



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

July 2021

Changing the World's Energy Future

Rebecca E Smith



DISCLAIMER

This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness, of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trade mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

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

Rebecca E Smith

July 2021

**Idaho National Laboratory
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

**Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517**



July 14, 2021

Rebecca Smith
Staff Engineer

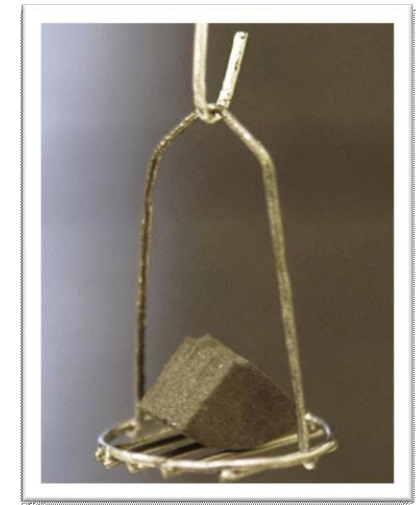
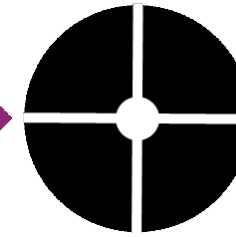
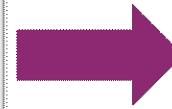
Graphite Oxidation Studies

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

**Advanced Reactor
Technologies**

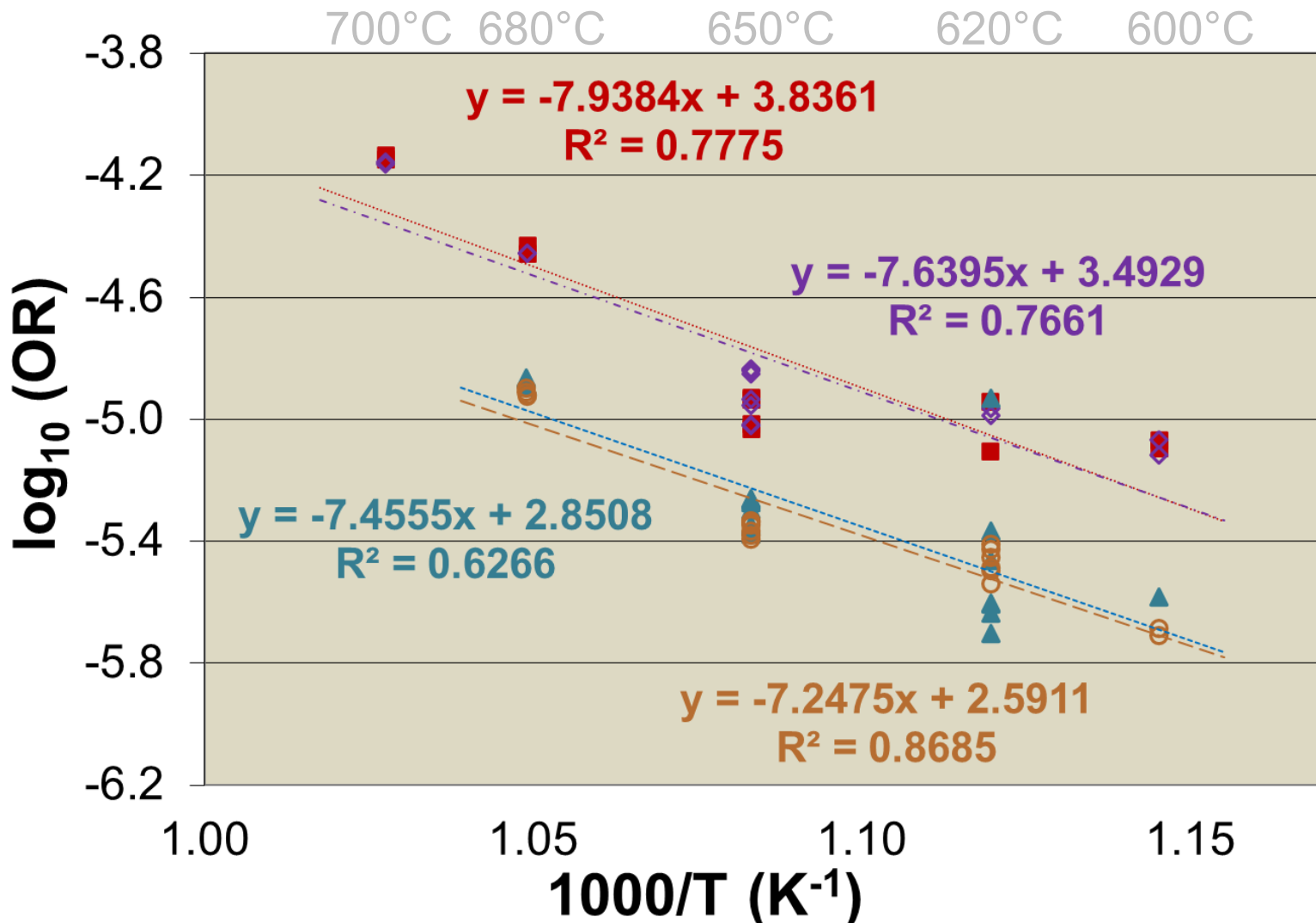
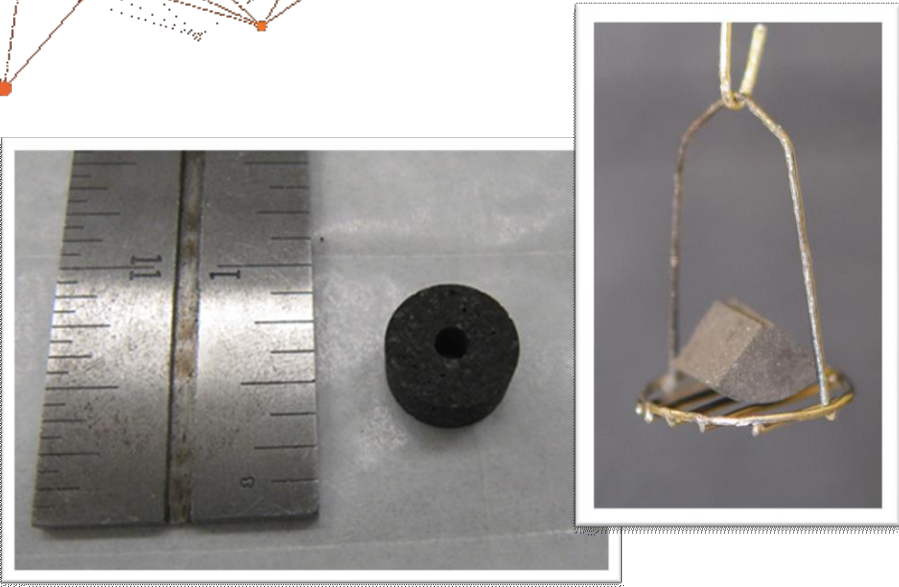


Introduction



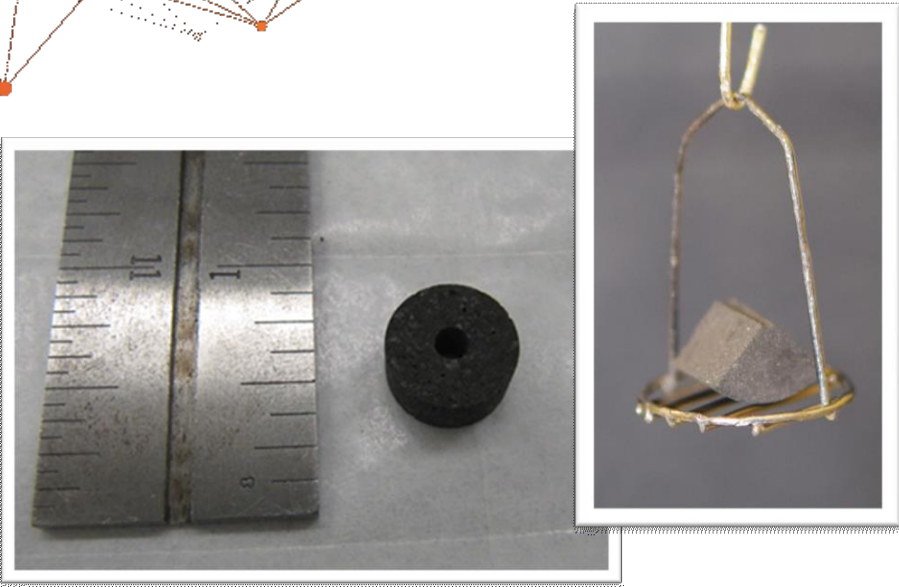
- Comparison of Graphite Oxidation Rates for Irradiated and Unirradiated NBG-25 (Rebecca Smith and Austin Matthews, INL)
 - Annealing effect over range of oxidation temperatures
 - Irradiation effect (~6.5 dpa) over range of oxidation temperatures
 - Dose dependency of irradiation effect
- Generation 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



