AGR power stations, which use a mix of gilsocarbon graphite grades. The model was fitted to gilsocarbon and ATR-2E data then calibrated to station-specific data for gilsocarbon grades. A similar approach may be taken for other reactors, accounting for differences in grade and irradiation environment.

The most complete set of irradiated data is for ATR-2E, a historic extruded, medium-grain, near-isotropic German graphite grade made using pitch coke. Good irradiation data exists for several other grades covering different coke sources and forming methods (e.g. summary on next slide).

The overall fitting approach starts from historic data and theory, with most parameters being common to all grades. A subset of parameters will then be calibrated based on grade-specific data for use in stress analysis.

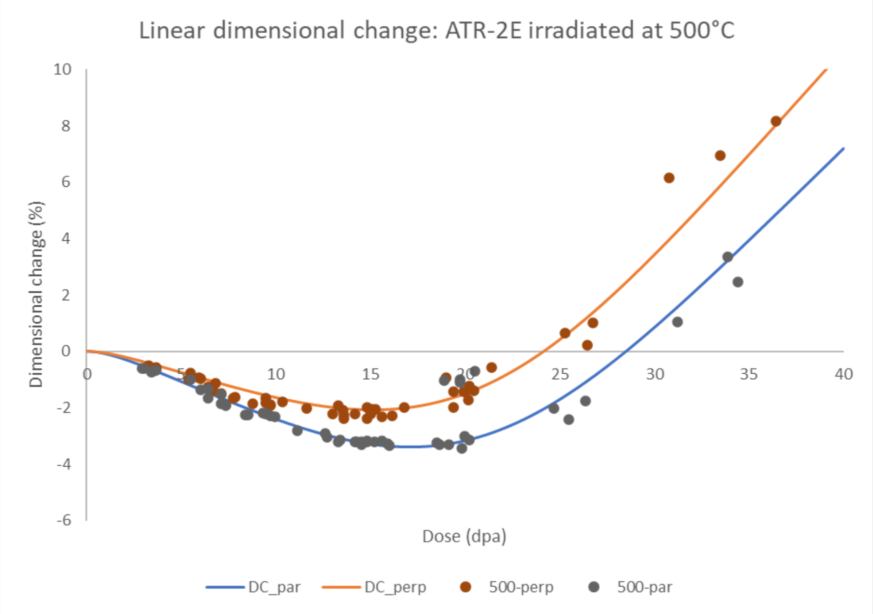


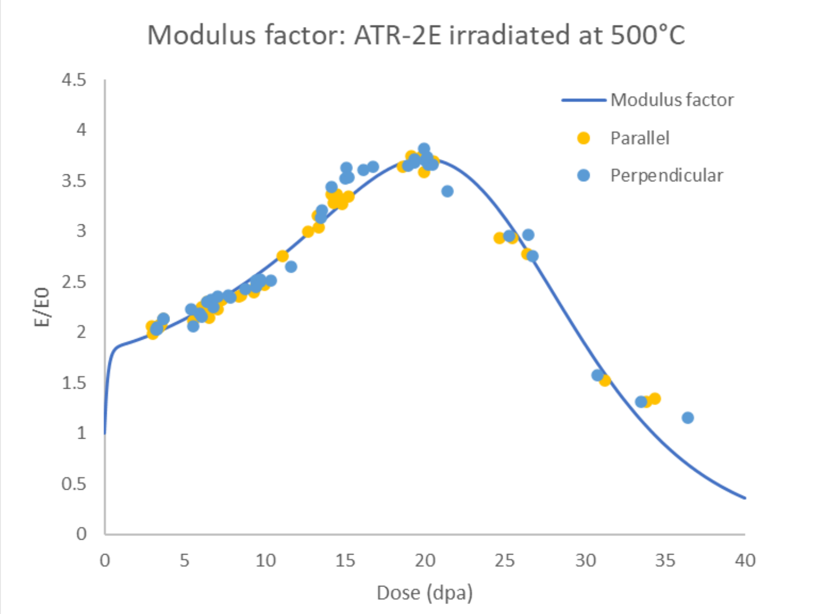
Summary of Historic Data – Example Grades

