July 14, 2021

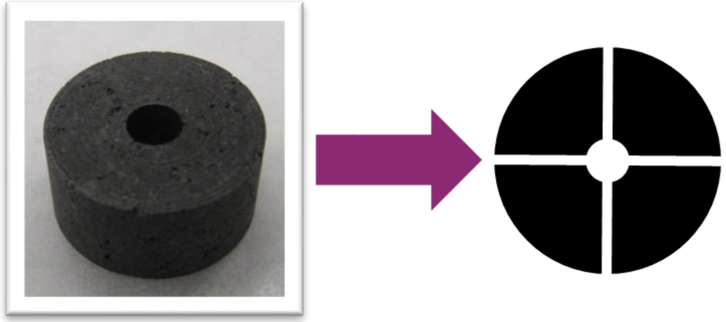
Rebecca Smith
Staff Engineer

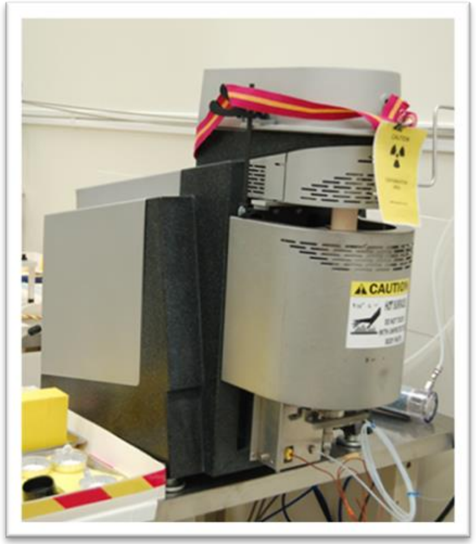
Graphite Oxidation Studies

Irradiated Graphite, GIF Summary, ASME Task Force, ASTM Activities

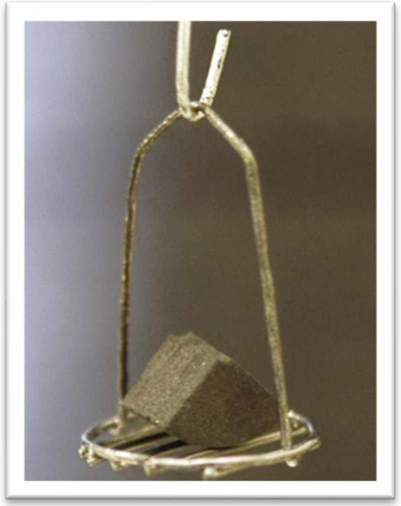
Advanced Reactor Technologies

Introduction

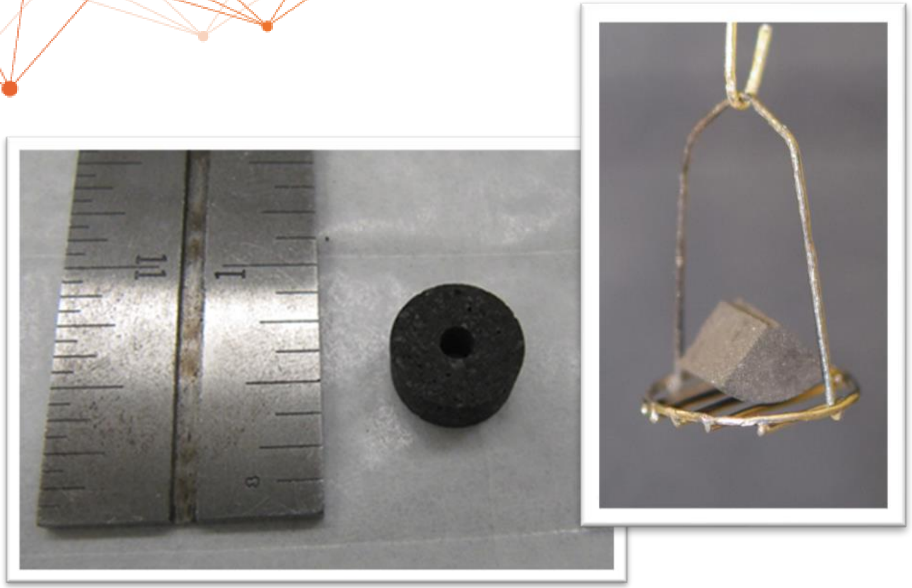


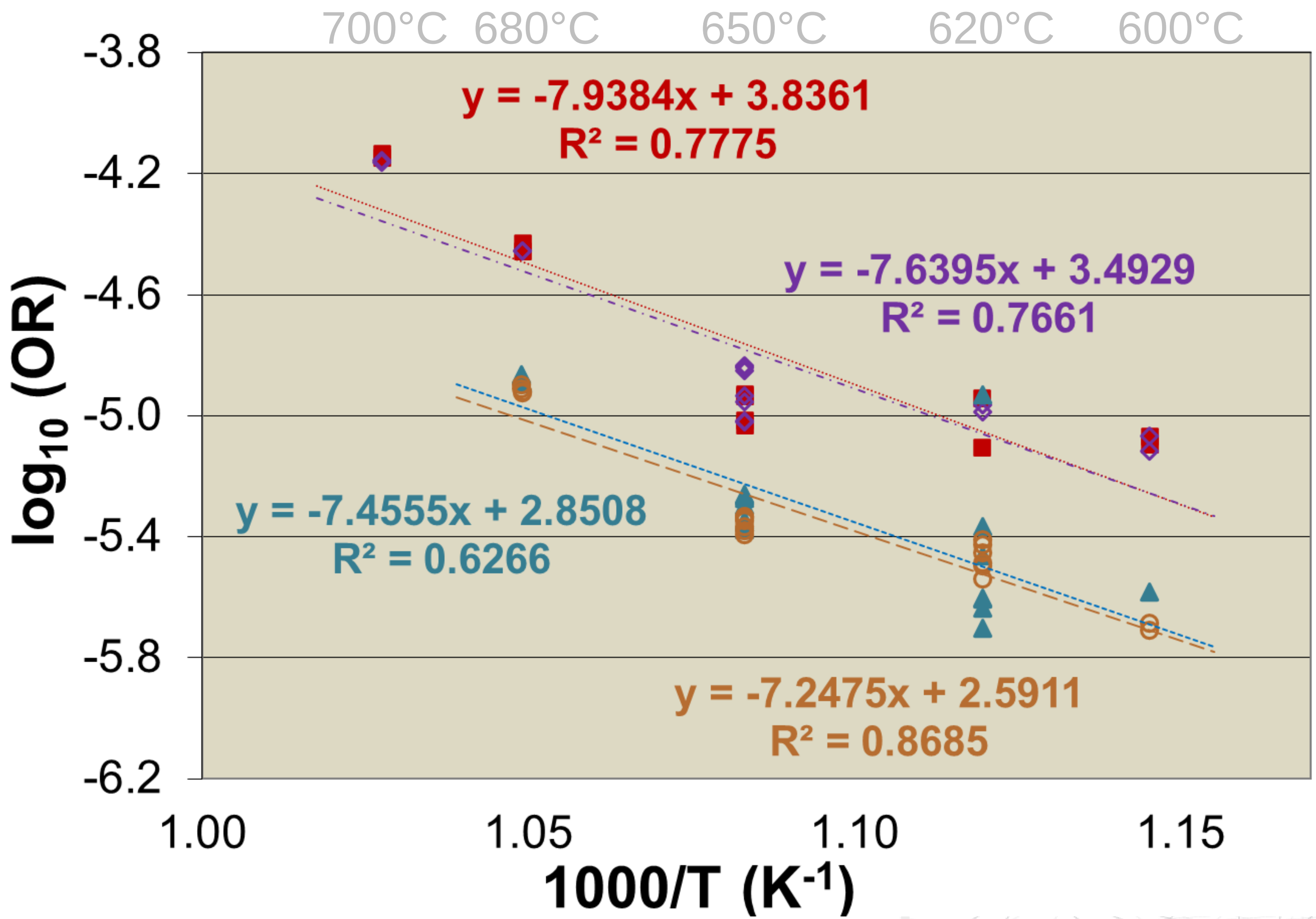


- Comparison of Graphite Oxidation Rates for Irradiated and Unirradiated NBG-25 (Rebecca Smith and Austin Matthews, INL)
  - Annealing effect over range of oxidation temperatures
  - Irradiation effect (~6.5 dpa) over range of oxidation temperatures
  - Dose dependency of irradiation effect
- Generation IV International Forum High Level Deliverable Summary of DOE ART Historic Oxidation Research (Cristian Contescu, ORNL)
  - Publications issued over the last ~10 years
  - Acute and chronic oxidation
- ASME Graphite Oxidation Task Force
  (C. Contescu, Paul Ryan, ORNL, Joe Bass, A. Matthews, R. Smith, INL)
  - Collaborative effort headed by ORNL and engaging INL and others
  - Initial review of relevant oxidation discussion in ASME code
- ASTM Activities (C. Contescu)
  - Virtual Meetings
  - New and Revised Standards

