ORNL/TM-2021/1892

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

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March 2021

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

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Physical Sciences Directorate
Chemical Sciences Division

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Prepared by
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Oak Ridge, TN 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

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ACRONYMS

ARD	Advanced Reactor Development
ART	Advanced Reactor Technologies
ASA	active surface area
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BLH	Boltzmann-enhanced Langmuir–Hinshelwood
DOE	Department of Energy
FTIR	Fourier-transform Infrared Reflection
GIF	Generation IV International Forum
GWG	Graphite Working Group
HTGR	High Temperature Gas-cooled Reactor
HTR	High Temperature Reactor
ICAPP	International Conference on Advancements in Power Plants
INGSM	International Nuclear Graphite Specialists Meeting
INL	Idaho National Laboratory
JAEA	Japan Atomic Energy Institute
JRC	Joint Research Center
KAERI	Korea Atomic Energy Research Institute
LH	Langmuir–Hinshelwood
MHTGR	Modular High Temperature Gas-cooled Reactor
MSR	Molten Salt Reactor
NE	Nuclear Energy
NERI	Nuclear Energy Research Imitative
NEUP	Nuclear Energy Universities Program
NGNP	Next Generation Nuclear Plant
NSUF	Nuclear Science User Facility
NQA	Nuclear Quality Assurance
ORNL	Oak Ridge National Laboratory
PA	Project Arrangement
PMB	Project Management Board
PP	Project Plan
R&D	research and development
RSA	reactive surface area
TGA	thermogravimetric analyzer
TSA	total surface area
UK	United Kingdom
USA	United States of America
U.S.-DOE	United States Department of Energy
VHTR	Very High Temperature Reactor
XPS	X-ray Photoelectron Spectroscopy

ACKNOWLEDGMENT

This work was supported by the U. S. Department of Energy, Office of Nuclear Energy, under the Advanced Reactor Technologies (ART) – Gas Cooled Reactor (GCR) Program. Oak Ridge National Laboratory is managed by UT-Battelle under contract DE-AC05-00R22725.

The author acknowledges invaluable support from colleagues at Oak Ridge National Laboratory (ORNL) and Idaho National Laboratory (INL) who provided suggestions for this document's structure and content and critically reviewed the manuscript: Drs. Ryan Paul (ORNL) and Rebecca Smith (INL). The support and critical reading of the final document by Dr. Will Windes (INL), National Coordinator of R&D activities on graphite materials for nuclear reactors, is highly acknowledged.

ABSTRACT

The objective of this report is to facilitate sharing of graphite oxidation research in support of the development and deployment of new nuclear power systems, first with the members of the Generation IV International Forum (GIF), and ultimately with the broader international community. The report summarizes the research and development activities funded by the United States Department of Energy from 2006 (the inception of the VHTR system arrangement) through present (2021). This work encompasses multiple aspects of acute and chronic oxidation of nuclear graphite in air and in steam, such as reaction kinetics and mechanism, experimental methodologies, consequences of oxidation to graphite materials properties, and model development. Due to the prominent use of graphite in very high temperature reactors (VHTR), chronic oxidation focuses on the very slow, but continuous chemical attack by the impurities that may be present in in the helium coolant, such as very low levels of moisture (steam). On the other hand, acute oxidation addresses fast chemical reactions of either oxygen or water in the improbable event of breaching the helium barrier followed by air or team ingress. The status of graphite oxidation research on these two directions, acute and chronic oxidation, is summarized, an index of references is provided, and the activities planned for closing remaining knowledge gaps are outlined.

This report is being submitted to the GIF Graphite Working Group (GWG) to serve as input for the GWG high-level deliverable to the Project Management Board of the Project Arrangement on Materials, which is scheduled for 2022 (deliverable 3.1.1.4.a of Task 1.4 – Graphite Oxidation Behavior).

1. INTRODUCTION

The Generation IV International Forum (GIF) is a cooperative international endeavor aimed at development of the research needed to test the feasibility and performance of the fourth generation of nuclear systems, and to make them available for industrial deployment by 2030. The United States is one of the 13 countries, along with Euratom, representing the European Union, which are committed to coordinating research and development (R&D) of new nuclear systems.[1]

The current GIF Project Arrangement (PA) on Materials (2018–2022) has been extended for another 10 years (2020–2030). Work Package 1 (Graphite) of the extended Project Plan (PP) on Materials specifies technical tasks and High Level Deliverables for research and development (R&D) activities related to nuclear graphite use in Very High Temperature Reactors (VHTRs), one of the six reactor technologies supported by GIF. The graphite tasks include materials specification and acquisition, qualification and development of new grades, characterization of properties, and development of behavior models. Specifically, Task 1.4 (Graphite Oxidation Behavior) outlines planned activities related to acute oxidation of graphite by air and chronic oxidation by impurities in the helium coolant. High purity graphite is used in fuel elements, support structures, and reflectors and is exposed to high temperature, fast neutrons irradiation, and chemical interactions with the gaseous environment (helium coolant).

This report was prepared for the GIF Graphite Working Group (GWG) to serve as input for the GWG High Level Deliverable to the Project Management Board of the PA on Materials (deliverable 3.1.1.4.a). The document summarizes the R&D activities funded by the US Department of Energy (U.S.-DOE) from 2006 (the inception of the VHTR system arrangement) through the present. In addition to U.S.-DOE, other organizations participating in Task 1.4 of the current PA on Materials are the European Commission's Joint Research Center (JRC), the Korea Atomic Energy Research Institute (KAERI), and the Japan Atomic Energy Agency (JAEA). U.S.-DOE is the main contributor to graphite oxidation R&D, with an 85% commitment of total funding during 2018–2022.