- NBG-25 no anneal ¼ irradiated ~6.5 dpa buttons, TGA
- ◇ NBG-25 annealed ¼ irradiated ~6.5 dpa buttons, TGA
- ▲ NBG-25 no anneal ¼ combined unirradiated, TGA
- NBG-25 annealed ¼ combined unirradiated, TGA
- Linear (NBG-25 no anneal ¼ irradiated ~6.5 dpa buttons, TGA)
- - - Linear (NBG-25 annealed ¼ irradiated ~6.5 dpa buttons, TGA)
- - - Linear (NBG-25 no anneal ¼ combined unirradiated, TGA)
- - - Linear (NBG-25 annealed ¼ combined unirradiated, TGA)

Unirradiated & Irradiated – Observed Effect at ~6.5 dpa

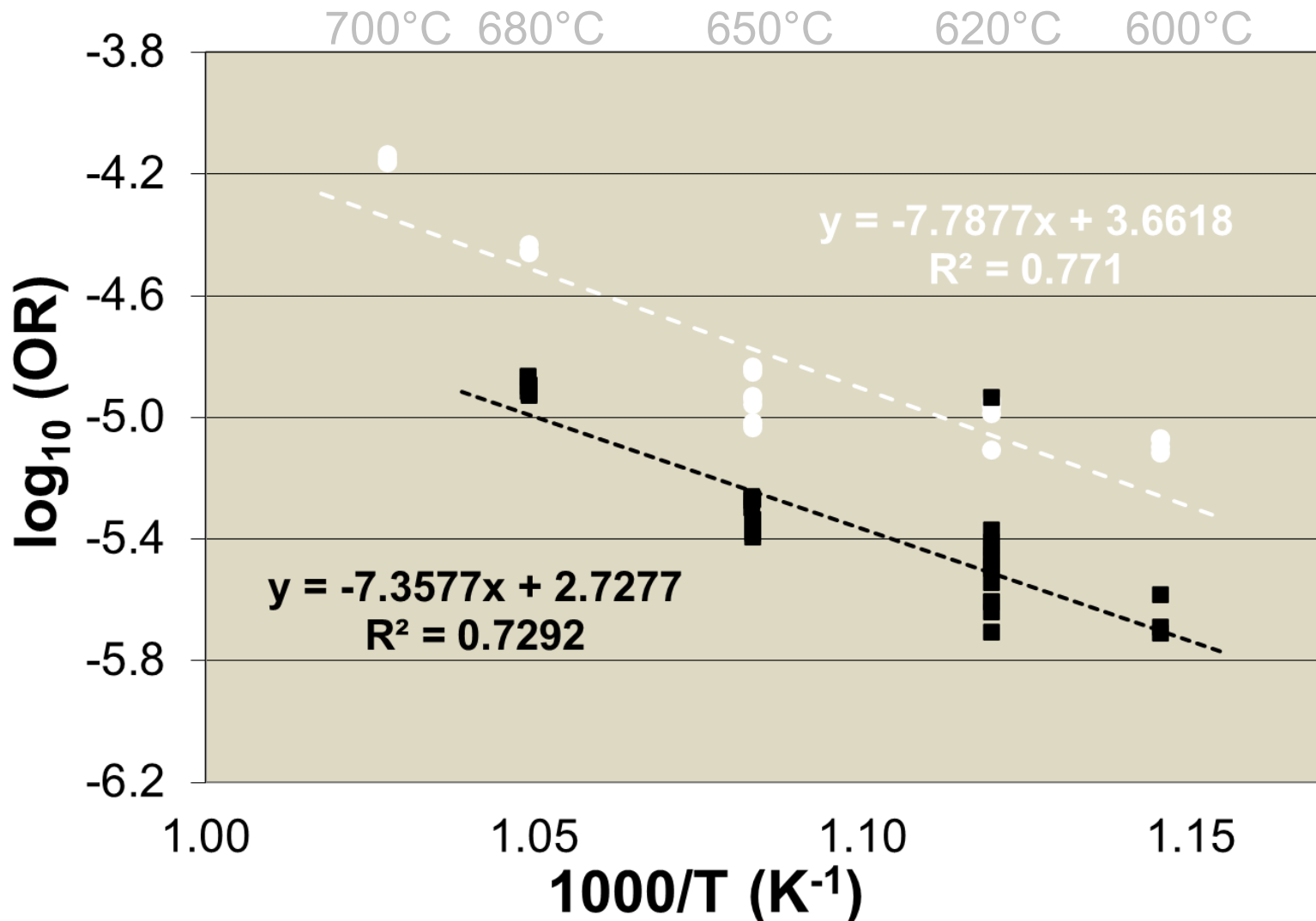


● NBG-25 all ¼ ~6.5 dpa irradiated buttons, TGA

■ NBG-25 all ¼ combined unirradiated, TGA

- - - Linear (NBG-25 all ¼ ~6.5 dpa irradiated buttons, TGA)

- - - Linear (NBG-25 all ¼ combined unirradiated, TGA)