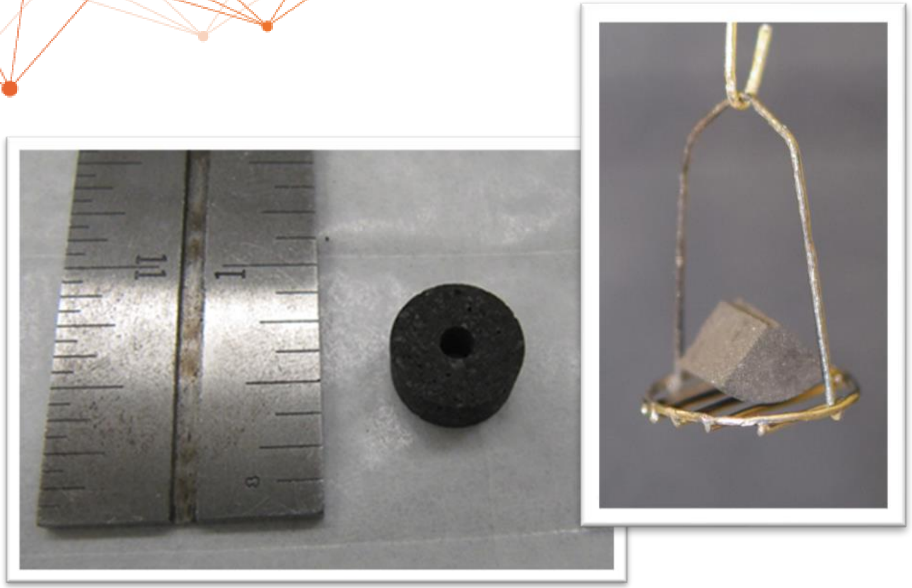


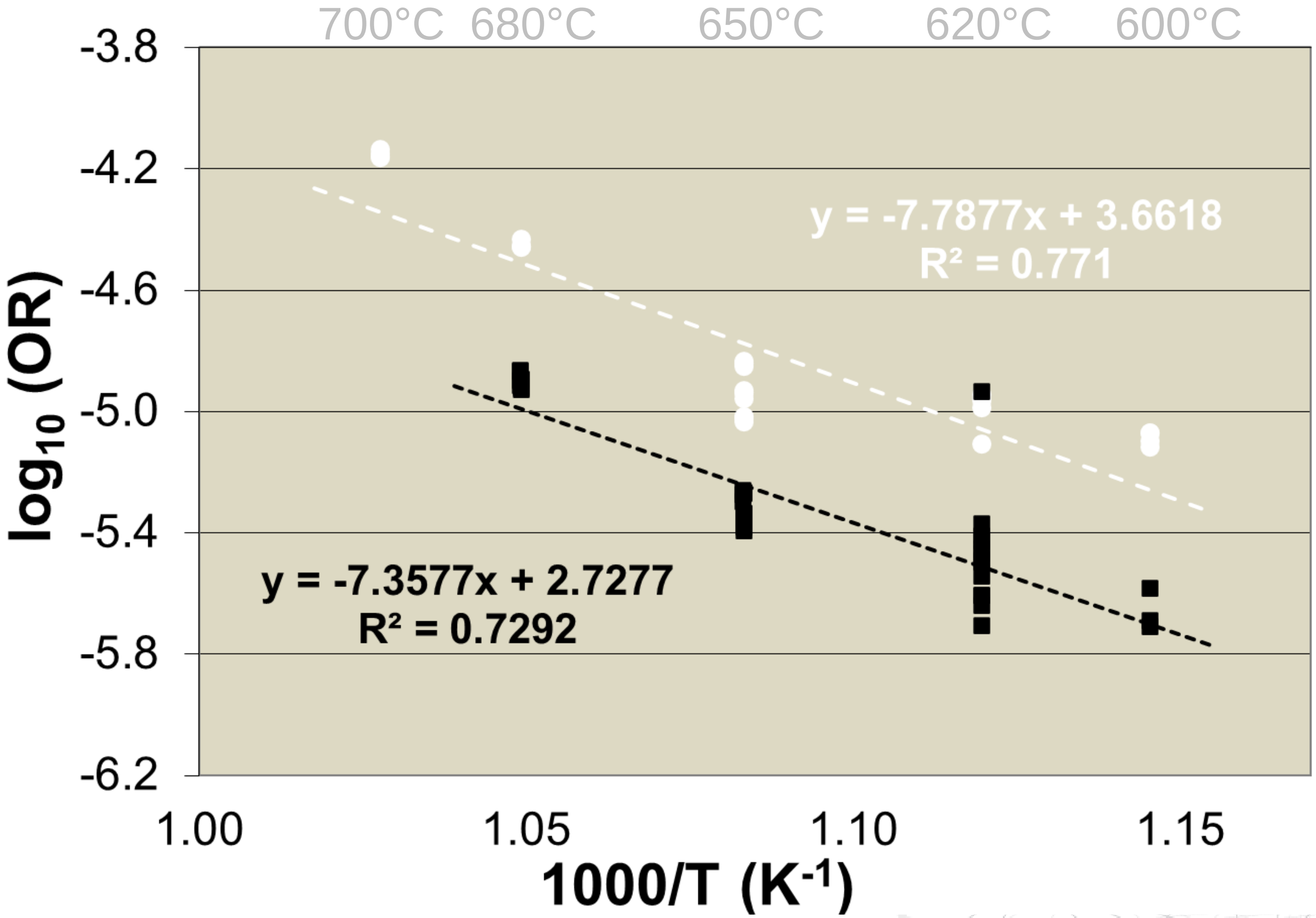
Unirradiated & Irradiated (~6.5 dpa), with and without Anneal



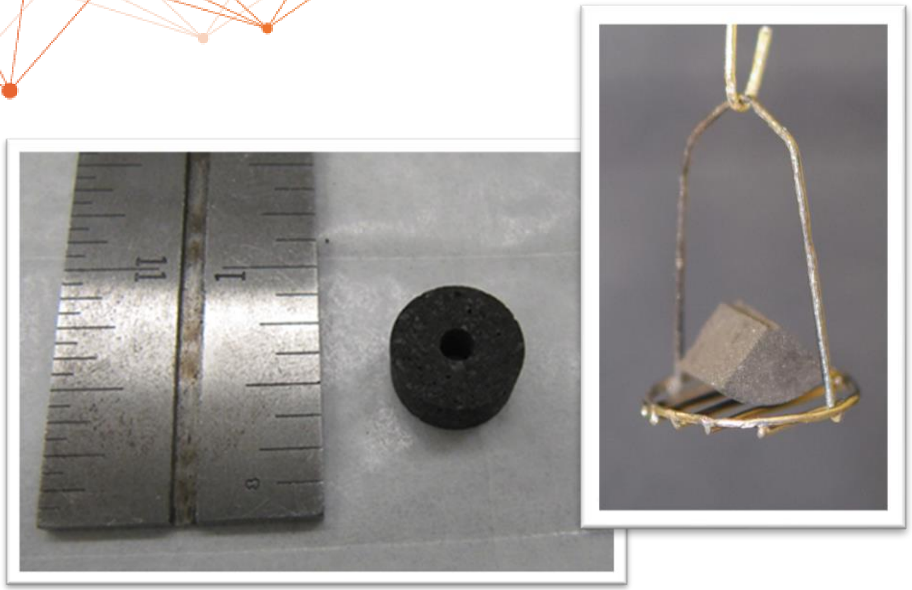


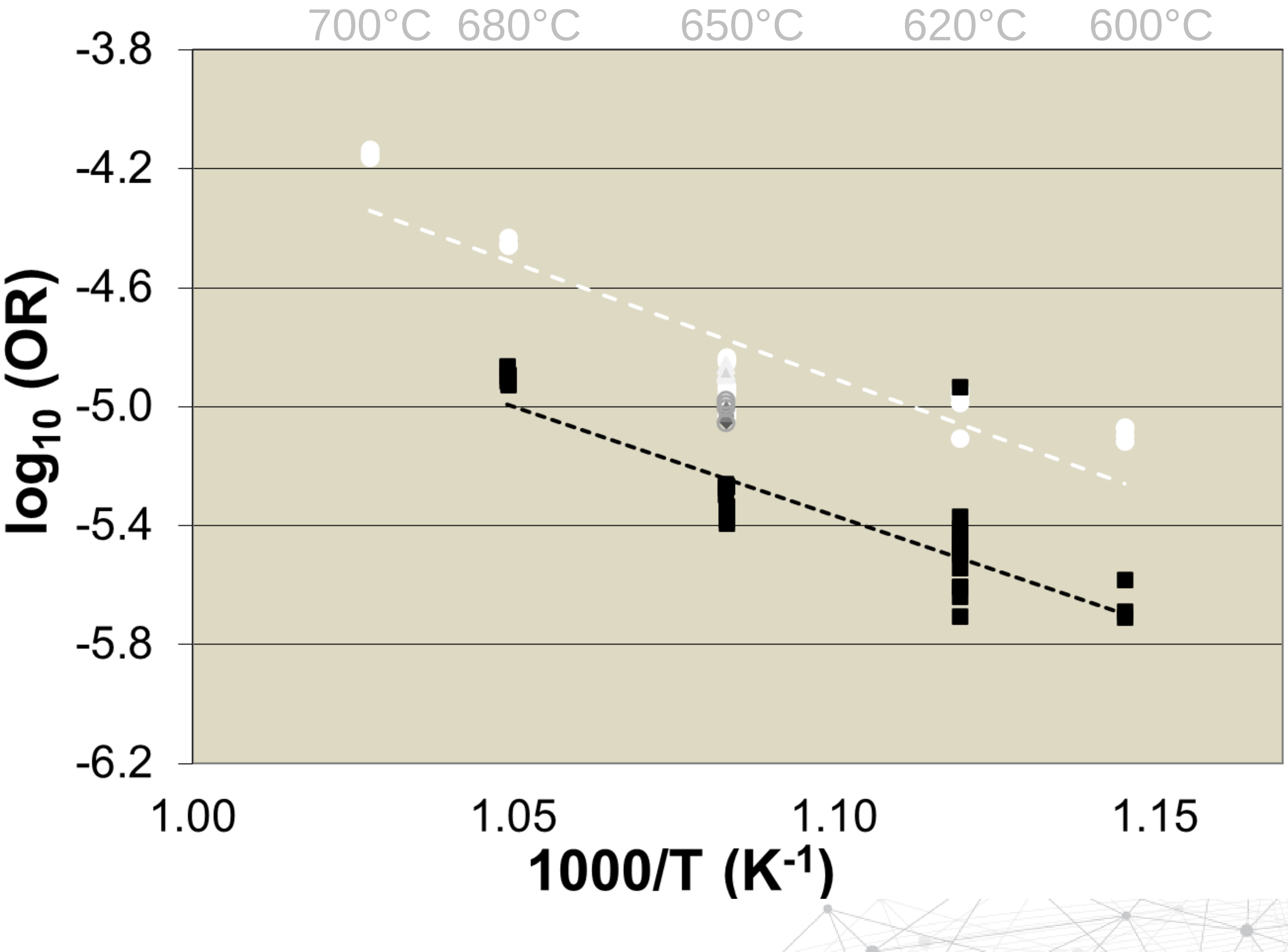
Unirradiated & Irradiated – Observed Effect at ~6.5 dpa