The main R&D work on graphite oxidation funded by U.S.-DOE Office of Nuclear Energy was performed at Idaho National Laboratory (INL) and Oak Ridge National Laboratory (ORNL) through two specific programs: Next Generation Nuclear Plants (NGNP) and Advanced Reactor Technologies (ART) – now called Advanced Reactor Development (ARD). In addition, smaller projects intended to stimulate collaboration between universities and national laboratories were funded by U.S.-DOE through competitive grants in programs such as Nuclear Energy University Programs (NEUP), Nuclear Science User Facilities, and Nuclear Energy Research Initiative. Researchers in national laboratories (INL and ORNL) were either collaborators or user-facility hosts for numerous competitive projects funded by U.S.-DOE.

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2. BACKGROUND

Graphite has been used as a neutron moderator in gas-cooled nuclear reactors since the 1940s and has performed remarkedly well over a broad range of environmental and irradiation conditions. The new generation of advanced reactors will continue to use graphite either in high- and very high temperature gas-cooled reactors (HTGRs, VHTRs) – with their more attractive modular version (MHTGRs) – or in molten salt reactors (MSRs). As a carbonaceous material, graphite is highly inert in aggressive chemical conditions, but it is easily oxidized in the presence of oxidants such as oxygen, water, carbon dioxide, etc. This tendency to oxidize creates a perception problem for public acceptance of the use of graphite in the cores of nuclear reactors. In fact, control of chemical attack is one of the primary objectives addressed during the safety design of high-temperature reactors. Licensing of new nuclear reactors is a rigorous process that demands comprehensive certifications that graphite oxidation behavior is both predictable and controllable in either normal or postulated accident conditions. An intense R&D effort has been pursued over the years for characterization of graphite's oxidation behavior in conditions related to normal operation of nuclear reactors and various off-normal scenarios. During normal operation, graphite will be exposed to ppm traces of moisture or other impurities in the helium coolant, which will predictably cause extremely slow but continuous (chronic) oxidation. On the other hand, rare off-normal events involving breaching of the helium pressure boundary may cause degradation of the reactor core support and the release of radionuclides within the primary cooling circuit. Events involving air or steam ingress that would potentially degrade the graphite core components, with significant radiological consequences, are so unlikely that they are not being considered in the design basis.[2]

Analysis of the progression and extent of graphite oxidation resulting from various type of events (either anticipated, design basis, or beyond design basis) is part of the licensing process. Reactor simulation codes and software need accurate experimental data on oxidation behavior for input. Data must be valid for a range of circumstances, from predictable to implausible, and be relevant to the graphite materials present in the reactor. In-core graphite components of HTGRs, VHTRs, and MHTGRs may be subjected to basically two different conditions that involve oxidation damage with potential consequences for reactor integrity and public safety.

- **An acute oxidation** event is an extremely unlikely accident, such as a breach of the helium pressure boundary accident followed by air or steam ingress, which may cause significant oxidation of graphite components over short periods of time. The effects of these beyond design limit events on graphite physical, mechanical, and thermal properties must be known. Detailed analysis and numerous simulations used for graphite licensing agree that self-sustained oxidation ("graphite fire") cannot occur because the decay heat is a decreasing source and the oxygen supply is limited. However, if significant oxidation occurs despite multiple barriers preventing graphite combustion, it may lead to physical damage within allowable tolerances to the fuel and reflector graphite structure. Therefore, understanding the oxidation behavior of the main graphite grades considered for qualification in nuclear reactors was, and continues to be, the object of intense scrutiny and modeling throughout the nuclear research community. The main achievements and the status of acute oxidation research activities in the United States are discussed in Section 3.1.

- **Chronic oxidation** will predictably occur during decades-long exposure of graphite components to the oxidative impurities (mostly moisture, but also traces of CO_2 and possibly O_2) that may be present in the helium coolant. Chemical attack by impurities is expected to cause extremely slow but continuous oxidation during reactor normal operation. This type of oxidation is less well known and is more difficult to study because of its extremely slow rate.

However, this process has the potential to change graphite properties, even though at extremely slow rates and on a limited scale. The long-term effects on mechanical, thermal, and physical properties can only be predicted based on a correct understanding of how fast, to what degree, and where this slow oxidation process will preferentially occur. The status and results of chronic activation research activities in the United States are presented in Section 3.2.

3. CURRENT STATUS

The activities summarized in this report cover the period approximately from 2006 through 2021 and cover the R&D activity for the entire period since the inception of the VHTR system arrangement until the current year. The main results are summarized below.

3.1 ACUTE OXIDATION BY AIR OR STEAM

Gas-cooled reactors can operate safely with helium gas in the cooling circuit (or with CO_2, as currently used in the United Kingdom), but the improbable event of air or steam ingress in the primary gas circuit may trigger acute graphite oxidation events that eventually would damage the physical integrity of in-core components. Self-sustained oxidation (uncontrolled "graphite burning") is not possible for graphite nuclear components because the four components needed for a sustained reaction (carbon fuel, heat, oxygen, and chain propagation) are severely restricted or eliminated from the crystallite length scale to full-size graphite components. However, analysis of off-normal severe oxidation events is required as part of the reactor licensing process. Sophisticated predictive models have been developed to represent the global oxidation behavior of graphite in various reactor zones. These models need accurate input data on chemical kinetics, oxidant transport, porosity development in the oxidized layer, and the lasting effects of structural degradation on mechanical and other properties of all graphite grades present in the VHTR unit. The goal is to provide designers, code builders, safety analysts, and regulatory agencies solid information on oxidation behavior and properties changes that is needed for making informed decisions on graphite selection and acquisition for new VHTR systems.