Unirradiated & Irradiated with Dose Dependency



● NBG-25 all ¼ ~6.5 dpa irradiated buttons, TGA

■ NBG-25 all ¼ combined unirradiated, TGA

◆ 2.52 dpa

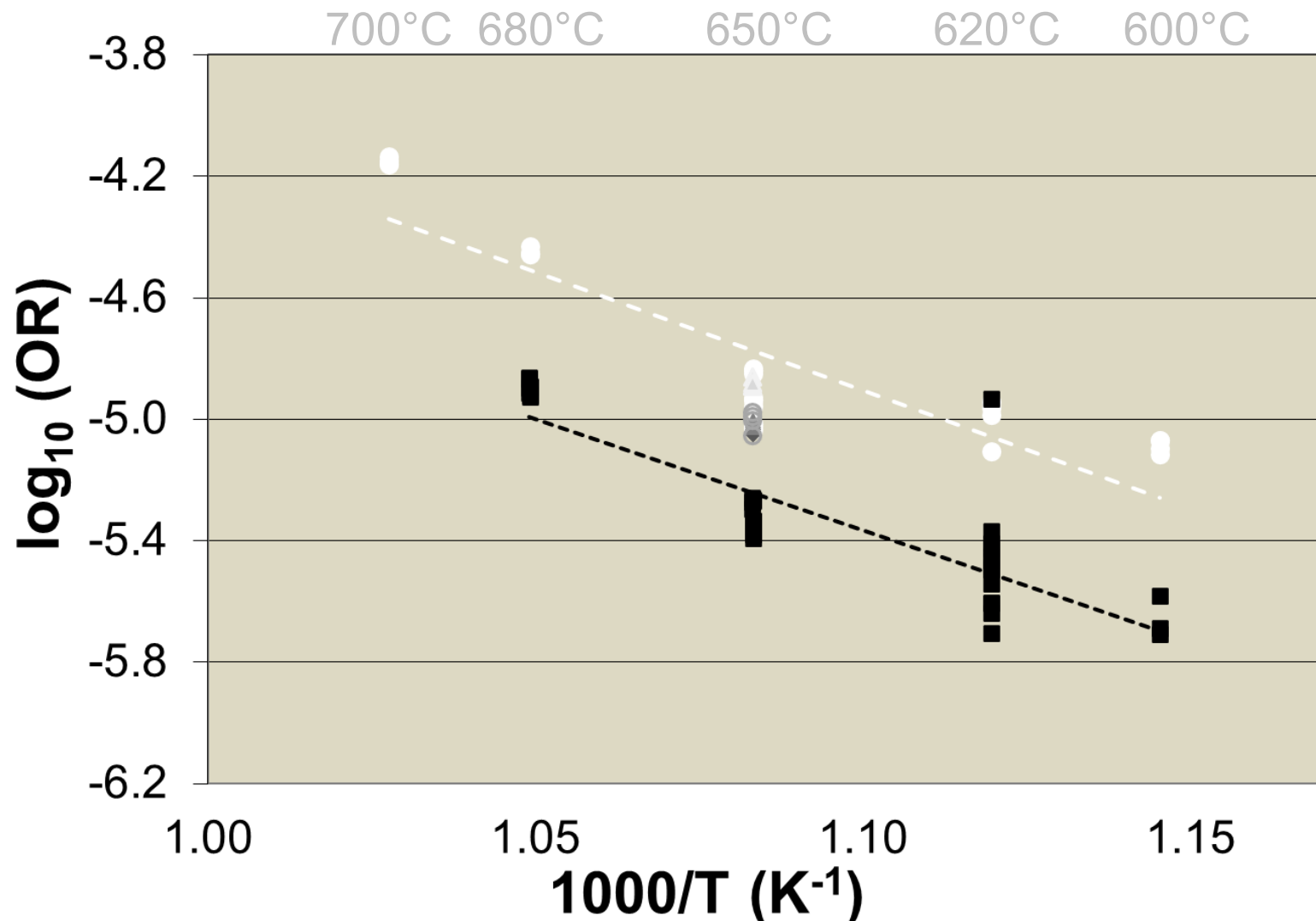
▲ 3.59 dpa

○ 4.48 dpa

△ 5.43 dpa

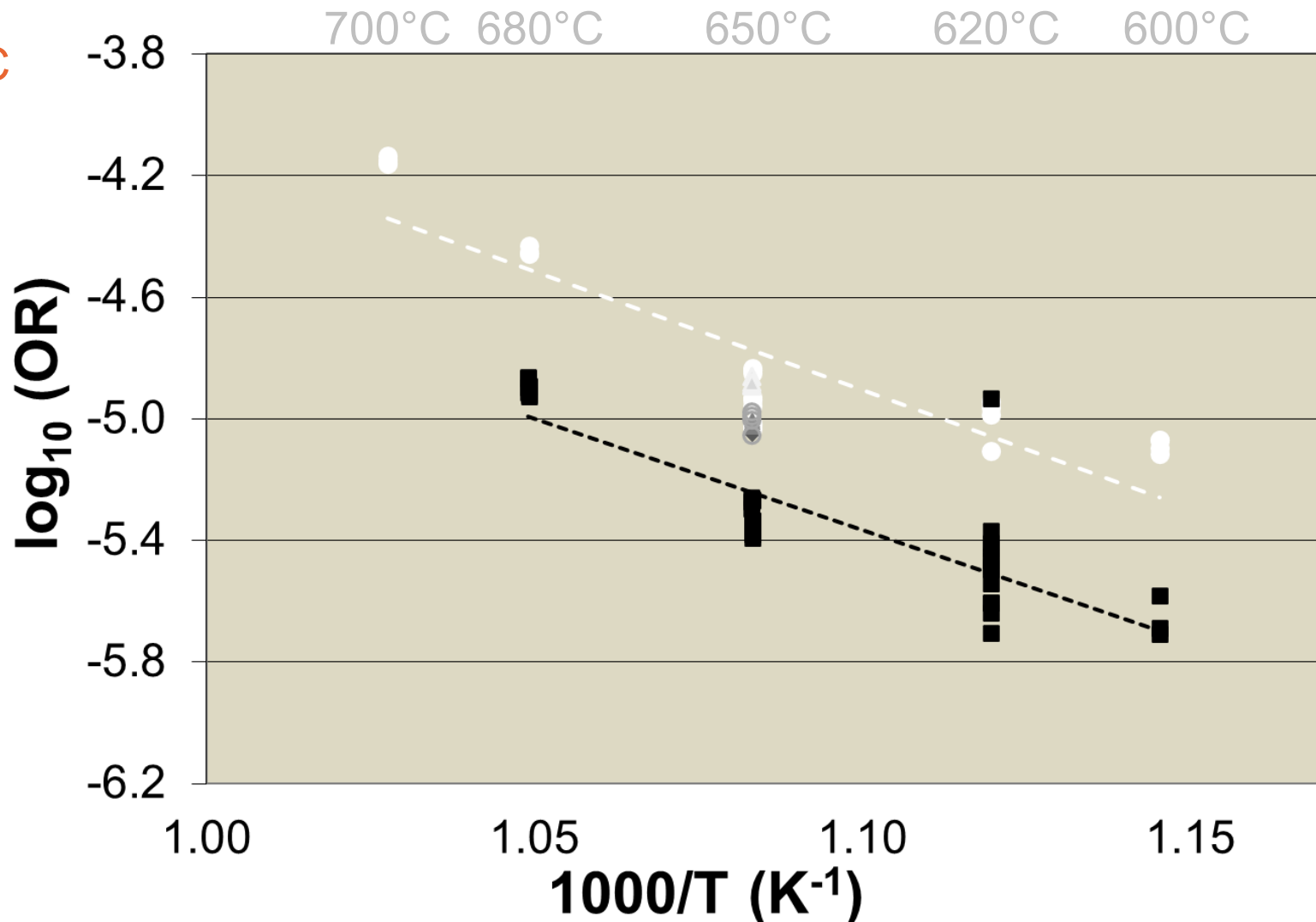
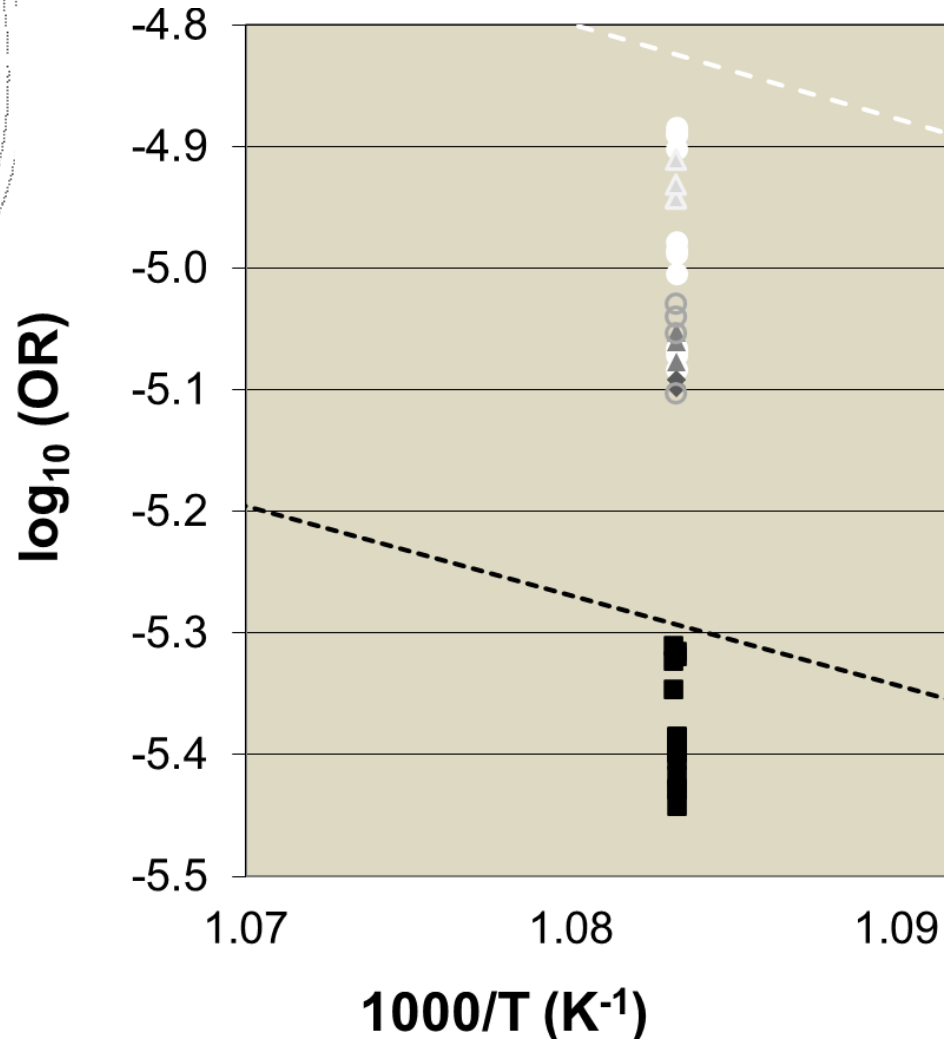
--- Linear (NBG-25 all ¼ ~6.5 dpa irradiated buttons, TGA)

---- Linear (NBG-25 all ¼ combined unirradiated, TGA)