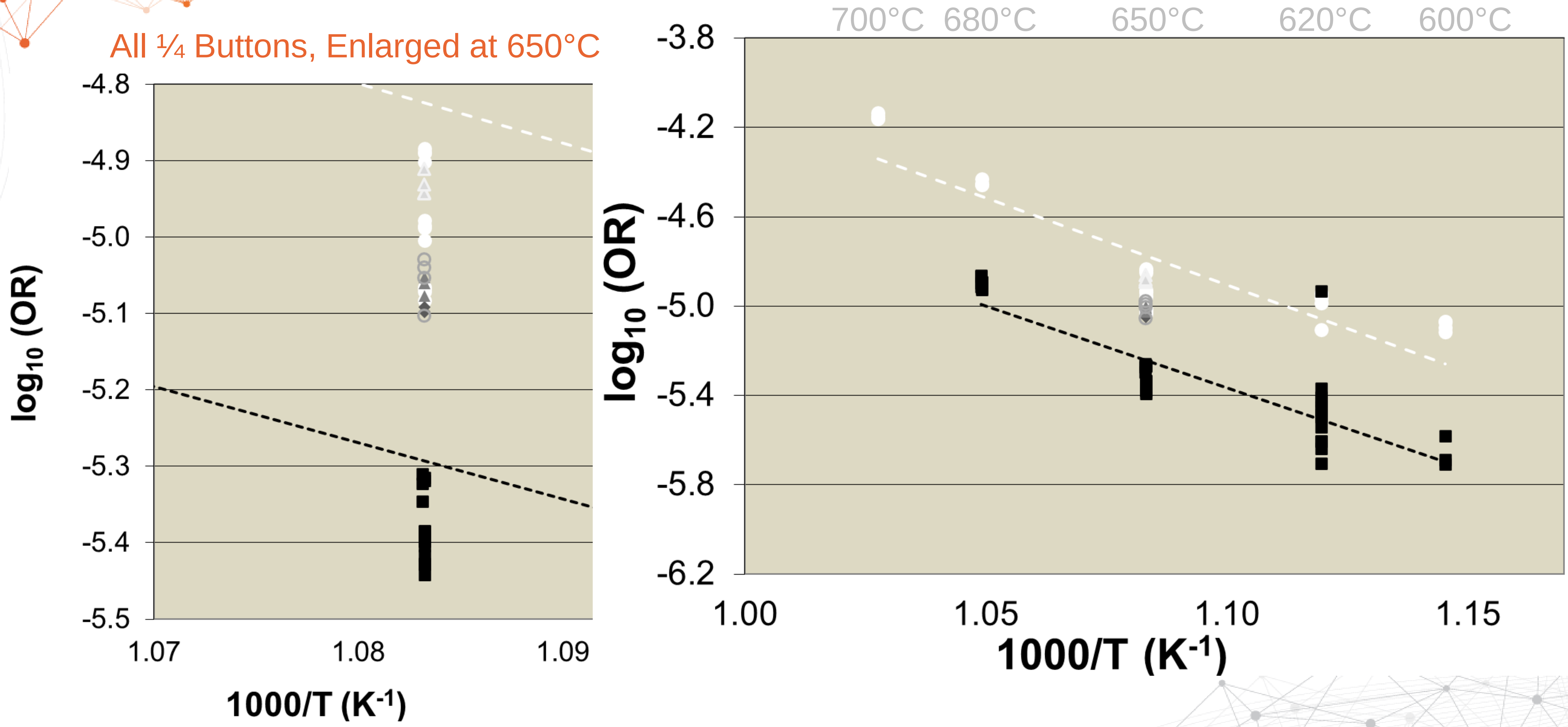
Unirradiated & Irradiated with Dose Dependency