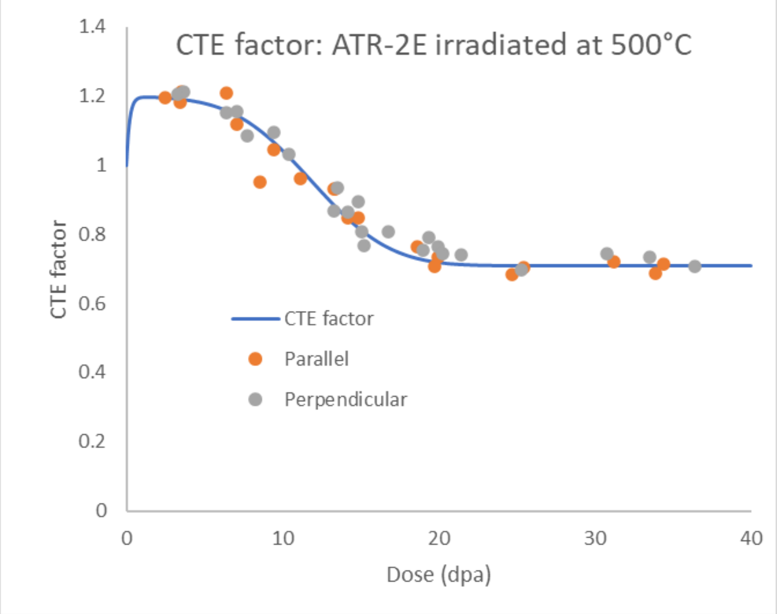
Grade name	Coke type	Forming method	Approx. temperature range (°C)
ATR-2E	Pitch	Extrusion	300-1100
ATR-2R	Pitch	Vibro-molding	300-600
IM1-24	Gilsonite	Molding	300-1400
IG-110 (still available)	Petroleum (fine grain)	Iso-molding	240-1100
H-451	Petroleum	Extrusion	400-1450
G-347A (still available)	Pitch (fine grain)	Iso-molding	300-700

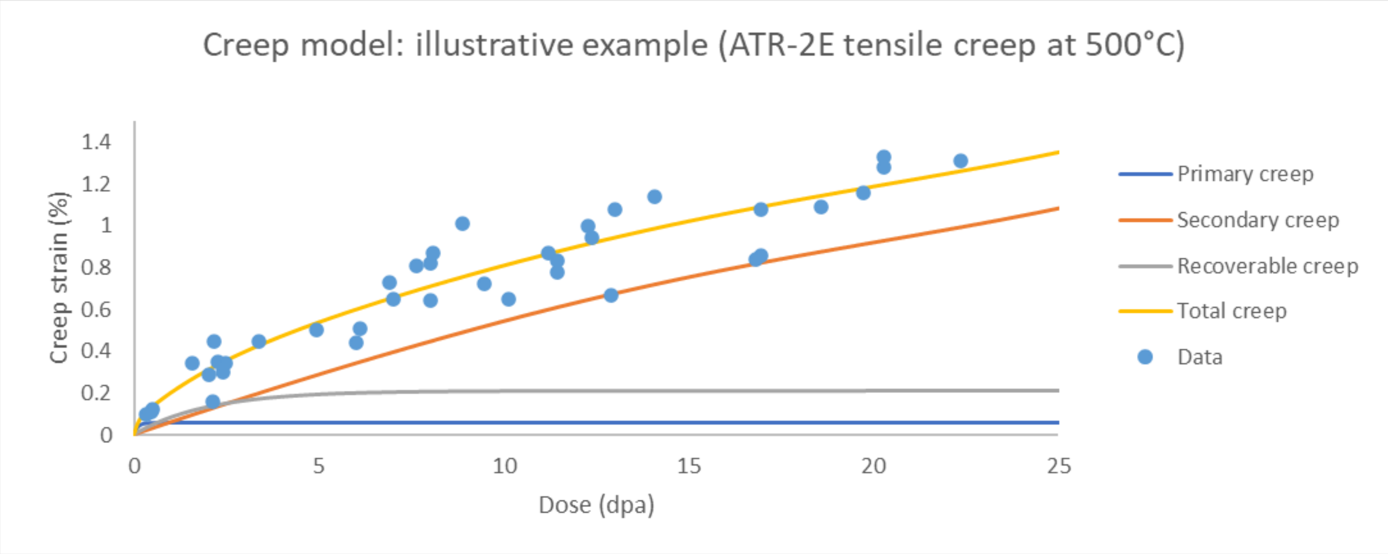
Table shows selected grades and approximate irradiation temperature ranges (not all properties are available for all temperatures).