The action list on acute graphite oxidation derived from the Work Package on Graphite consists of the following steps:

1. Develop and consensually adopt a standard procedure for the kinetic characterization of graphite oxidation by air that provides consistent and reproducible results validated by interlaboratory testing.

2. Perform systematic and accurate measurements for the characterization of kinetic constants for air-oxidation of graphite in well-controlled conditions.

3. Determine oxidation effects on graphite properties (e.g., density profile, porosity development, degradation of mechanical strength and elastic modulus).

4. Characterize the effective diffusivity of specific gases in the pore structures of various graphite grades and determine the relationship between gas transport and graphite microstructure.

5. Develop models connecting kinetics and oxidant transport in the bulk of graphite and correlate them with observations on the temporal (kinetics) and spatial (penetration depth) progress of oxidation.

6. Assist in scaling up the oxidation behavior of small-size specimens to the actual performance of full-size components in assumed conditions of accident scenarios.

The accomplishments so far for these tasks are summarized in the following subsections.

3.1.1 Standardization of oxidation rate measurements and adaptation for small specimens

- A standard method for measuring graphite oxidation rates in air in controlled and reproductible conditions was consensually adopted by ASTM International (American Society for Testing and Materials) as ASTM D7542 in 2009.[3]

- The procedure was tested in an interlaboratory study with international participation, including graphite vendors and three national laboratories. The latest approved version (ASTM D7542-15) was revised in 2015.
- The method recommends using test specimens of a standard shape which are oxidized in a vertical furnace with abundant air supply (as needed to avoid starvation by lack of oxygen) in the temperature range in which oxidation is under kinetic control. The rates of isothermal weight loss (between 5 and 10%) are used to calculate the apparent activation energy that quantifies the effect of temperature on oxidation rates. The results provide a standardized way to compare graphite grades through the temperature effects on the rates of acute oxidation in air.

- Systematic and reproducible oxidation rate measurements performed according to ASTM D7542 recommendations have shown the extent by which the graphite microstructure determines the reactivity toward oxygen.
  - Oxidation rates were measured in standard conditions for the main graphite grades selected by the graphite qualification strategy,[4] and data are available for NBG-10;[5] PCEA;[6] NBG-18, and IG-110.[7]
  - Comparing oxidation behavior in standard conditions for the graphite grades revealed the effects of microstructure for the following grades: IG-110, NBG-25, PCEA (both purified and not purified), BAN, NBG-17, and NBG-18.[8]
  - In general, the larger the graphite grain size is, the lower the total surface area, and the higher the oxidation resistance, e.g., IG-110 < PCEA < NBG-18.[8,9]
  - It was confirmed that purified PCEA graphite has lower oxidation rates than before purification.[10]

- The need to characterize the oxidation behavior of irradiated graphite specimens was also considered. Irradiated specimens are too small to be tested according to ASTM D7542, but they fit in commercial thermogravimetric analysis (TGA) instruments. Comparing oxidation tests between large specimens tested according to ASTM D7542 and small specimens tested via TGA showed that concurrent kinetic results can be obtained only in well-defined conditions and under strict control of the TGA tests. This conclusion is important for planning and analyzing the air oxidation kinetics of irradiated small specimens using commercial TGA instruments. It also has important consequences related to extrapolating oxidation results from small graphite test specimens into conclusions on the behavior of large graphite reactor components.
  - Graphite grades characterized by parallel oxidation tests in vertical furnace and TGA: AG 13-01;[5] NBG-18, IG-110.[7]
  - Graphite grades characterized by oxidation tests in TGA only: NBG-18, NBG-17, IG-110, IG-11;[11] NBG-18;[12] IG-110;[13] graphitic matrix.[14]

3.1.2 Systematic observation of properties degradation with oxidation weight loss

- The effect of air oxidation on the degradation of mechanical properties was studied to clarify (1) the evolution of properties degradation with an increase in weight loss and (2) the difference in mechanical properties among specimens with equal weight losses but different density profiles of the oxidized layer, obtained from oxidation at different temperatures.
  - Graphite grades characterized: NBG-18, unpurified PCEA;[15] NBG-10, 2020;[5] graphitic fuel matrix;[16,17] purified PCEA;[18,10] NBG-10, IG-110;[19] H-451, IG-110;[20] NBG-18.[21]

- The microstructural changes after oxidation in air were investigated in various conditions, in correlation with the evolution of porosity; surface chemistry; and total, active, and reactive surface area (or TSA, ASA, RSA, respectively).

Several methods were used for microstructure and porosity characterization in oxidized graphite: optical microscopy with computer-added image analysis;[18,22,23] acoustic microscopy with image analysis;[24] electron microscopy;[17,25] Raman spectroscopy,[5,17] Fourier-transform infrared spectroscopy (FTIR);[12.13,14] X-ray photoelectron spectroscopy (XPS);[12,13,14] laser-based ultrasonic methods;[26] X-ray computer tomography and thermogravimetry.[27]
  - Graphite grades characterized: NBG-18;[12] IG-110;[13,18,23] NBG-18, PCEA, IG-110; [27] graphitic fuel matrix.[14,17]

- The effects of oxidation-induced porosity and microcracks on elastic moduli were characterized by a laser-based, contactless ultrasonic method. The results showed that the longitudinal and shear moduli, along with the Young's modulus, decrease with increasing graphite porosity. This variation was explained by models describing the effect of porosity on material stiffness.
  - Graphite grades characterized: oxidized IG-110 and NBG-18.[28]
  - Other graphite grades included in the analysis, based on literature information: HLM, H-451, PCIB, PGX, 2020, BAN, IG-110, IG-430, NBG-10, NBG-17, NBG-18, NBG-25, PCEA.[29]