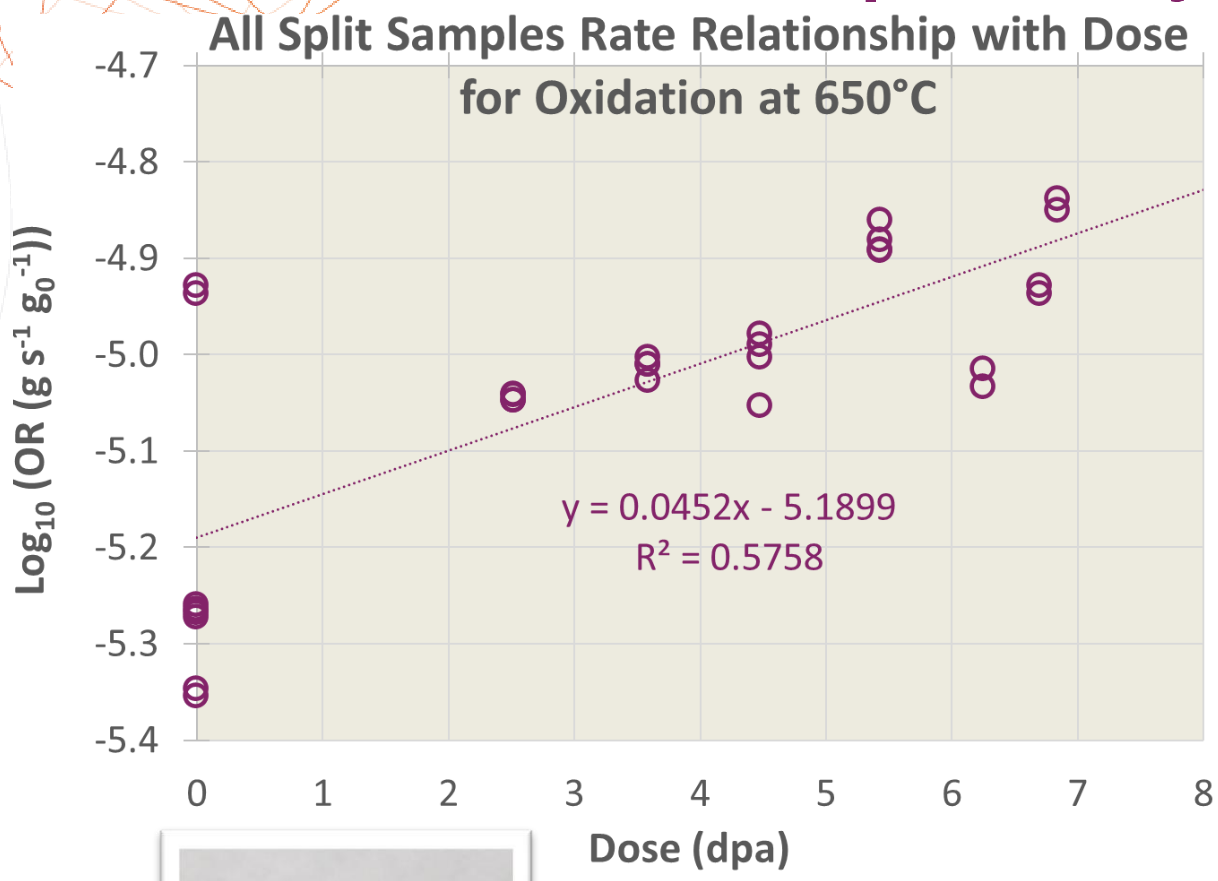


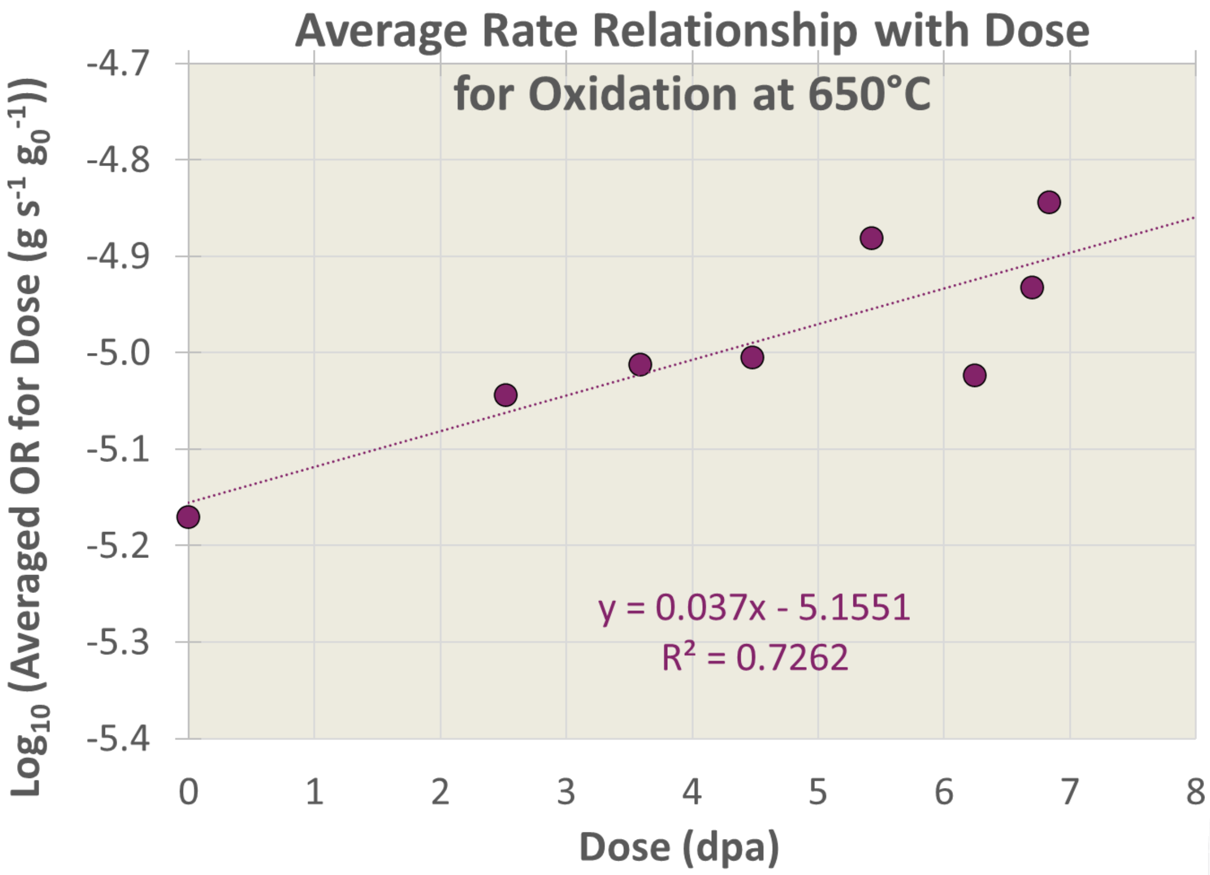
Unirradiated & Irradiated with Dose Dependency

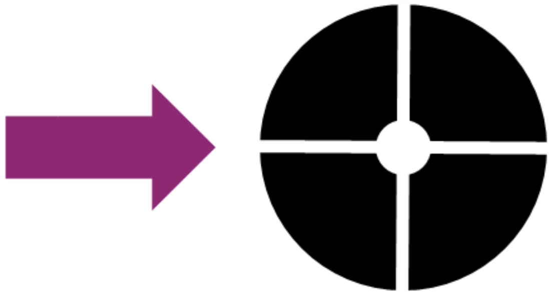
All ¼ Buttons, Enlarged at 650°C



Dose Dependency at 650°C



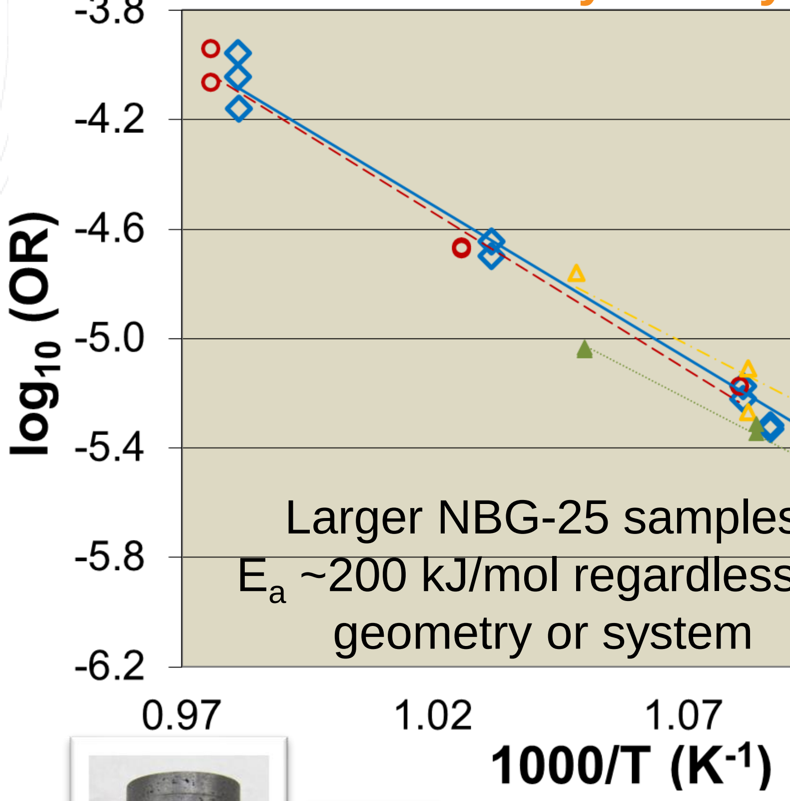




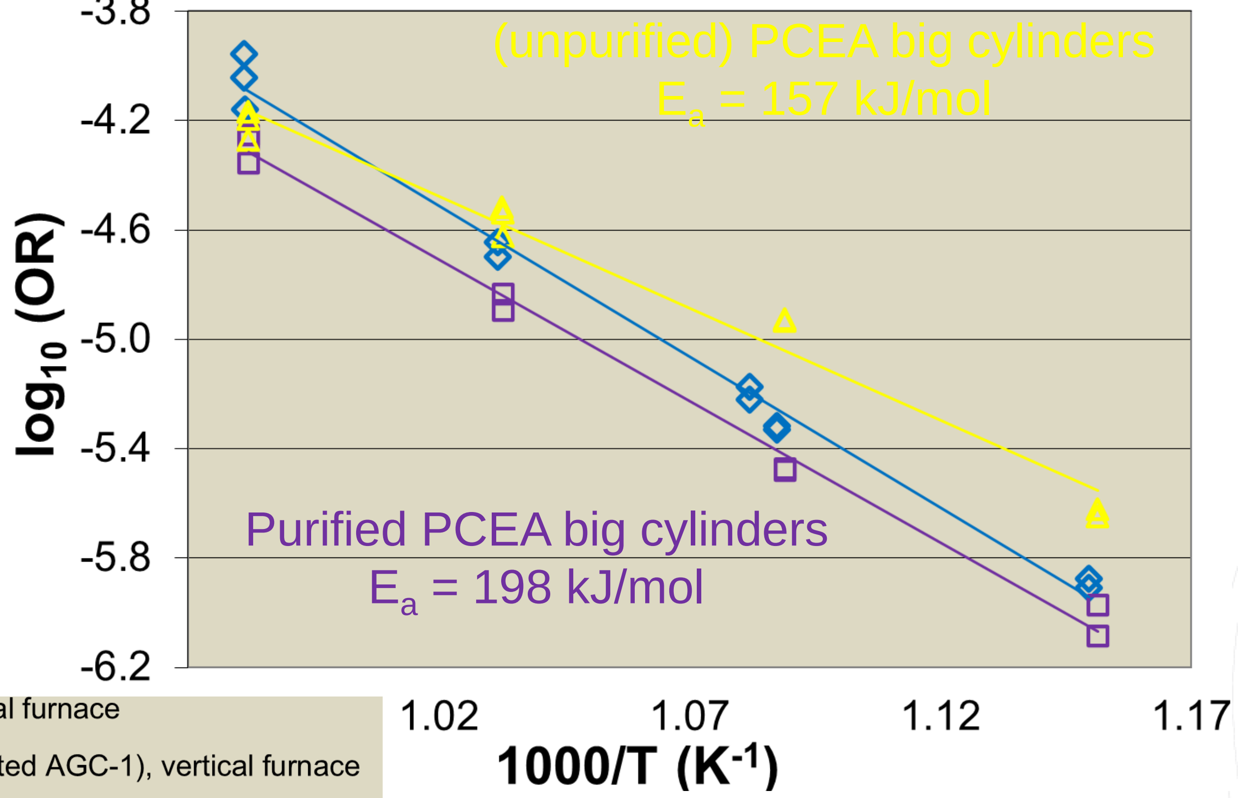
Approximately 10% Increase in Oxidation Rate for Each 1 dpa of Irradiation