Example Fits: ATR-2E at 500°C (Illustrative)



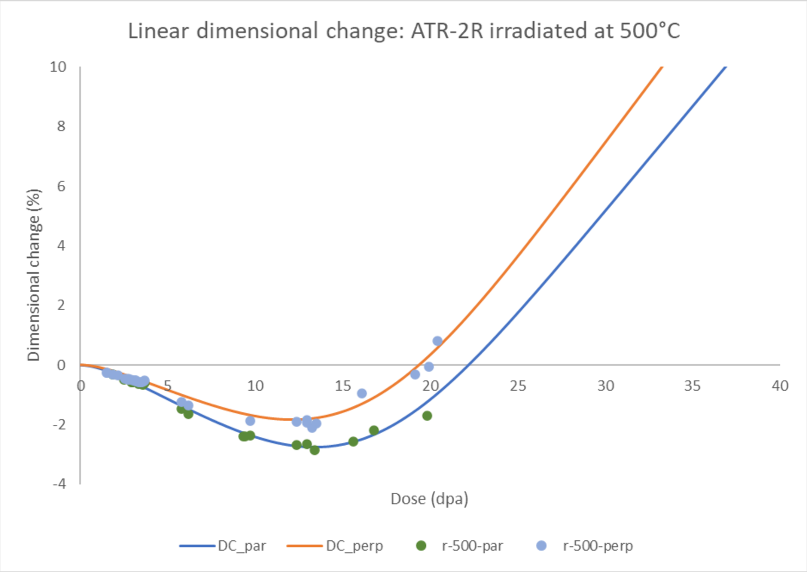




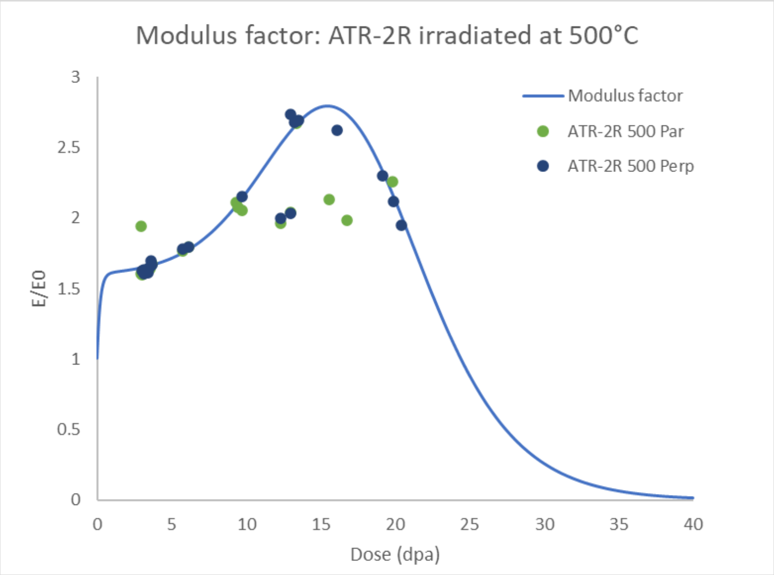


Example: Calibration to ATR-2R (Illustrative)

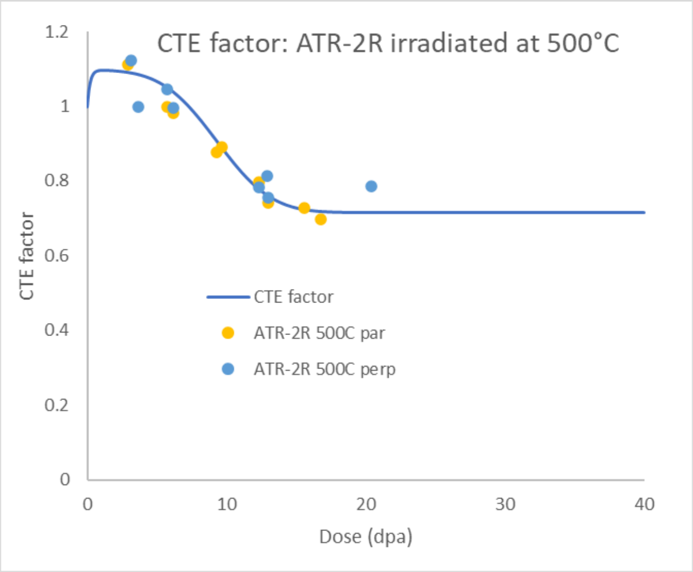
Using the parameter fit for ATR-2E (extruded grade), adjust a limited subset of parameters to fit data for ATR-2R (molded grade). Allows reasonable confidence in predictions despite relatively limited data.