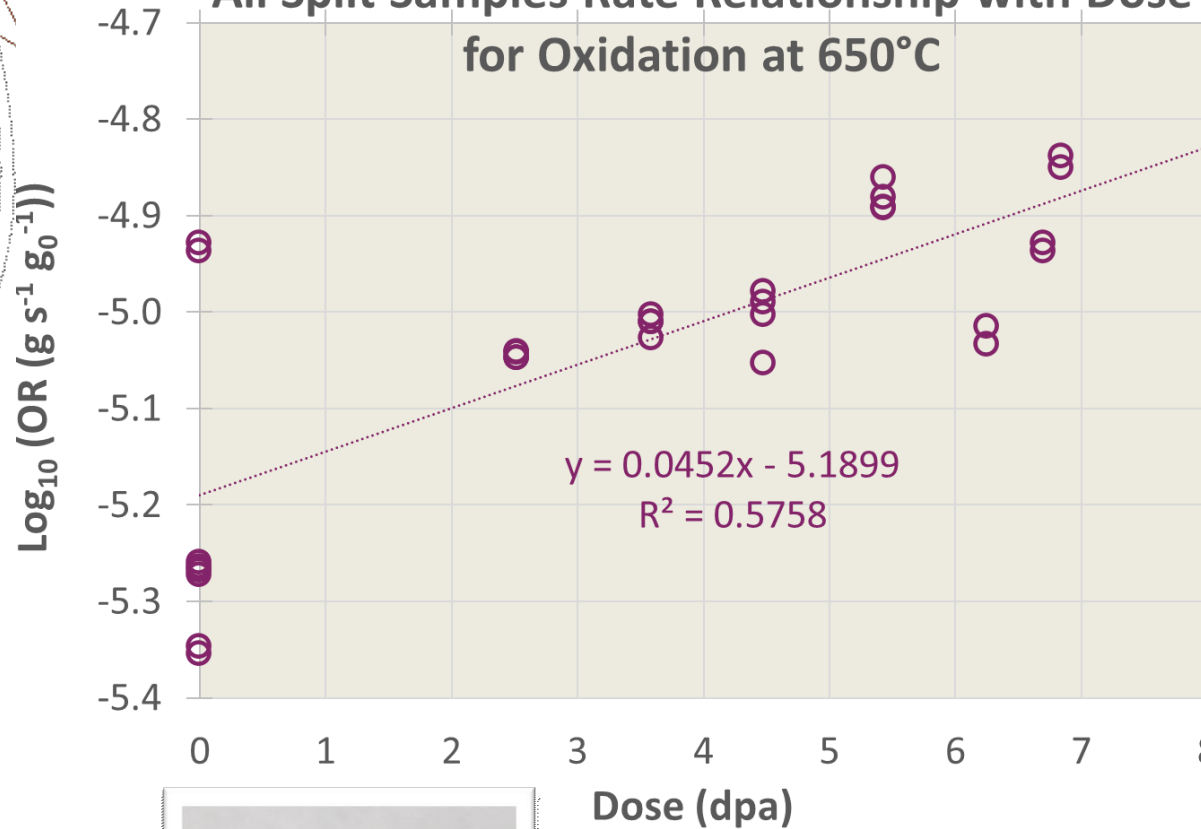
Unirradiated & Irradiated with Dose Dependency

All 1/4 Buttons, Enlarged at 650°C

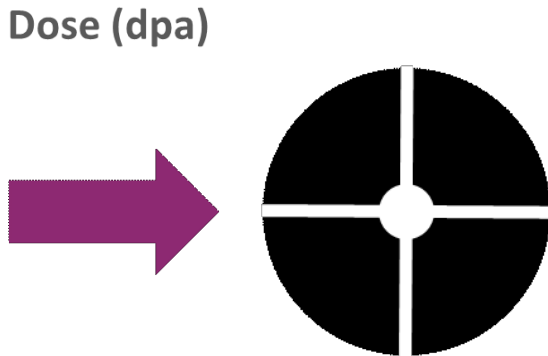
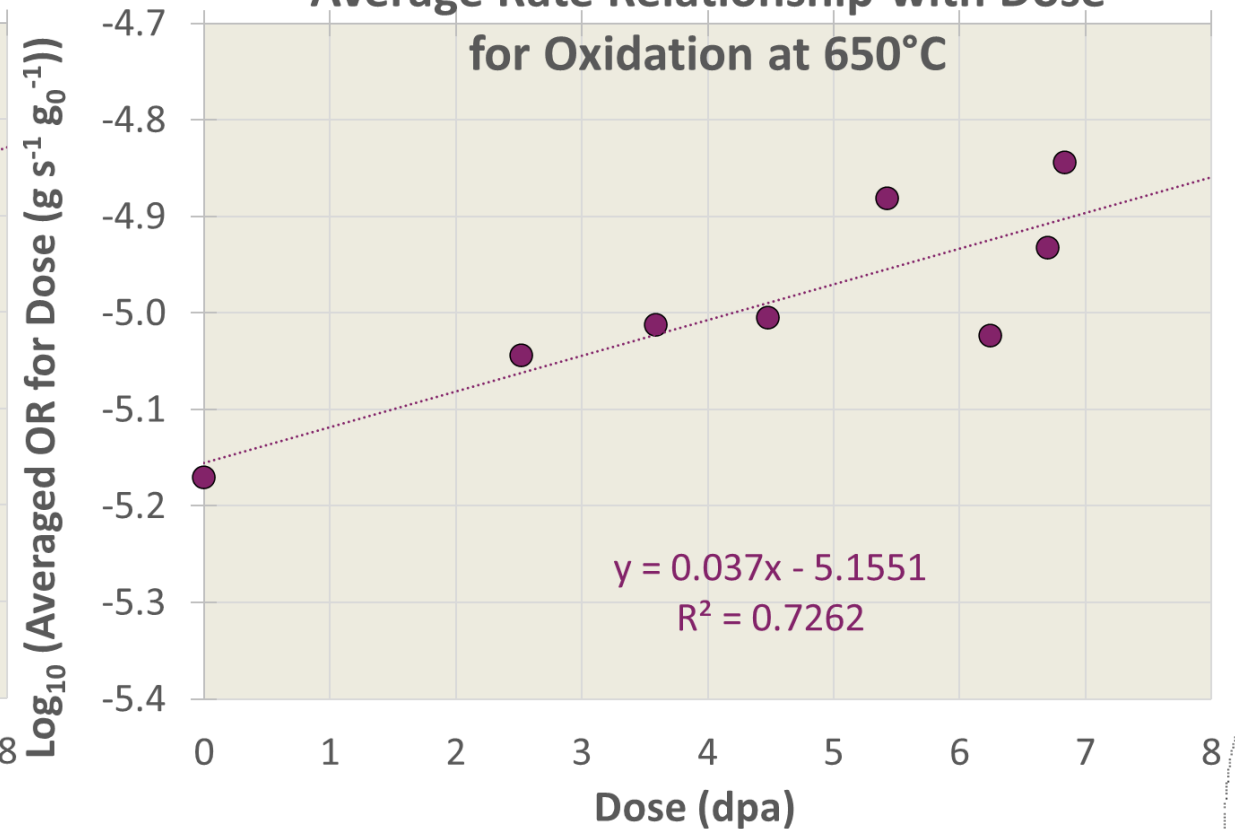