- Research was initiated for the development of oxidation-resistant graphite and characterization of its oxidation behavior.
  - The oxidation rate in air at 740 °C of nuclear graphite doped with up to 6 % volume boron carbide (B_4C) was 20 times slower than that of undoped graphite.[30]
  - As-fabricated boronated graphite had a lower compression strength than the unmodified graphite. However, oxidized boronated graphite maintained a higher compression strength than did the oxidized non-boronated graphite.[31]

3.1.3 Model development for acute oxidation in air and accident scenario simulations

- The role of graphite as an important factor in limiting in-core component oxidation and protecting the fuel in MHTGRs was addressed in a new multiscale analysis of oxidation mechanisms.[2]
  - The report addresses public concerns regarding the use of graphite in MHTGRs. It also demonstrates – with arguments from the international knowledgebase on graphite oxidation – that the unique crystal structure and microstructure of graphite, from the atomic scale to full-size components, eliminates at least one of the three elements needed for uncontrolled combustion of graphite in air (heat, unimpeded oxygen access, and chain reaction). It is demonstrated with arguments that "graphite burning" is not possible.[2]

- Basic principles were outlined for modeling of oxidant penetration depth versus intrinsic graphite properties (porosity, microstructure) and extrinsic oxidation conditions (temperature, air flow rate, specimen size).
  - The model combines linearized rate equations with effective diffusivity parameters and estimates the evolution of penetration depth versus time and temperature. [32,33]

- A new model was developed for the oxygen transfer mechanism and the estimation of projected kinetic rate constants under variable conditions. [34]
  - The model is based on the reaction mechanisms at the graphite/oxygen interface and uses physically meaningful parameters that can be directly compared with the experimental and theoretical literature on graphite oxidation. Kinetic constants for oxidation of NBG-18 graphite were calculated at various conditions and compared with reported literature values. [34]

- Effective gas diffusivity in several graphite grades was measured to evaluate this important parameter that controls the transport rate of an oxidant in the porous structure of graphite. Together

with the rate of chemical reactions, the effective diffusivity determines the penetration depth and density profile of the oxidized layer.
    - Systems (gases and graphite grades characterized): Ar and N_2 from Ar-N_2 mixtures in graphites 2114, IG-110, IG-430, NBG-17, NBG-18, PCEA. [18,35]

- A multi-species chemical oxidation model was developed and validated with experimental and/or literature reports. The model accounts for consistent prediction of graphite oxidation rates and density profile development in oxidized specimens of various shapes, sizes, and graphite types. [36]
    - The model describes oxidation progress and allows for the calculation of activation energies and active surface area as a function of carbon consumption.[36]
    - The model was validated using in house–measured kinetic data on graphite PCEA oxidation in air [6] and literature reports on other graphite grades: IG-110, IG-430, NBG-25.[37]

- A comprehensive review of kinetic, transport, and microstructural factors interplay in the graphite oxidation process led to the development of a comprehensive oxidation model. [38]
    - The microstructurally informed model, kinetically independent of graphite grades, describes local and observed oxidation rates under a wide range of conditions applicable to air-ingress.[38]

- A previously developed model was used for predicting transient gasification of a full-scale NBG-18 coolant channel of a VHTR prismatic fuel element in conditions representing the unlikely event of accidental air ingress. [39,40]
    - A transient diffusion and flow model for multi-species composition of bulk gas in the cooling channel was developed and coupled with calculated weigh loss tables for NBG-18 gasification as a function of temperature and pressure. The results show that graphite weight loss is higher at the channel entrance and decreases rapidly with axial distance within the channel.[39,40]

3.2 CHRONIC OXIDATION BY TRACES OF MOISTURE IN HELIUM COOLANT

Graphite will undergo extremely slow but continuous oxidation by traces of moisture that will predictably be present, albeit at very low levels, in the helium coolant of VHTRs. Over the reactor lifetime, this chronic oxidation may cause degradation of mechanical strength and of other properties if the porous oxidized layer penetrates deeply enough from the exposed surface into the bulk of components. There is a stringent need to understand the behavior of graphite grades selected for reactor use during prolonged exposure to the chemical attack of moisture traces in helium at high temperatures. The goal of this research direction is to collect information and develop predictive models for lifetime chronic oxidation behavior of VHTR graphite components under normal operating conditions and beyond. Because direct rate measurements of these extremely slow processes are not feasible, information on kinetic parameters for oxidation by moisture could be obtained only from accelerated oxidation tests, with higher water pressures and even higher temperatures than the design conditions for normal operation.

The action list on chronic graphite oxidation derived from the Work Package on Graphite consists of the following steps:

1. Measure oxidation rates, determine and validate a comprehensive kinetic model suitable for prediction of intrinsic oxidation rates as a function of temperature and oxidant gas composition.

2. Measure the effective diffusivity of water vapor in the graphite pore system for accurate estimation of in-pore transport of moisture in the graphite grades of interest.

3. Obtain experimental information on the spatial and temporal evolution of the oxidized layer in selected graphite grades, as a function of temperature and water partial pressure.

4. Combine kinetics, transport, and direct observations of the oxidized layer into a comprehensive predictive model for chronic oxidation behavior, oxidant penetration, and porosity development.

5. Use the above information to estimate the impact of chronic oxidation on full-scale graphite components after prolonged exposure to moisture traces in helium coolant in VHTRs.

The accomplishments so far for these tasks are summarized in the following subsections.

3.2.1 Accelerated oxidation rate measurements in moist helium at various temperatures

- Accelerated oxidation rate measurements were performed in conditions relevant to normal operation and beyond (low moisture concentrations in helium and variable temperatures).
  - An experimental methodology for accelerated oxidation rate measurements in kinetic conditions (with minimal diffusion control) and the routine for data analysis was established and validated. [41]
  - Careful experiments revealed the limitations of the classical LH (Langmuir–Hinshelwood) kinetic model and led to the development of an improved BLH (Boltzmann-enhanced Langmuir–Hinshelwood) model. [41]
  - The newly developed BLH model provided reliable results for oxidation rates varying by more than three orders of magnitude, caused by water pressures varying by about 1000 times and temperatures varying by 350 °C.