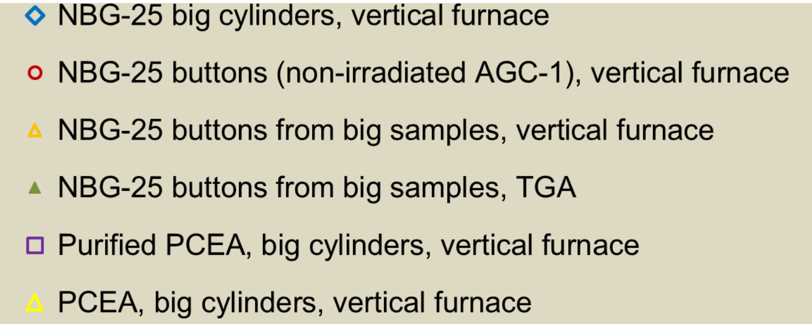
Comparison of Effective Activation Energies Suggests Presence of Catalyst (Older Data for Larger Samples)

Behavior of NBG-25 Samples with Geometry and System



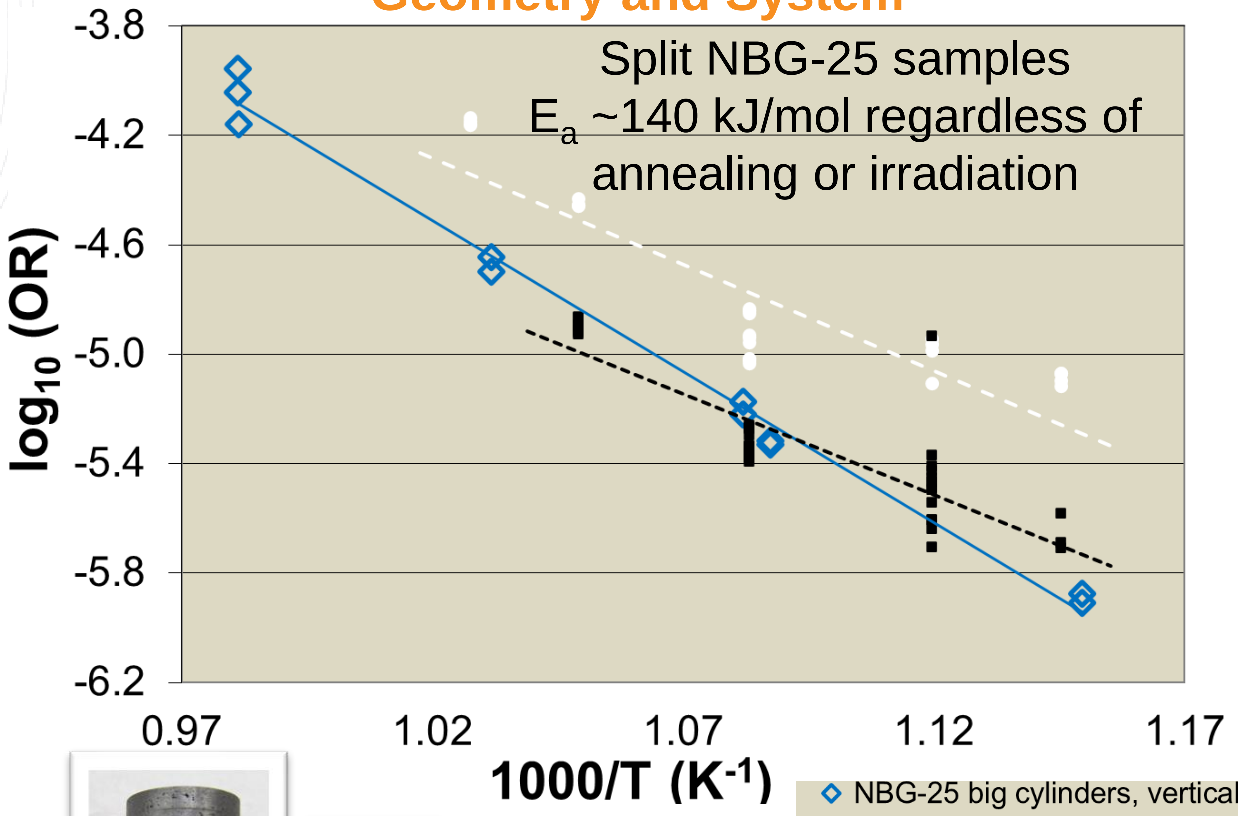
Behavior of Graphite Grades with and without Known Contaminants



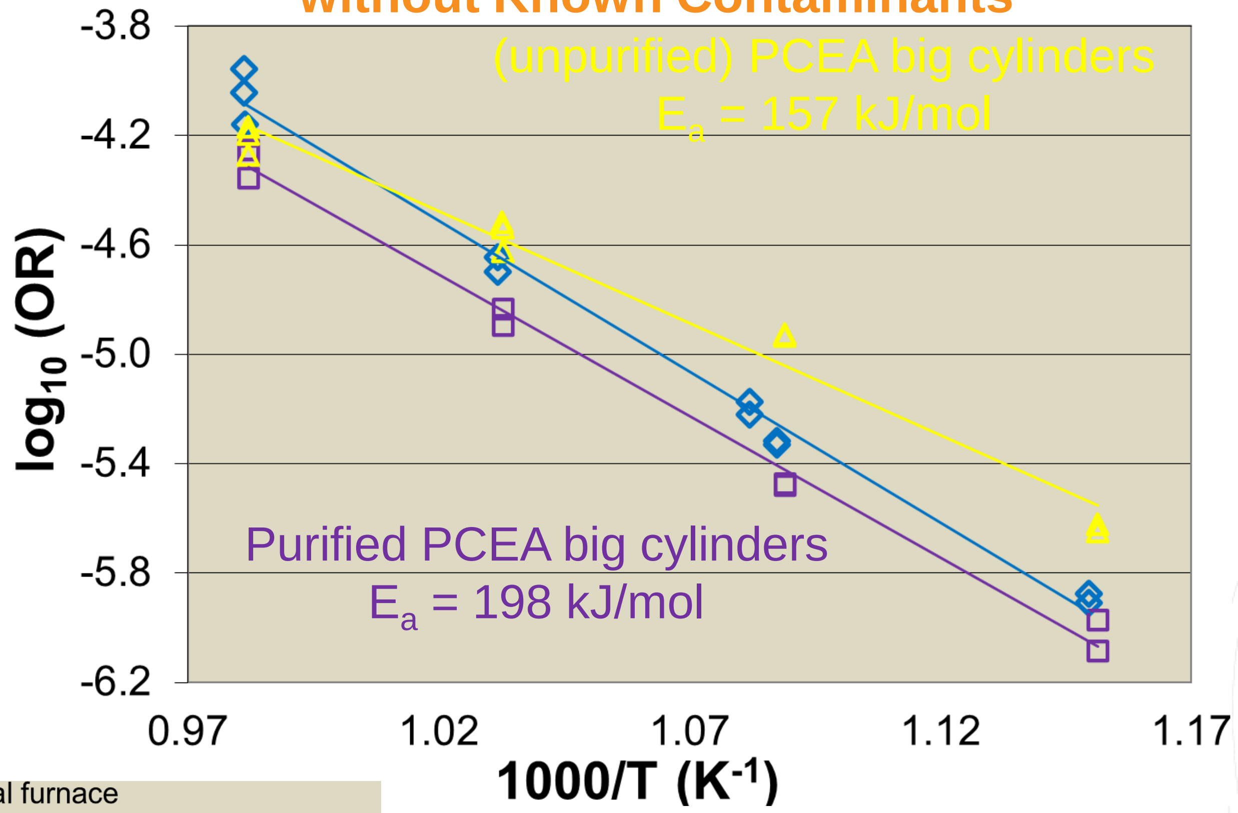


Comparison of Effective Activation Energies Suggests Presence of Catalyst in Split Samples, Not Larger NBG-25

Behavior of NBG-25 Samples with Geometry and System



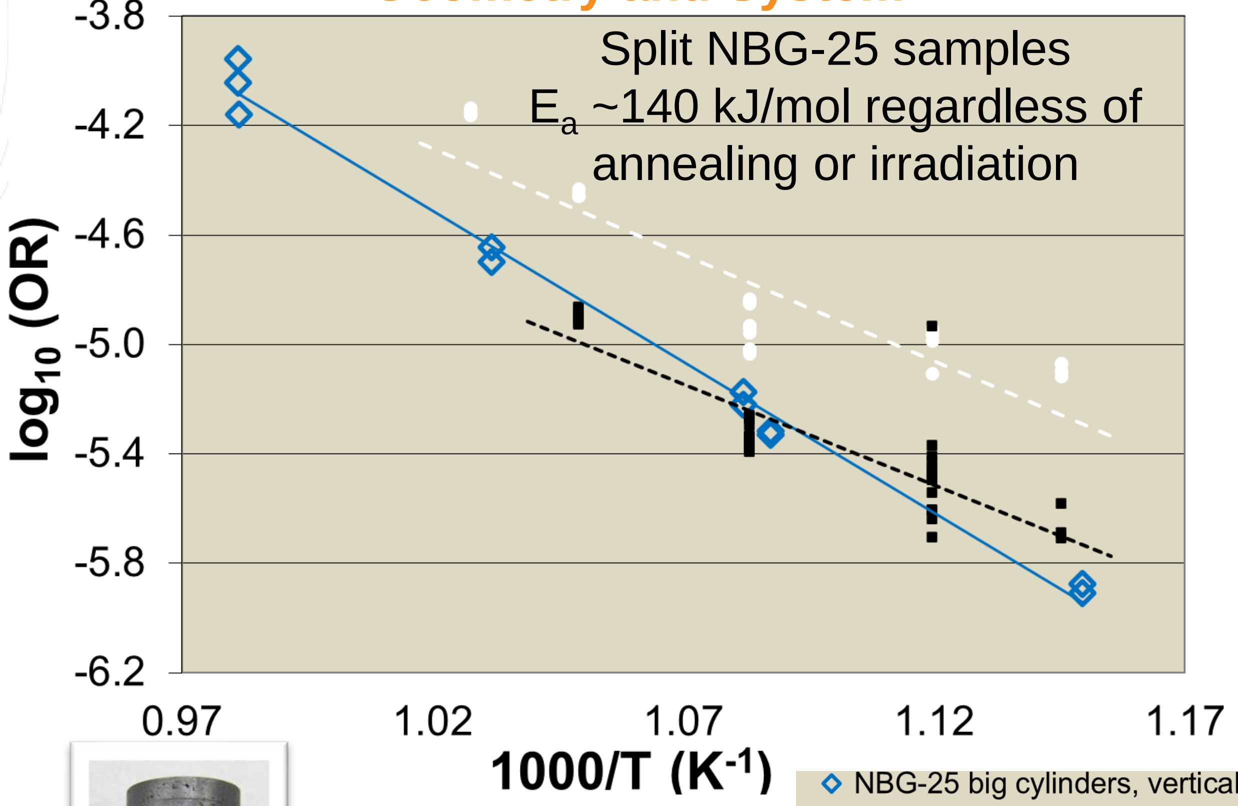
Behavior of Graphite Grades with and without Known Contaminants