Dose Dependency at 650°C

All Split Samples Rate Relationship with Dose for Oxidation at 650°C



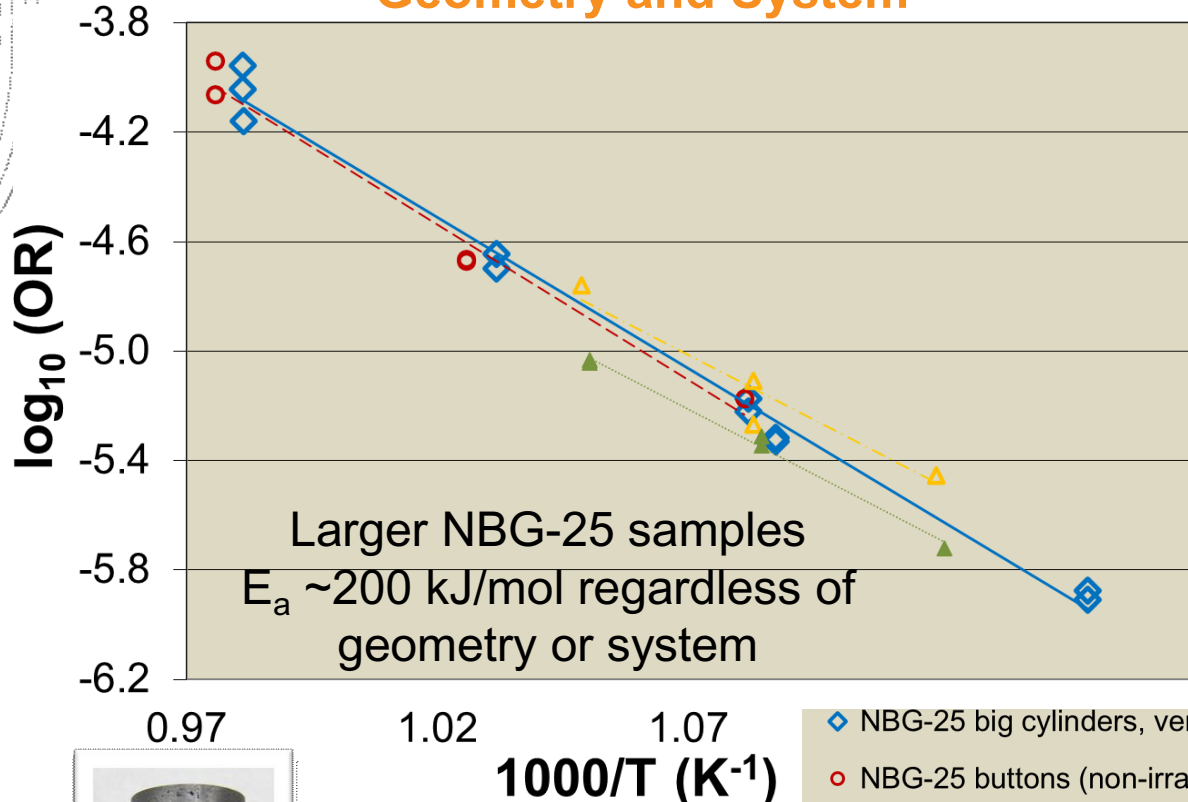
Average Rate Relationship with Dose for Oxidation at 650°C



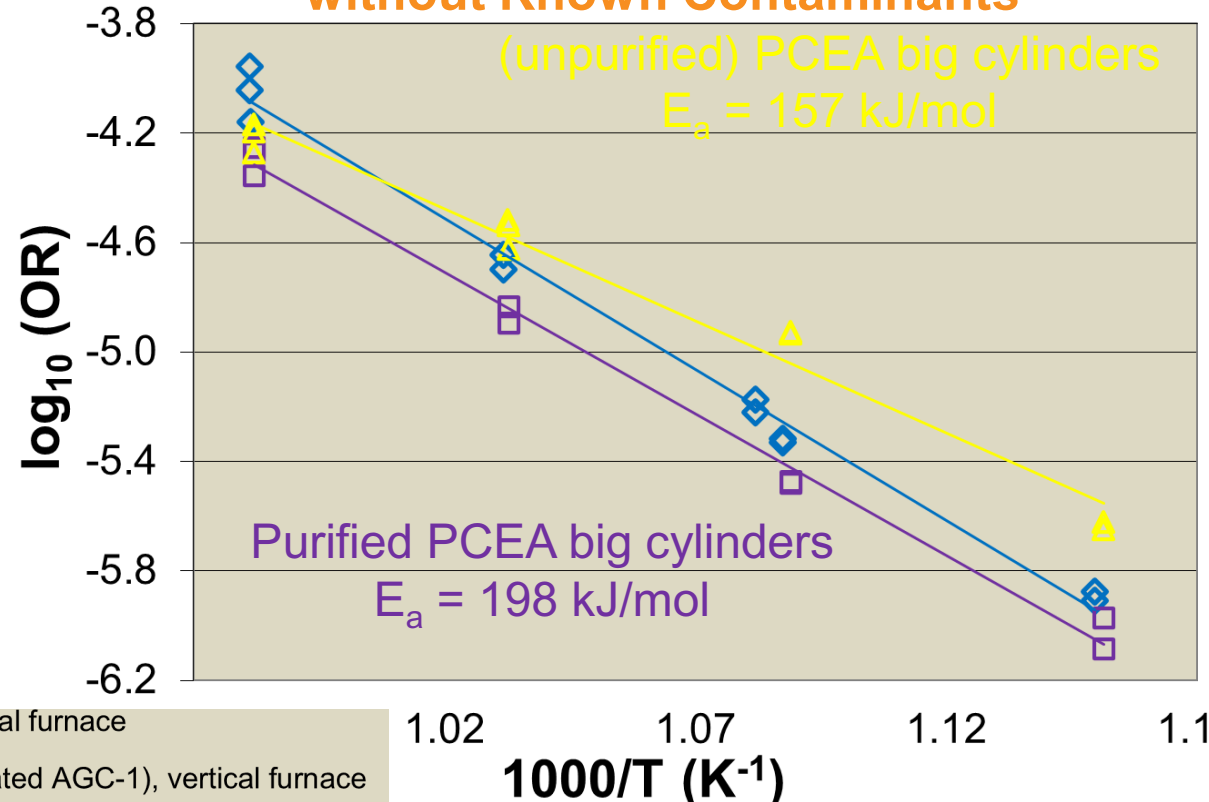
Approximately 10% Increase in Oxidation Rate for Each 1 dpa of Irradiation

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

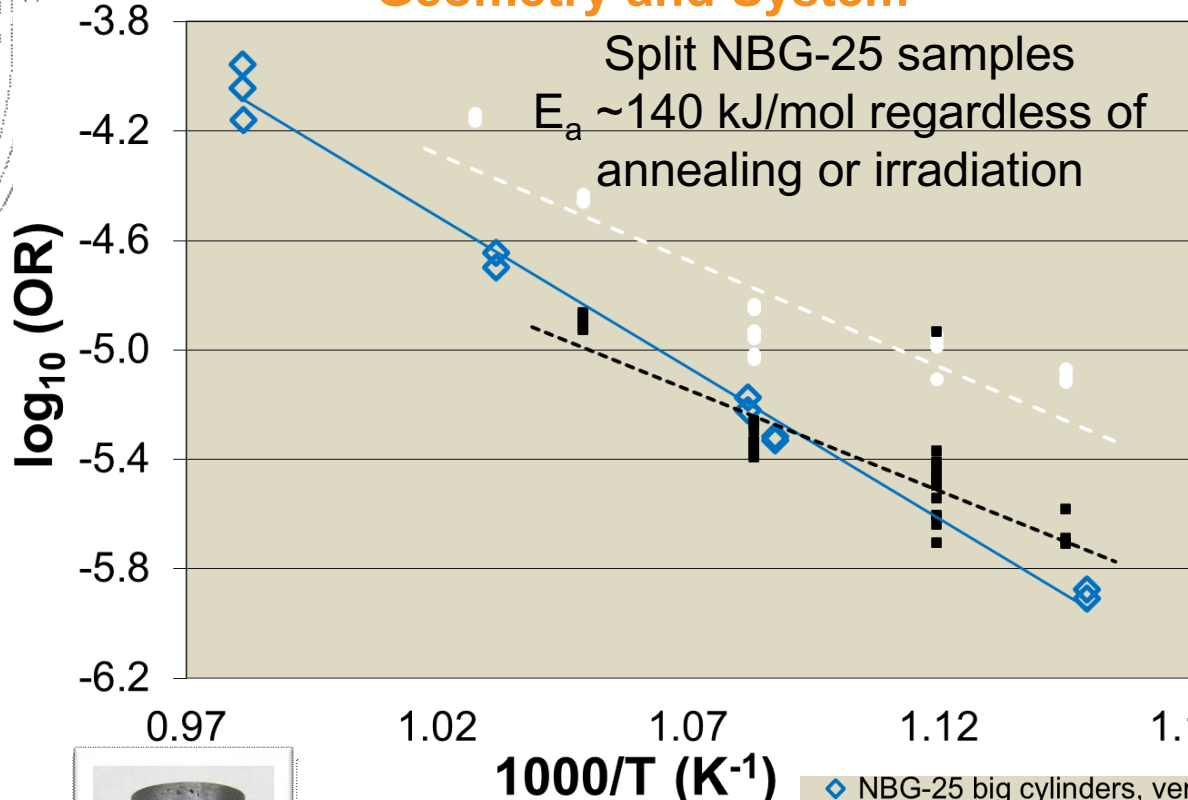


- ◆ NBG-25 big cylinders, vertical furnace
- NBG-25 buttons (non-irradiated AGC-1), vertical furnace
- ▲ NBG-25 buttons from big samples, vertical furnace
- ▲ NBG-25 buttons from big samples, TGA
- Purified PCEA, big cylinders, vertical furnace
- ▲ PCEA, big cylinders, vertical furnace