- Both the LH and the newly developed BLH kinetic models were tested with rate data collected in accelerated tests of four graphite grades performed in H_2O/He mixtures. [41] .[42] [43]
  - Measurements have shown that rates of oxidation by moisture increase faster with temperature than was predicted by the classical LH kinetic model, especially at high moisture contents in helium, i.e., in conditions beyond the normal operating regime of VHTRs. These conditions may occur during off-normal events (steam ingress) and had to be characterized as well.
  - Kinetic parameters for LH and BLH oxidation models were determined for four major graphite grades: IG-110;[41] PCEA;[44] NBG-17;[45] 2114;[46] and graphitic fuel matrix.[47]
  - Globally, the experiments showed that the LH kinetic model was more accurate at moderate temperatures (800–1000 °C) and low partial water pressures (2–100 Pa), while the BLH kinetic model returned more accurate predictions over a broader range of temperatures (800 to 1100 °C) and water pressure conditions (2–2000 Pa). Over this range of conditions, the oxidation rates by moisture varied by three orders of magnitude.[48]

3.2.2 Effective diffusivity measurements of water vapor in helium in selected graphite grades

- Effective water diffusivity (caused by concentration differences) and water permeability (caused by total pressure differences) in the system H_2O-He were measured under controlled temperature, flow, and pressure conditions.
  - Results were obtained for grades PCEA and NBG-17;[49] PCEA, NBG-17, IG-110 and 2114.[48]
  - For each graphite grade, effective diffusivity is determined by similar structural factors regardless of the gas system (either H_2O-He,[49,48] or N_2/(N_2-Ar) and Ar/(N_2-Ar). [35]
  - The higher the open porosity (or the lower the apparent density), the higher was the effective diffusivity in this selection of graphites.[35,48]

3.2.3 Predictions of chronic oxidation behavior and degradation of material properties

- Theoretical analysis of graphite chronic oxidation led to formulation of the Wichner model, [32,33] which outlines the data analysis strategy based on the experimental plan implemented for four graphite grades.
  - The Wichner model [32,33] combines kinetics and transport phenomena and describes density profiles and strength degradation in oxidized graphite. The model predicted that the maximum penetration depth of the oxidant will depend on temperature, not on the time of exposure or the level of weight loss.

- The Wichner model was verified and validated for chronic oxidation behavior of nuclear graphite by moisture.
  - The following strategy was used: [32,33]
    - Measure accelerated oxidation rates and estimate kinetic parameters for LH and BLH models.
    - Determine water effective diffusivity from H_2O-He mixtures from independent measurements using thin graphite slabs (same grades).
    - Analyze density profiles in the oxidized layers produced at various temperatures.
    - Predict oxidant penetration depth versus temperature and compare with direct observations of oxidized layer density profiles.
  - Predictions by the BLH model were closer to measured observations for PCEA, NBG-17 and 2114 grades; but no satisfactory agreement could be found for superfine grade IG-110.[48]
  - Although each graphite grade behaved differently, all results showed that the maximum penetration depth of a well-developed oxidized layer was only a few millimeters at low temperature (e.g. 1–2 mm at 850 °C) and was even thinner at higher temperatures.

- Limitations and recommended ranges of the two kinetic models (LH and BLH) were as follows.
  - Oxidation by moisture of a graphitized fuel matrix was performed under a broader range of conditions, reaching up to extremely high temperatures (800–1400 °C) and water partial pressures (2 Pa–30 kPa) which are specific to a steam ingress accident scenario.[47] The BLH model provided better fitting of rate data at extreme temperatures and water pressures, whereas the LH model worked better at moderate temperatures (< 1000 °C) and lower water partial pressures (<100 Pa).
  - It appeared that the LH model is more appropriate for modeling chronic oxidation under normal VHTR operating conditions, while the BLH model should be used for analysis of off-normal events, such as steam ingress accidents. However, this conclusion still needs to be verified experimentally for nuclear graphites at extreme conditions.

- The parameters of the chronic oxidation model for four graphite grades were used for the development of a multi-physics model of full-scale oxidation of cooling channel graphite after prolonged exposure to moist helium in normal operation conditions.
  - The results showed that the oxidized layer will be 1–2 mm thick at graphite component surfaces and only in the bottom fuel blocks.[50,51]

3.3 CITATION INDEX: GRAPHITE GRADES CHARACTERIZED, INFORMATION AVAILABLE, AND REFERENCED SOURCES

This citation index shows the types of information available for each graphite grade that has been characterized within the scope of this report along with links to the cited reference sources.

	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	7, 8, 11, 12	8, 11	5		6, 8, 9, 10				11	7, 8, 9, 11,13		8, 9	30	14, 16
Structural characterization	27				27					18, 23, 27				
Effective diffusivity	35	35			35		35			35	35			
Effect on porosity	18, 22, 27		24		18, 22, 27	22				22, 27				
Effect on strength	15, 19		5, 19		10, 18			5		19, 20			31	16
Effect on elastic modulus	28									28				
Model development	34, 39, 40			37	6					37	38			
Chronic oxidation														
Oxidation rates by moisture		42, 43, 45, 48			42, 43, 44, 48		42, 43, 46, 48			41, 42, 43, 48				47
Structural characterization		45			44		46			41				
Effective diffusivity		48, 49			48, 49		49			49				
Model development		48, 50, 51			48, 50, 51		48, 50, 51			48, 50, 51				

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4. CONCLUSION: SIGNIFICANCE AND RECOMMENDATIONS

4.1 SIGNIFICANCE OF RESULTS

Preventing or minimizing the chemical attack of graphite components is one of the major concerns that designers and safety analysts must address in the licensing process for advanced reactors. Two different types of oxidative degradation processes may affect graphite properties and structural integrity: acute oxidation in the highly improbable event of an off-normal event, such as air or steam ingress; and chronic oxidation under the continuous attack of moisture or CO_2 traces (at the ppm level) that would usually occur in the helium coolant.