Calibrate:
- Scaling factors on A_{DC} (both orientations)
- Scaling factor on μ_{DC}



Calibrate:
- Scaling factor on P (pinning)
- Scaling factor on C (structural connectivity term)
- Exponential DC terms (optional)



Calibrate:
- Scaling factor on P_{CTE} (pinning)
- Scaling factor on D (structural connectivity term)

Matters to Consider When Interpreting Irradiation Data

When interpreting irradiation data, some important matters must be born in mind:

- Irradiation temperature is uncertain and variable. Most properties depend on the irradiation temperature.
- Machining can induce stresses in small specimens which are relieved during the initial period of irradiation, leading to an additional component of measured dimensional change that is not directly applicable to reactor components
- Specimens are irradiated at high temperature in inert gas but generally measured in room temperature air. Correction for the difference between measurement and irradiation temperature can be important. Strength tends to be lower in atmospheric air than in dry reactor coolant.
- At low irradiation temperatures (<300-350°C), there is some evidence for flux-dependence of irradiation damage. Separating the potential 'equivalent temperature' effect from irradiation temperature uncertainty is challenging.
- Often, irradiation temperature in MTR samples is positively correlated with dose as both depend on the local radiation flux. This complicates the task of identifying trends with dose at a constant temperature. Data from experiments with good temperature control is preferred for model formulation. More variable data can be used to determine grade-specific properties.
- Changes to sample dimensions during irradiation can lead to unexpected temperature variation and/or stuck/constrained samples. This is a particular concern in creep experiments. Small differences in temperature between the loaded and reference specimen in a creep experiment can give the appearance of a large additional 'creep strain' at high dose.

References

A Structurally-based model of irradiated graphite properties, J. Nuc. Mat., 2008, M.R. Bradford and A.G. Steer

Qualitative Prediction of Graphite Material Properties, Presentation to INGSM-9, 2008, M. R. Bradford and M. Joyce

A Pragmatic Approach to the Use of Reactor Inspection Data, Presentation to INGSM-10, 2009, M. Joyce and M. R. Bradford

Some Observations on the Low Dose Behaviour of CTE and the Potential Implications for Reactor and MTR Experiment Design, Presentation to INGSM-6, 2005, M. R. Bradford, M. A. Davies and A. G. Steer

Assessment of EDF's graphite materials properties model in NP/SC 7766 V10 SS1 (Operation of HNB R3 to a burn up of 16.425TWd) and implications for the predicted brick stresses, dimensions and overall damage tolerance assessment, ONR-OFD-AR-19-093 Rev 0, 2020, UK Office for Nuclear Regulation

High Dose Fast Neutron Irradiation of Highly Oriented Pyrolytic Graphite, Carbon, 1971, B. T. Kelly and J. E. Brocklehurst

Physics of Graphite, 1981, B. T. Kelly

A revised description of graphite irradiation induced creep, J. Nuc. Mat, 2008, M. A. Davies and M. R. Bradford

Graphite Irradiation Induced Creep, Presentation to INGSM-8, 2007, M. A. Davies and M. R Bradford

A Review of the Graphite Irradiation Creep Data from the "OC-Series" of Experiments, ORNL/TM-2009/176, 2012, M. A. Davies and T. D. Burchell

Properties of ATR-2E Graphite and Property Changes due to Fast Neutron Irradiation, Jül-4183, 2008, G. Haag

Closed Portion

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Summary
of
Current and Planned Data
for
Material Model Calibration for Xe-100

Xe-100 Graphite Reflector Regions

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Xe-100 Temperature/Dose Envelope (Approximate; Subject to Change)

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ATR-2E Data Compared to Xe-100 Temperature/Dose Envelope

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National Lab/Institute	Title/Author(s)	Temperature Range (°C)	Maximum Dose (dpa)	Creep Data?
INL	Baseline, AGC-1, AGC-2, AGC-3	550-800	7	Yes
Petten	Innograph	750-950	17	No

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National Lab/Institute	Title/Author(s)	Temperature Range (°C)	Maximum Dose (dpa)	Creep Data?
ORNL	Campbell/Katoh	250-700	25-30	Yes
	Snead	400	6.8	Yes
INL	Baseline, AGC-1, AGC-2, AGC-3	550-800	7	Yes
Petten	Innograph	750-950	17	No
JAERI	Oku	750-1000	1.6	Yes

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Future Data - IG-110 and NBG-18

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Future Meetings

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- Present model implementation for finite element analysis

Questions