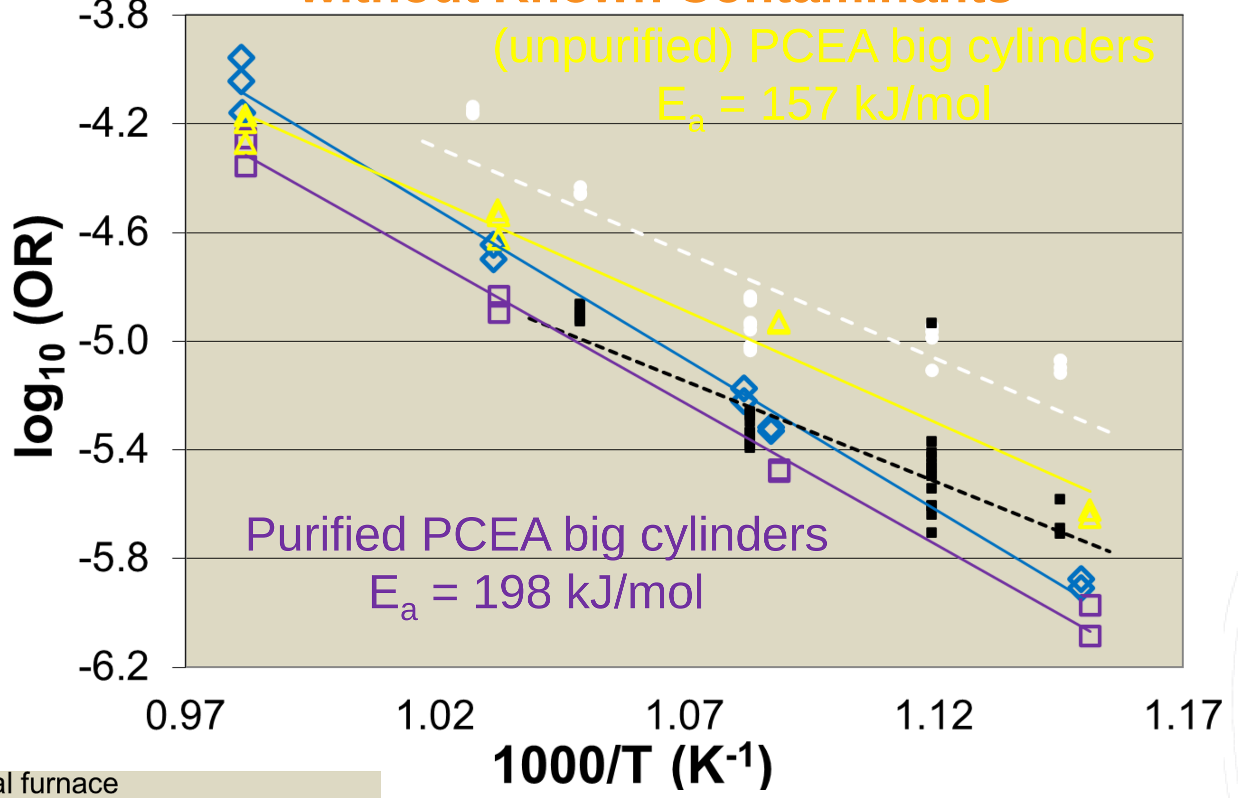
- NBG-25 big cylinders, vertical furnace
- NBG-25 all ¼ ~6.5 dpa irradiated buttons, TGA
- NBG-25 all ¼ combined unirradiated, TGA
- Purified PCEA, big cylinders, vertical furnace
- PCEA, big cylinders, vertical furnace

Comparison of Effective Activation Energies Suggests Presence of Catalyst in Split Samples, Like Observed with PCEA

Behavior of NBG-25 Samples with Geometry and System



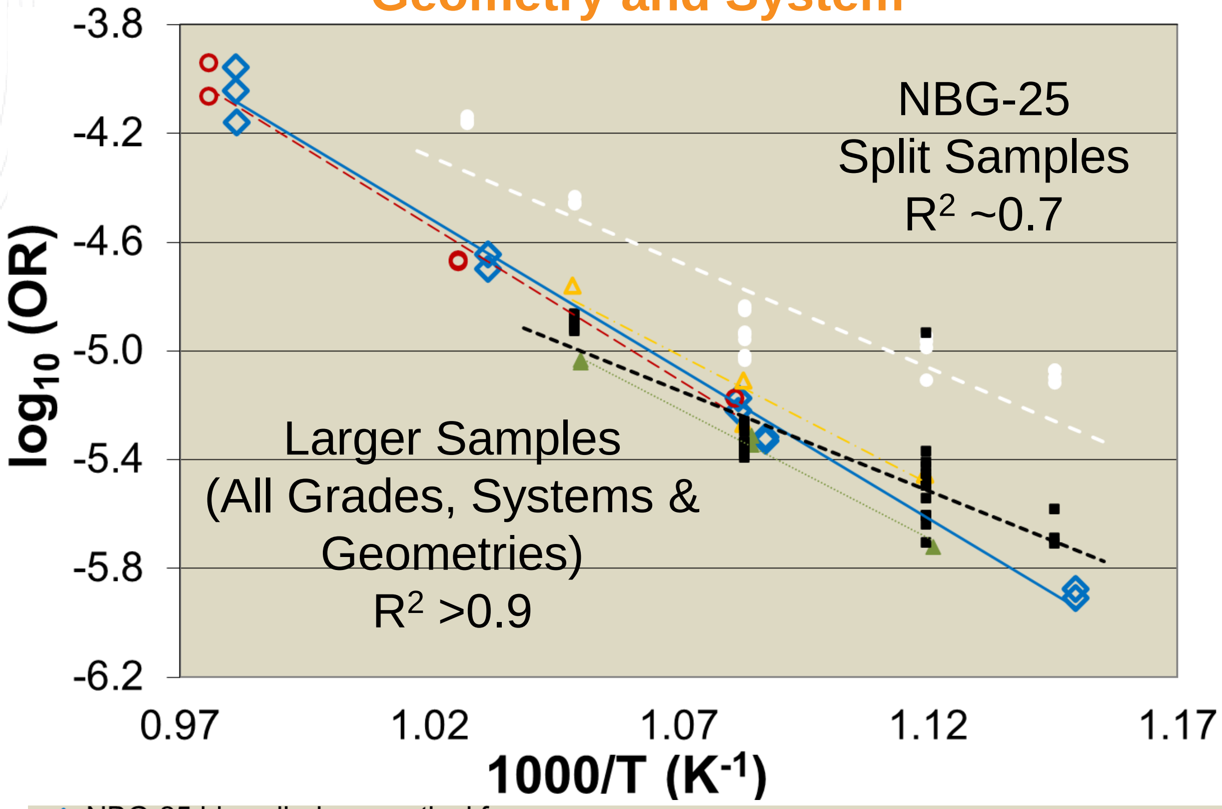
Behavior of Graphite Grades with and without Known Contaminants