Chronic oxidation will always occur, continuously but extremely slowly. Its effects may be significant over the decades-long lifetime of a gas-cooled reactor. Despite the rigorous control of chemical impurity levels in the helium coolant, traces of moisture may be, and most probably will be introduced at various times (e.g., during revisions, refueling) in the normal operation cycle of the reactor. Oxidation by moisture is thermodynamically unfavorable below 700–750 °C, and it is still extremely slow at 800–850 °C. For example, in helium with a moisture content ten times higher than the maximum design limit, the weight-normalized predicted oxidation rates are slower than 10^{-9} s^{-1} (approximately 1% weight loss in 3000 years!). Because extremely slow reactions cannot be monitored in real time, the experiments used accelerated oxidation tests in conditions where the diffusion effects were minimized as much as possible. Several years of chronic oxidation research on the main graphite grades (PCEA, NBG-17, IG-110, 2114)[42,43,44,45,46] showed similar behavior patterns: the structural damage caused by chronic oxidation due to moisture will be limited to a thin layer at the exposed surface of graphite components.[32,33,48] The thickness of this oxidized layer will be narrower at higher temperatures and broader at lower temperatures, but it will not exceed a few millimeters even in the most unfavorable conditions. This limited surface damage may be less of a concern for massive structural elements (support posts, reflector) but it must be considered for the design of prismatic fuel blocks with millimeter-thin walls separating gas and fuel channels. Nevertheless, given the extremely low oxidation rates, it will take a very long time (many decades) for the damage expected in the fully developed oxidized layer to degrade local mechanical properties beyond the levels considered safe for graphite physical integrity.

Data from U.S.-DOE funded research on oxidation by moisture were used to predict chronic oxidation of large-scale components during long-time operation of HTGRs. Researchers from three US universities sponsored by the NEUP program developed a multi-physics model for chronic oxidation of a full-scale graphite coolant channel operating for 36 month in 6.4 MPa helium with 1.2 Pa H_2O and 10 Pa H_2 at 800–1400 K.[50,51] The results showed that oxidation would be expected to occur only in the three of four fuel blocks at the reactor bottom (where temperature is higher) and that the oxidized layer would be in general about 1.5 mm thin or less. This result matches early estimates by General Atomics[52] of minimal effects of chronic oxidation by moisture on graphite components at normal operating conditions in HTGRs.

In contrast, **acute oxidation** after an air- or water-ingress accident is a beyond-design event; i.e. its occurrence is judged to be so improbable that it is not fully considered in the design process.[2] This judgment is supported by all knowledge accumulated so far. Multiscale analysis of oxidation conditions, from graphite crystallites to full-scale components, demonstrates that the three conditions for self-sustained, uncontrolled combustion (unlimited oxygen access, heat source, and chain reaction propagation) cannot be simultaneously met for high-purity, high-density, highly crystalline nuclear graphite. Simply said, "graphite does not burn."[2,38]

However, consistent with the thorough analysis of the regulatory process, beyond-design accident sequences must be examined to fully understand the complexity of the nuclear plant design. This is done using sophisticated simulation codes and computer programs. They need reliable input data, for every grade

of graphite present in the reactor, concerning oxidation kinetics, oxidant transport, pore structure development, and possible effects on local properties. As previously presented, numerous measurements performed with the graphite grades of interest for VHTR led to the accumulation of a large volume of information on oxidation behavior in the kinetic regime, oxidant transport through graphite porosity, porosity development, and effects on local mechanical properties. Oxidation by air is a complex process that involves gaseous chemical species with different reactivities, their transport through viscous or Knudsen diffusion into the bulk of graphite, desorption, and reverse diffusion of gaseous oxidation products.[38] Chemical reactions accelerate with the absolute temperature (T) according to an exponential relationship (Arrhenius equation), while the rates of diffusion processes vary proportionally with $\sqrt{T^3}$. The overall behavior is always controlled by the slowest process. At lower temperatures (<650 °C), chemical reactions are slower than diffusion, and the process is under the chemical kinetics control (Regime 1). Because of faster diffusion rates, oxidation spreads deeply into the graphite bulk and may cause extended structural damage. As the temperature increases (~650–750 °C), the chemical reaction rates become comparable with the diffusion rates, and the overall process enters a transition stage at which slow in-pore diffusion limits bulk penetration and produces a density gradient under the surface (Regime 2). At even higher temperatures (>750 °C), chemical rates become so fast that the oxidant is rapidly consumed at (or near) the external graphite surface, which is rapidly gasified. The limiting factor is the mass transfer through the boundary layer at the gas–solid interface, which depends mostly on the concentration and flow pattern of the oxidant near the external surface (Regime 3). It should be acknowledged that these temperature limits are approximative, since the transitions from one regime to another depend on a series of intrinsic and extrinsic factors [8,38] that may vary significantly among graphite grades, reactor design, and local circumstances.