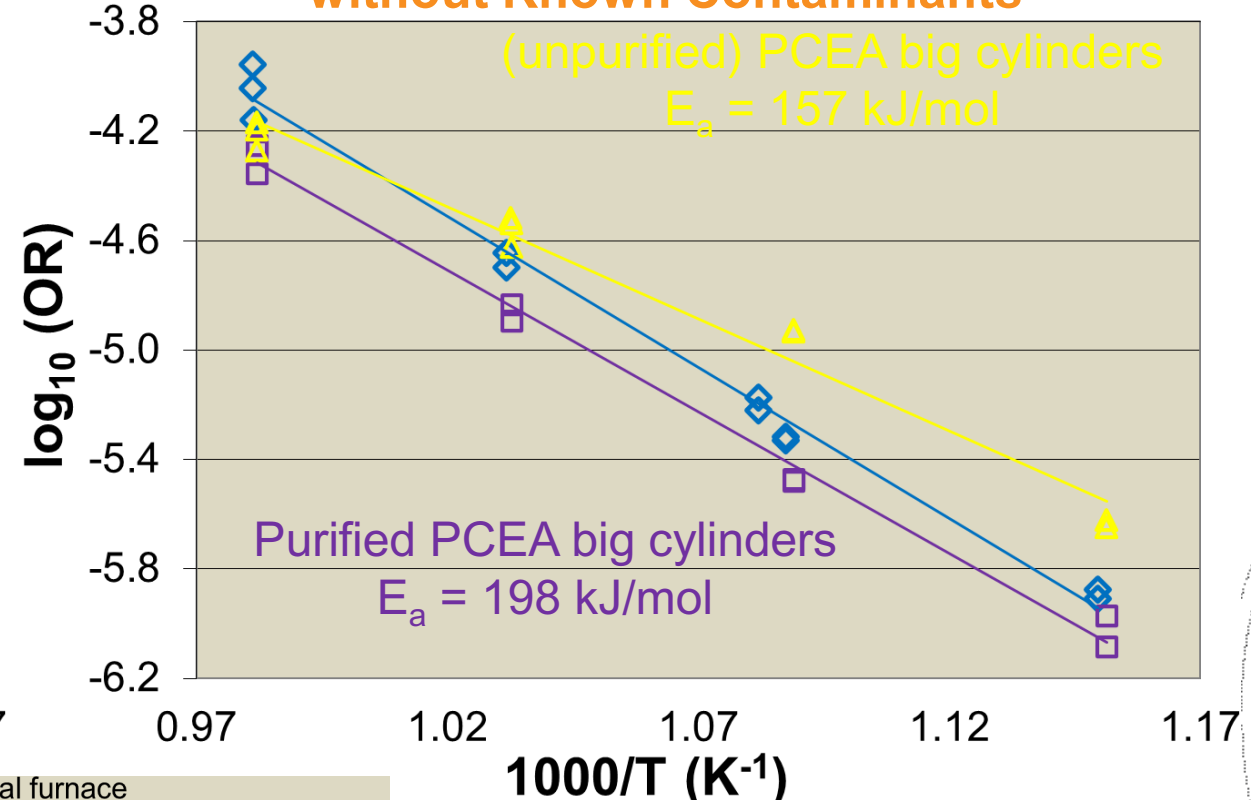


Comparison of Effective Activation Energies Suggests Presence of Catalyst in Split Samples, Not Larger NBG-25

Behavior of NBG-25 Samples with Geometry and System



Behavior of Graphite Grades with and without Known Contaminants

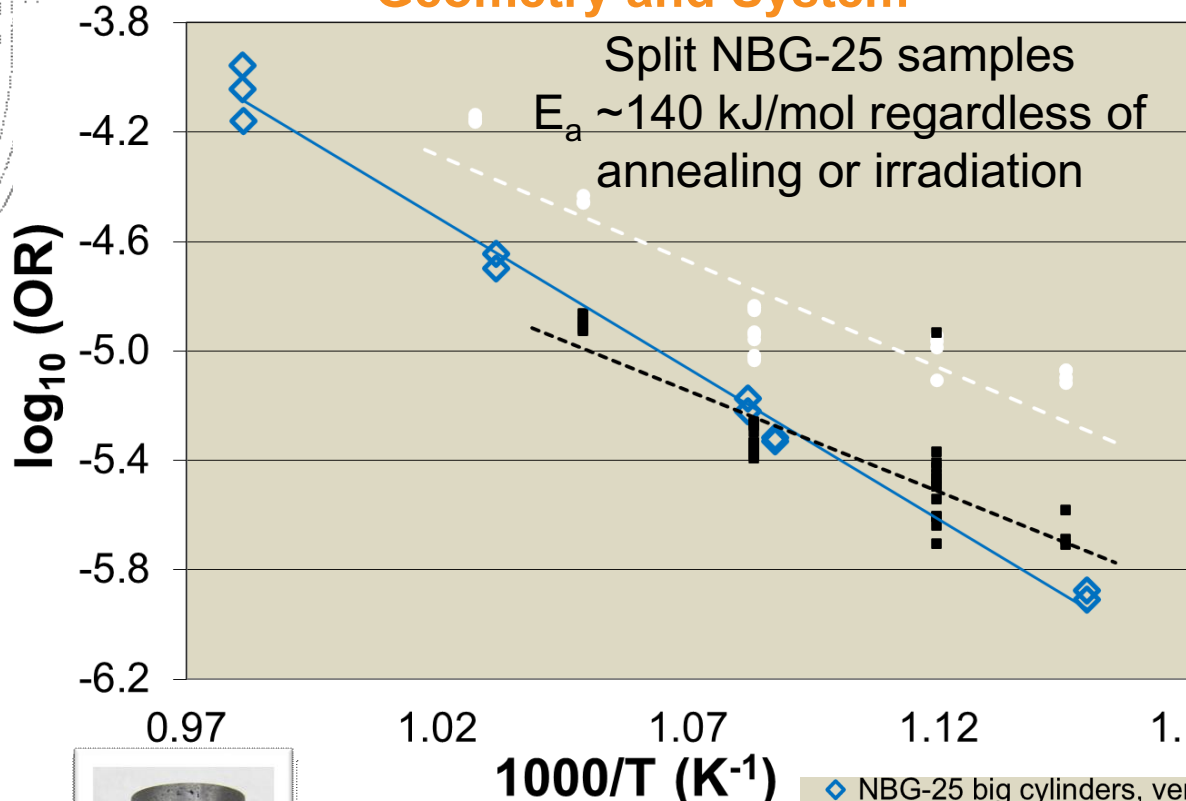


- ◆ NBG-25 big cylinders, vertical furnace
- NBG-25 all ¼ ~6.5 dpa irradiated buttons, TGA
- NBG-25 all ¼ combined unirradiated, TGA
- Purified PCEA, big cylinders, vertical furnace
- △ PCEA, big cylinders, vertical furnace