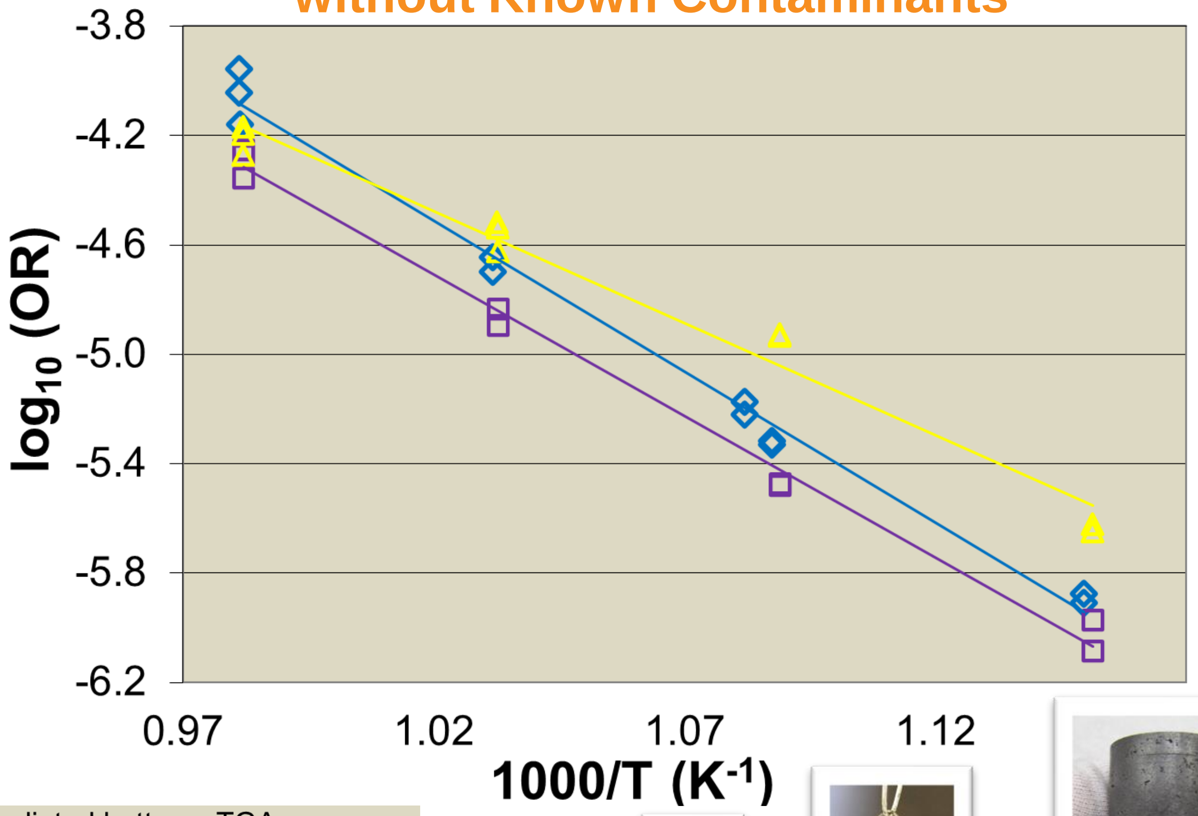
- ◇ NBG-25 big cylinders, vertical furnace
- ● NBG-25 all ¼ ~6.5 dpa irradiated buttons, TGA
- ▪ NBG-25 all ¼ combined unirradiated, TGA
- □ Purified PCEA, big cylinders, vertical furnace
- △ PCEA, big cylinders, vertical furnace

More Scatter in All Split Samples Compared to Others, Unirradiated Splits Fair Fit Overall, Definite Correlation to Dose

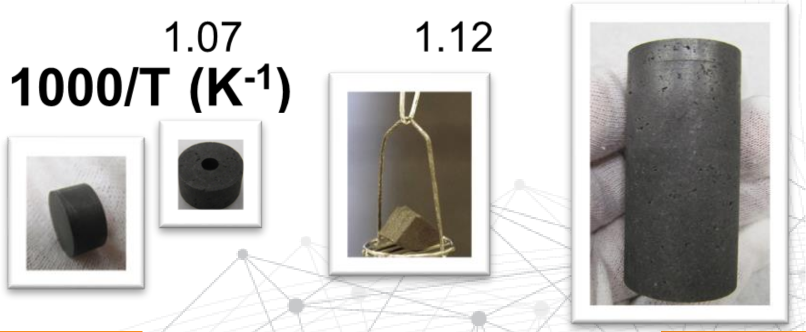
Behavior of NBG-25 Samples with Geometry and System



Behavior of Graphite Grades with and without Known Contaminants

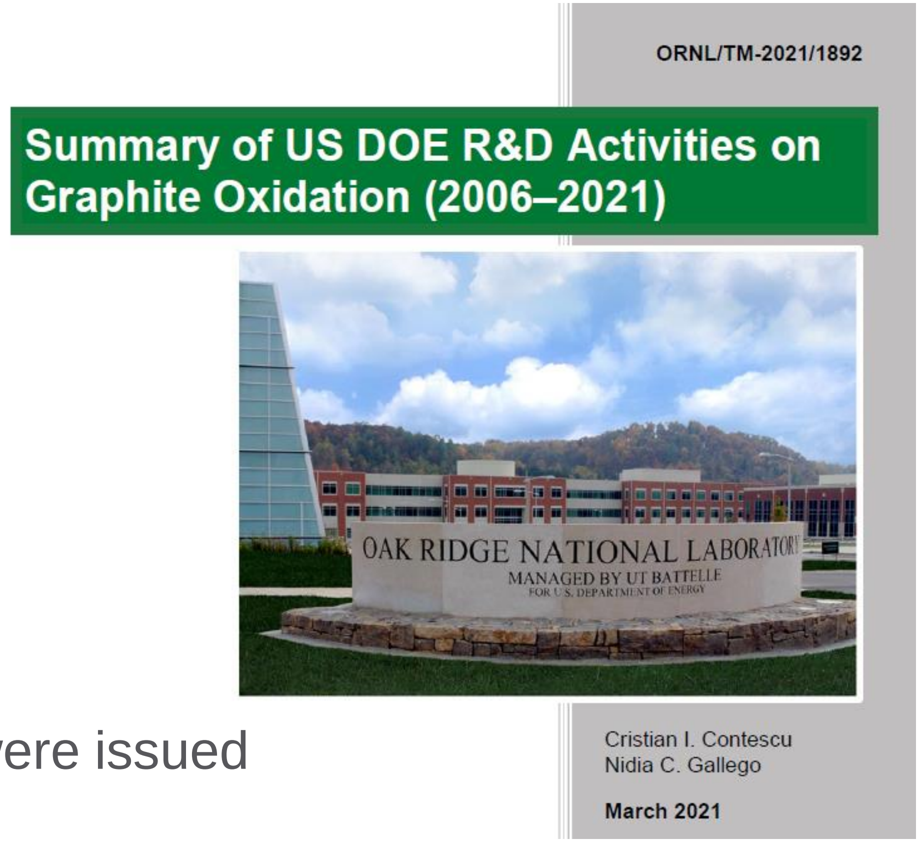


- ◇ NBG-25 big cylinders, vertical furnace
- ○ NBG-25 buttons (non-irradiated AGC-1), vertical furnace
- △ NBG-25 buttons from big samples, vertical furnace
- ▲ NBG-25 buttons from big samples, TGA
- ● NBG-25 all ¼ ~6.5 dpa irradiated buttons, TGA
- ■ NBG-25 all ¼ combined unirradiated, TGA
- □ Purified PCEA, big cylinders, vertical furnace
- △ PCEA, big cylinders, vertical furnace



International Collaboration: Generation IV International Forum

- Summary report on R&D activities funded by DOE-NE on graphite oxidation (2006-2021)
  - Completed (March 2021)
  - Will serve as input to Graphite Working Group for the High-Level Deliverable to the Project Management Board on Materials GIF
  - Outlines progress made on understanding graphite chronic and acute oxidation, effects on properties, and model development