Most of the research done so far was focused on characterization of the oxidation behavior of the main graphite grades in Regime 1 (kinetic control). Post-oxidation analysis led to the identification of specific structural parameters, which may entail different courses of properties degradation. Most simulations of oxidation effects used the traditional approach in which oxidation behavior is represented by the Arrhenius equation with constant (apparent) activation energy and pre-exponential factors. Although easy to integrate with thermal-hydraulic codes, this approach is valid only within the temperature range of the experimental data. Moreover, this analysis ignores the complexity of chemical reactions, including kinetic and thermal effects associated with the generation of oxidation products (CO and CO_2), which may affect global evaluation of accident scenarios. Occasionally, early transitions from Regime 1 to Regime 2 were observed in experiments in which the rate of oxygen supply was (purposely or not) too low to sustain faster chemical rates as the temperature increased. With a few exceptions, most oxidation rates measured in commercial TGA equipment [11,12,13,14] were affected by oxidant starving at high temperatures, as shown by the down-shift of transition temperatures between Regime 1 and Regime 2.[5]

A different approach was pursued by researchers at the University of New Mexico at Albuquerque funded by an NEUP project. They developed a complex finite element model based on chemical-reaction kinetics,[6,36,37] which was coupled with calculations for CO and CO_2 production fluxes and associated thermal effects from their respective heats of formation. The analysis covered multispecies diffusion and variable flow conditions at temperatures corresponding to all three oxidation regimes.[39,40] Transient gasification of NBG-18 graphite in a 0.8 m coolant channel was modeled for various conditions of laminar flow. The results confirmed that oxidation of the graphite channel caused by air ingress would be non-uniform, with significantly higher weight losses occurring near the entrance of the cooling channel. The authors underscored the importance of local temperature increase from the heat of formation of CO and CO_2.

4.2 KNOWLEDGE GAPS AND FURTHER RESEARCH NEEDS

There still remain some research gaps related to both types of oxidation (chronic and acute) that nuclear graphite (and Matrix A3[*]) will, or may be, exposed to in VHTRs. Research focused on the following directions is needed to address these gaps.

4.2.1 Chronic oxidation

- Neutron irradiation effects on chronic oxidation behavior
- Degradation of properties (physical, mechanical, thermal) caused by chronic oxidation
- Chronic oxidation by CO_2 impurities in helium coolant
- Combined effects of H_2O and CO_2 impurities in helium coolant on chronic oxidation

4.2.2 Acute oxidation

- Neutron irradiation effects on acute oxidation behavior are needed.

- Models are needed for the transition range between kinetic control (Regime 1) and in-pore diffusion control (Regime 2).

- Research is needed for degradation of properties (physical, mechanical, thermal) caused by acute oxidation in each of Regime 1 (quasi-uniform bulk oxidation), Regime 2 (sub-surface density gradients), and Regime 3 (thin surface oxidized layers).

- Enhanced filler oxidation rates at extreme temperatures (e.g. 900–1200 °C) after oxidation and consumption of the binder phase are needed.
  - Binder-depleted graphite during low-temperature oxidation is expected to sustain more severe damage through filler attack if oxidation continues with faster rates at elevated temperatures.

- Predictive models are needed for the variation of isothermal oxidation rates vs. weight loss (or time) from the earliest moments of chemical attack.
  - Assessment of oxidation behavior up to the first 10 % weight loss limit specified by ASME codes requires explicit knowledge of weight loss variation versus time and temperature.
  - Microstructurally informed models need reliable experimental data on structure-related ASA and its relationship with RSA with the progress of oxidation.

- Flexible predictive models, interfaced with thermal-hydraulic analysis of external conditions and supported by complex experimental results, are needed for projecting the oxidation behavior of full-scale graphite components of various shapes and sizes.

[*] Fuel Matrix A3 is the binder material that holds TRISO fuel microspheres in fuel compacts (for prismatic reactors) and pebbles (for pebble bed reactors). Being a carbon-based material, it is sensitive to oxidation like all other nuclear graphite components. However, because of its different manufacturing process and lower final treatment temperature than nuclear graphites, Matrix A3 may have a different oxidation than graphite. For consistent evaluation of oxidation resistance of **all** carbon-based materials present in the reactor core, it is desirable that the research on chronic and acute oxidation of Matrix A3 be carried out using the same procedures and the expertise developed historically for oxidation studies of nuclear graphite materials. At present, oxidation of Matrix A3 is part of the fuel development tasks.

5. INFORMATION DISSEMINATION

The dissemination of information resulting from R&D activities on graphite oxidation supported by U.S.-DOE during the reference period of this report followed four main routes:

1. Peer-reviewed journal publications in the open scientific and technical literature, of which *Journal of Nuclear Materials* and *Carbon* journal held the highest incidence.

2. Technical reports and memoranda issued by national laboratories and marked for unlimited public distribution, which are available from the Office of Scientific and Technical Information website (https://www.osti.gov/).

3. Presentations at professional conferences, meetings, and workshops, such as the International Nuclear Graphite Specialists Meetings (INGSM), annual Carbon Conferences, International Conference on Advancement in Power Plants (ICAPP), and meetings of American Society for Standards and Materials (ASTM International) and American Society for Mechanical Engineering (ASME).

4. The Gen IV Materials Handbook, the materials properties database managed by ORNL. It is currently released for access by all the VHTR Materials Project Management Board signatories, including Australia, China, European Union, France, Japan, South Korea, United States, and Switzerland. The database contains raw data and analytical results on oxidation kinetics by air of several graphite grades measured according to ASTM D7542. Data from oxidation by moisture are in the course of being uploaded.

During the time frame covered in this report, a total of 48 publications have been issued as either peer-reviewed journal articles or technical reports from national laboratories and participants in university research projects. Figure 1 shows the distribution of total publications according to their type (mainly journals, institutional reports) and subject (acute or chronic oxidation). The number of publications on acute oxidation (37) is more than three times higher than the number of publications on chronic oxidation (11). Figure 2 shows the uneven distribution of total publications by their year of issuance.