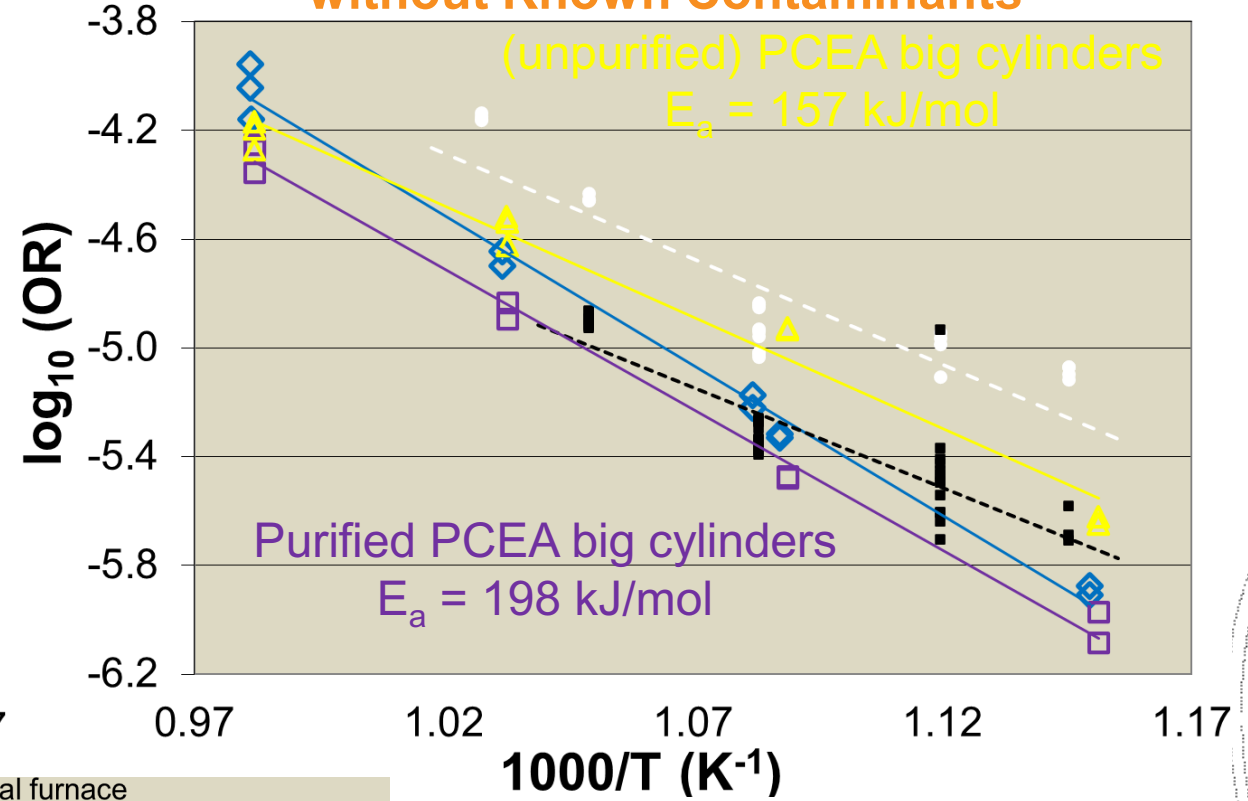


Comparison of Effective Activation Energies Suggests Presence of Catalyst in Split Samples, Like Observed with PCEA

Behavior of NBG-25 Samples with Geometry and System



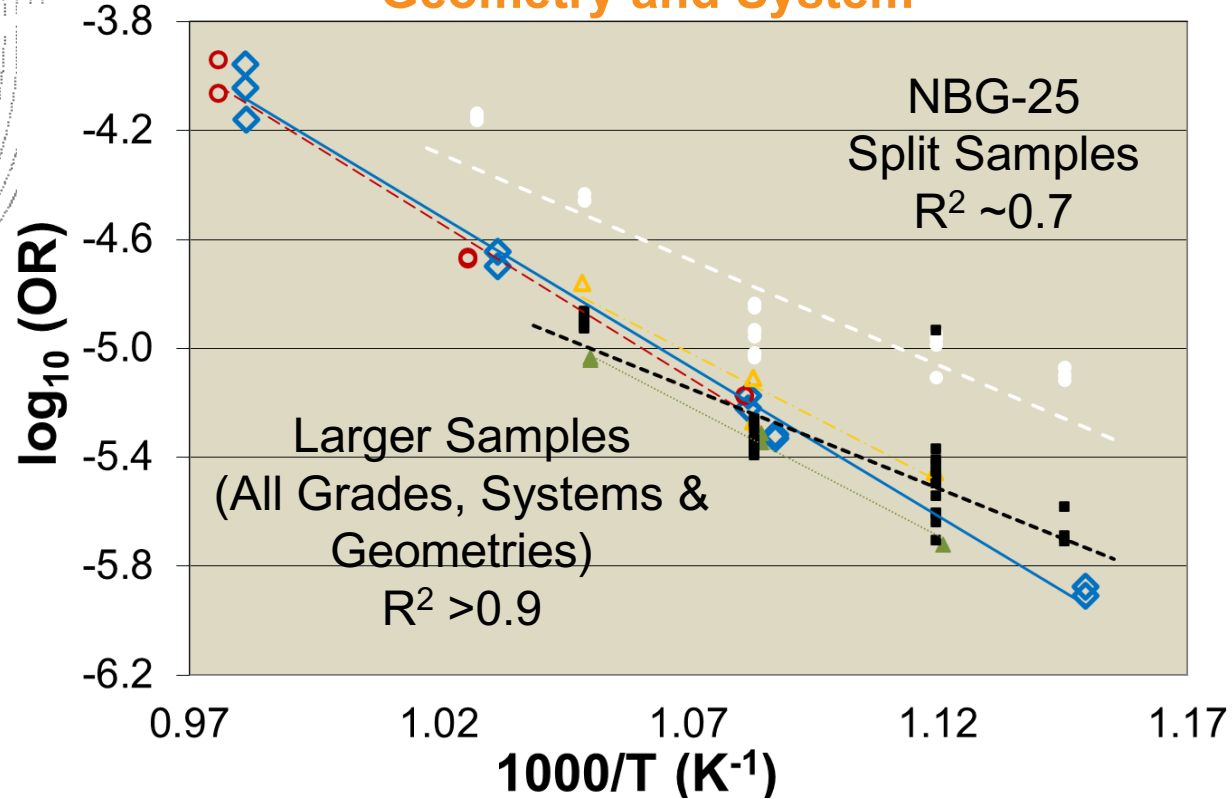
Behavior of Graphite Grades with and without Known Contaminants



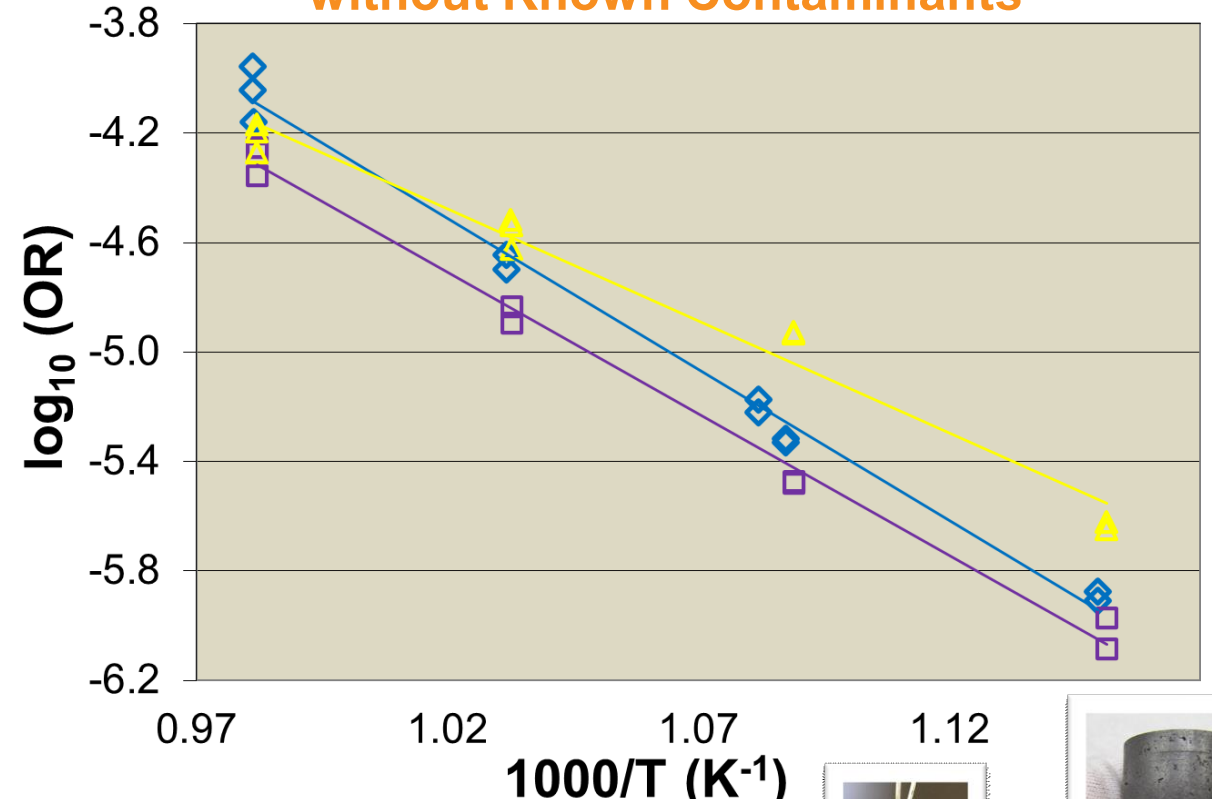
- ◆ NBG-25 big cylinders, vertical furnace
- NBG-25 all ¼ ~6.5 dpa irradiated buttons, TGA
- NBG-25 all ¼ combined unirradiated, TGA
- Purified PCEA, big cylinders, vertical furnace
- △ PCEA, big cylinders, vertical furnace

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

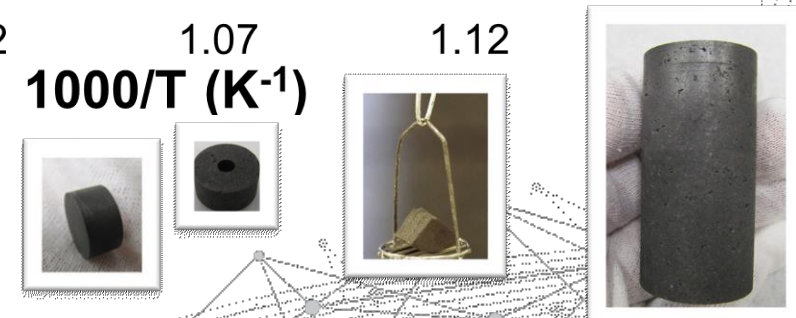
Behavior of NBG-25 Samples with Geometry and System



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

ORNL/TM-2021/1892

Summary of US DOE R&D Activities on Graphite Oxidation (2006–2021)

- 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 scientific 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.)