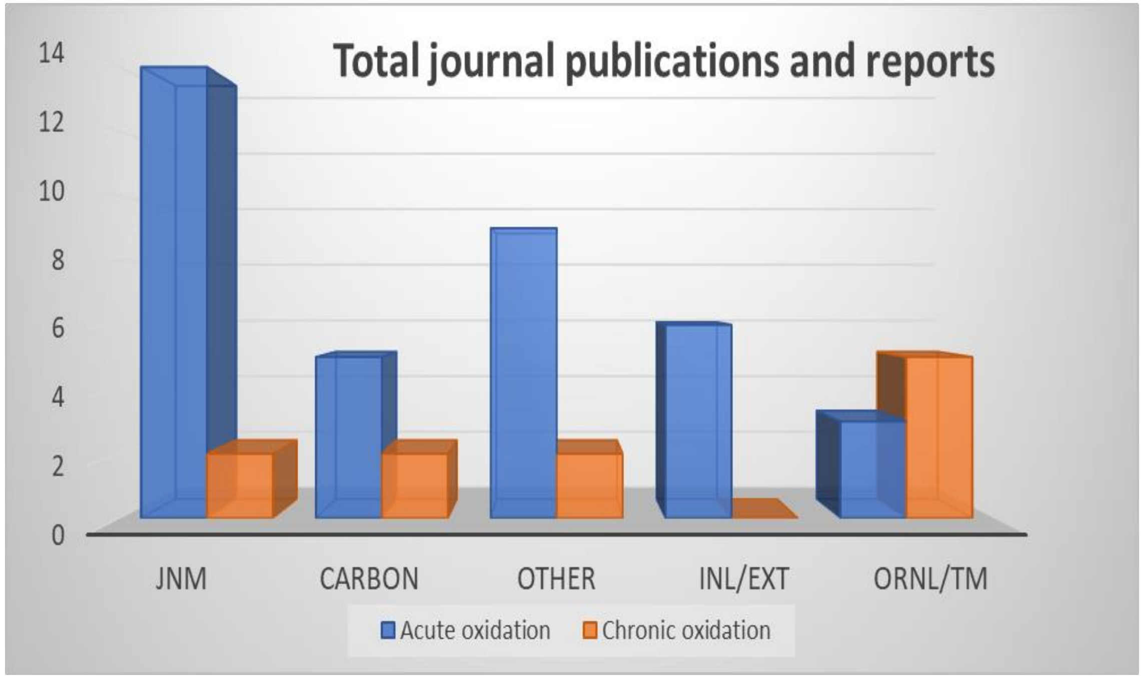


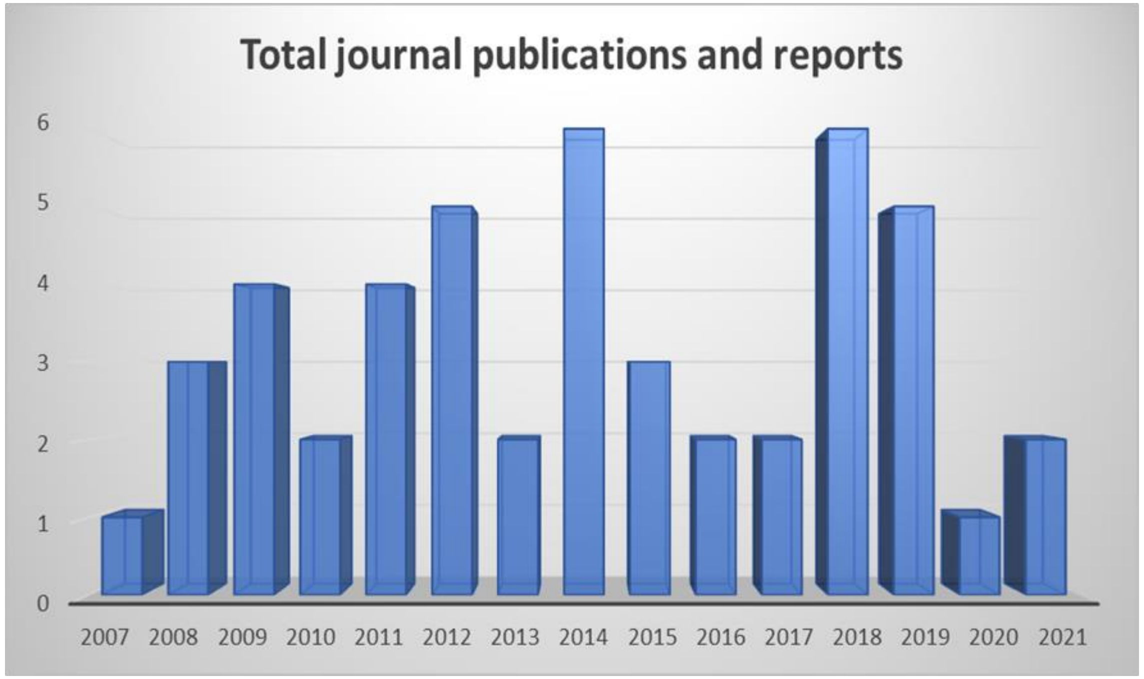
- A total of 48 technical reports and scientifical publications were issued during 2006-2021.
  - These were from R&D activities supported by DOE-NE through National Laboratories and competitive programs with U.S. Universities (NEUP, NSUF, NERI).
  - This number does not include presentations at international meetings (INGSM, ICAPP, ASME, ASTM, Carbon Conference, etc.)

Publications Distribution by Graphite Grade and Properties

	NBG-18	NBG-17	NBG-10	NBG-25	PCEA	PGX	2114	2020	IG-11	IG-110	IG-430	BAN	Boronated graphite	Fuel matrix A3
ACUTE OXIDATION														
Oxidation rates in air	4	2	1		4				1	5		2	1	2
Structural characterization	1				1					3				
Effective diffusivity	1	1			1		1			1	1			
Effect on porosity	3		1		3	1				2				
Effect on strength	2		2		2			1		2			1	1
Effect on elastic modulus	1									1				
Model development	3			1	1					1	1			
CHRONIC OXIDATION														
Oxidation rates by moisture		4			4		4			4				1
Structural characterization		1			1		1			1				
Effective diffusivity		2			2		1			1				
Model development		3			3		3			3				

Publications distribution by type and year



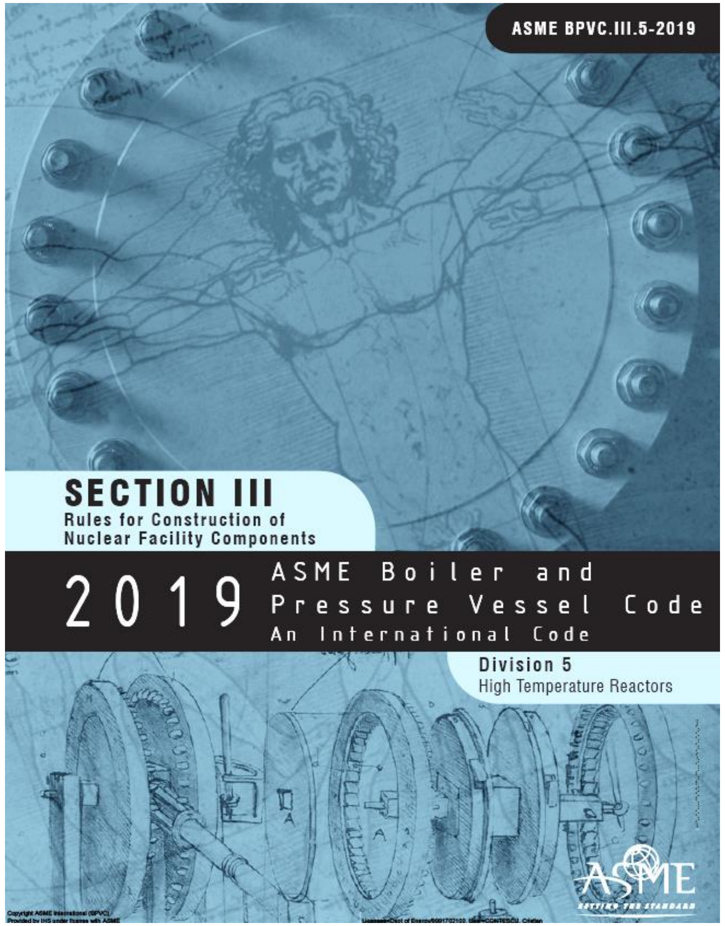


Other methods of information dissemination include

- Activities through international organizations such as (ASME, ASTM, IAEA) and experts forums (Carbon Conferences, INGSM, ICAPP)
- Gen IV Materials Handbook (managed by ORNL)

ASME Task Group on Oxidation

- A Task Group was formed to address gap issues on graphite oxidation in the ASME BPVC Section III Division 5 – High Temperature Reactors
- Examine the ASME code approach to graphite oxidation
- Propose a generic strategy for quantification of oxidation-induced property changes
- Draft white paper(s) to justify proposed changes, supported by authoritative publications in literature
- A short list of obvious changes will be discussed and balloted at the July 2021 meeting of ASME Non-Metal Working Group
- Effort led by ORNL with INL support
- Includes subject matter experts with diversified background from national laboratories, universities, and graphite vendors from US and UK.



Obvious Changes to be Discussed and Balloted

- Drop “radiolytic oxidation” from HHA-2230 and HHA-3140
  - Radiolytic oxidation is typical for CO_2-cooled AGRs in the UK, but it is not expected in HTGRs and MSRs that use high-purity He as coolant.
- Drop “hydrogen” from HHA-3141
  - Hydrogen cannot cause graphite oxidation (on the contrary, H_2 slows down oxidation by water)
- Add “moisture” in HHA-3141
  - Moisture traces in the helium coolant will cause extremely slow, but continuous, chronic oxidation during normal operation during reactor’s service life.
- Add text to HHA-3141 to emphasize the localized character of oxidation which will create a density profile in the component’s subsurface penetrated by oxidant.
  - Using modeling for mapping the profile of weight loss (or density) versus penetration depth of oxidant is essential for calculation of strength and geometry reduction in oxidized components (HHA-3141) as required for stress analysis (HHA-3215).

ASTM Activities

ASTM D02.F Subcommittee on Manufactured Carbon and Graphite had virtual meetings in December 2020 and May-June 2021

- New standards:
  - Test Method for Sonic Velocity in Manufacture Carbon and Graphite Materials for use in obtaining Approximate Elastic Constants: Youngs Modulus, Shear Modulus and Poisson's Ratio.
- Revised and reapproved standards:
  - D7779 Test Method for Determination of Fracture Toughness of Graphite at Ambient Temperature
  - C0769 Test Method for Sonic Velocity in Manufactured Carbon and Graphite Materials for Use in Obtaining an Approximate Value of Young's Modulus
  - C0816 Test Method for Sulfur Content in Graphite by Combustion-Iodometric Titration Method
  - C1039 Test Methods for Apparent Porosity, Apparent Specific Gravity, and Bulk Density of Graphite Electrodes

Oxidation Work Continues

- Irradiated Graphite Oxidation
  - Test whether light buffing limits contamination
  - Consider additional grades (esp. with distinct grain size / microstructure)
  - Possible (non-linear) relations with additional dose
  - Develop model refinements to incorporate effects
- Collaborations all ongoing
  - GIF oxidation summary provides resource to existing publications by content
  - ASME oxidation-related updates, gaps, and guidance
  - ASTM test standards for graphite (including degradation from oxidation)