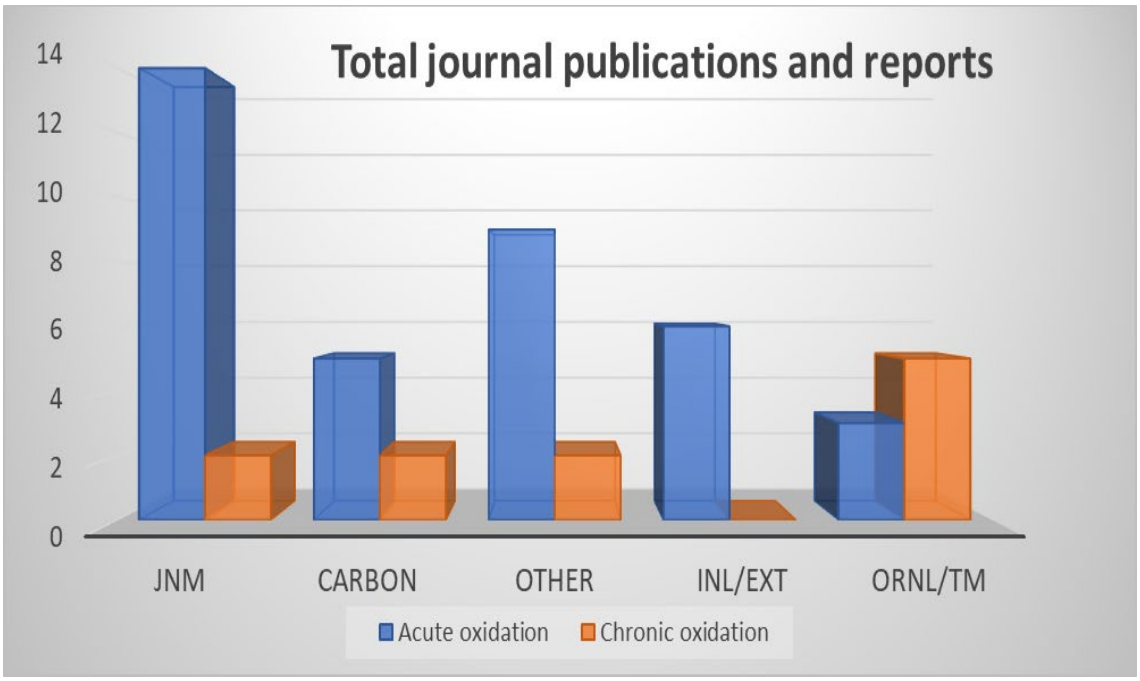

Figure 1. Distribution of graphite oxidation publications between journals and institutional reports and by subject (acute oxidation, chronic oxidation).

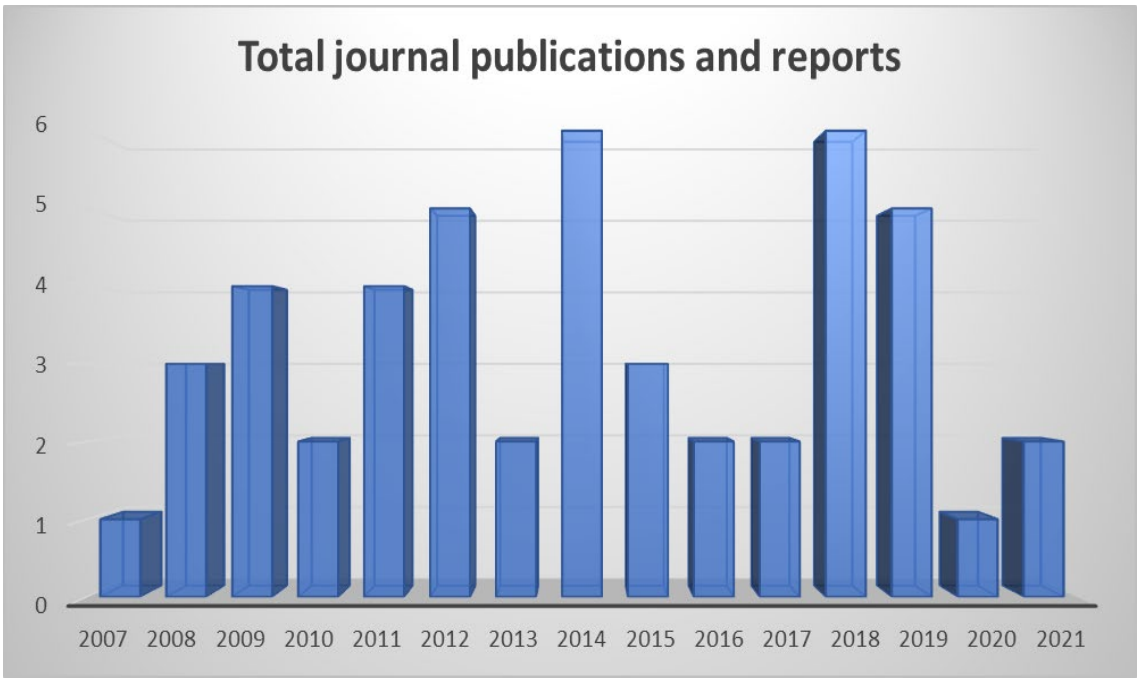

Figure 2. Distribution of total journal and report publications on graphite oxidation by year of publication.

6. QUALITY ASSURANCE

All research funded by U.S.-DOE and reported here was conducted in accordance with GIF quality assurance management guidelines, which require that

- All studies and testing be conducted according to an internationally accredited quality assurance program, i.e., Nuclear Quality Assurance 1 (NQA-1), in the United States

- All testings be conducted in accordance with consensually approved standards, i.e., ASTM, in the United States

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