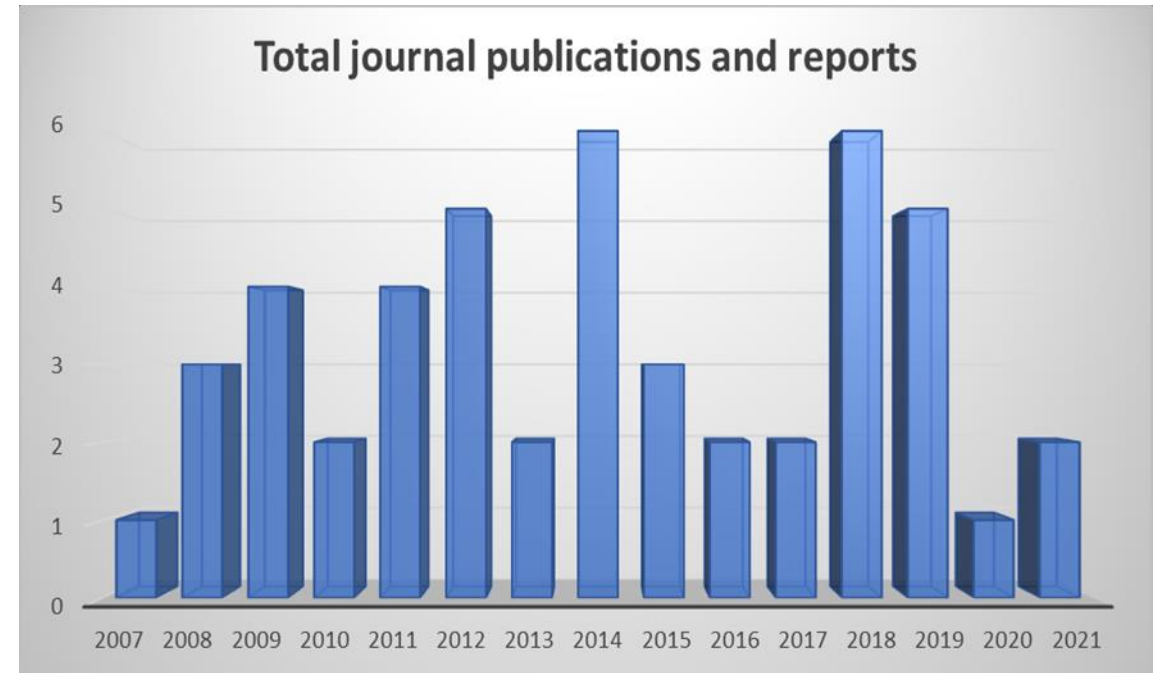
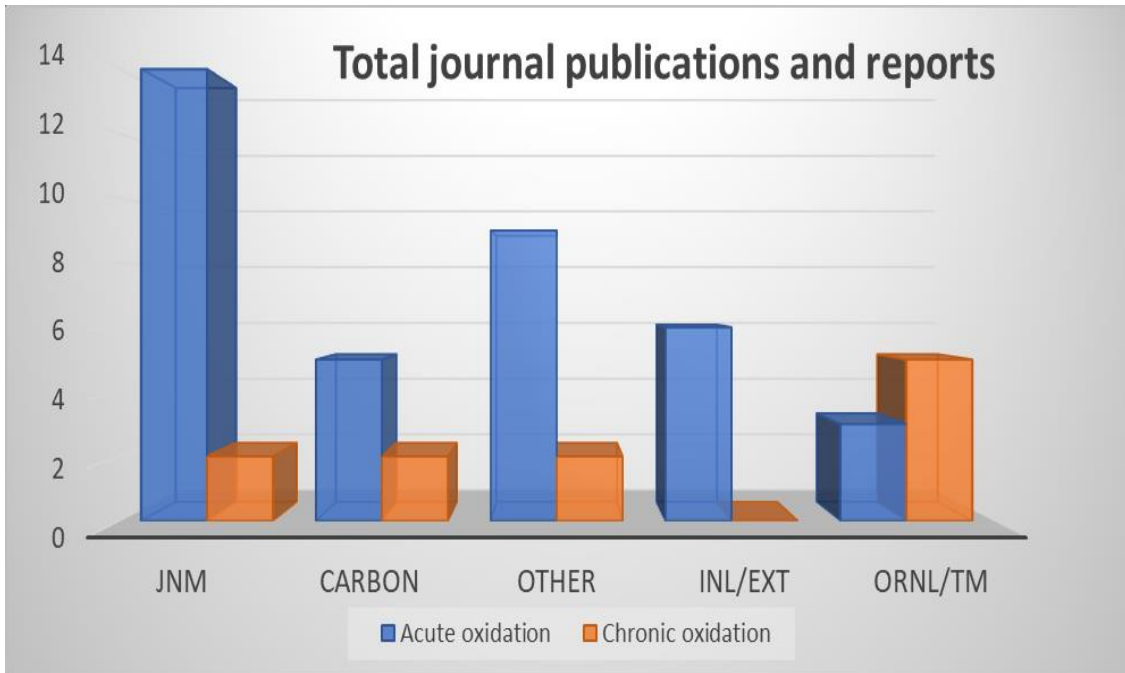
Cristian I. Contescu
Nidia C. Gallego

March 2021

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

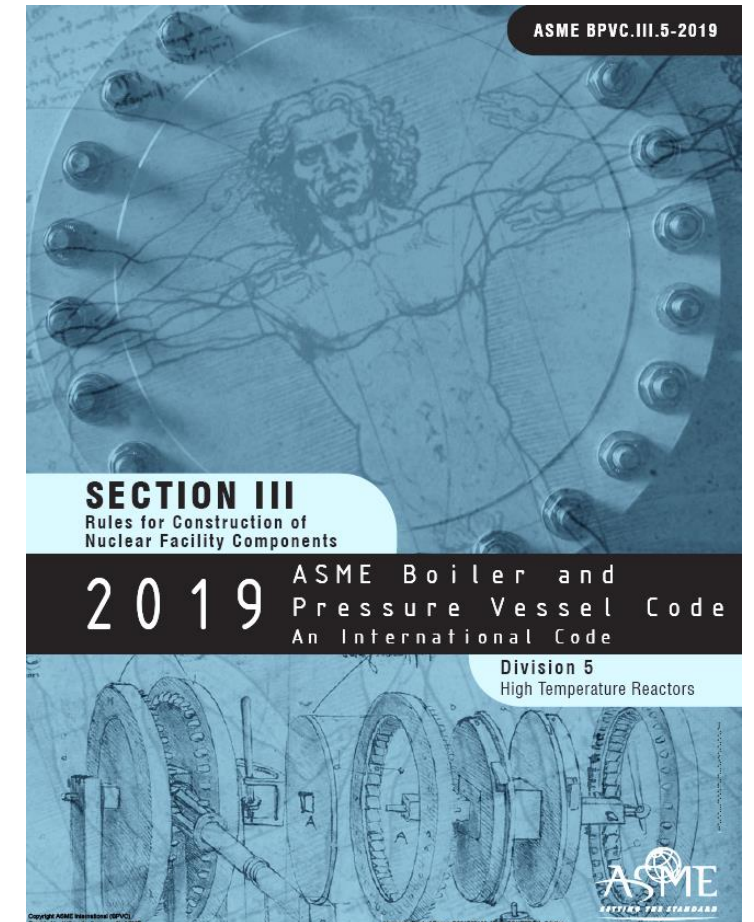


Other methods of information dissemination include

- 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 CO₂-cooled AGRs in the UK, but it is not expected in HTGRs and MSR that use high-purity He as coolant.
- Drop “hydrogen” from HHA-3141
 - Hydrogen cannot cause graphite oxidation (on the contrary, H₂ 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)

