Oxidation of Matrix Material in Helium with Varied Moisture Content

- Advanced Reactor Technologies
- Idaho National Laboratory

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Gas-Cooled Reactor
Fuels and Methods Program Review
June 18-19, 2019

ADVANCED REACTOR TECHNOLOGIES

Research Team

- Cristian Contescu; ORNL — Oxidation kinetics technical insight
- Grant Helmreich; ORNL — Technical insight
- Mike Howell; ORNL — SATS furnace operation
- John Hunn; ORNL — Programmatic oversight
- Jay Jellison; ORNL* — Anisotropy analysis
- Jo Jo Lee; ORNL — TGA operation and technical insight
- Robert Mee; University of Tennessee —Kinetics analysis
- Austin Schumacher; ORNL — Sample preparation
- John Stempien; INL — Technical insight

Program Goals and Objectives

- Determine oxidation kinetics of AGR-5/6/7 matrix material in varying water vapor environments
- Empirically measure oxidation rate at conditions relevant to water ingress accident conditions (high temperature, high steam)
- Characterize the structural variation between matrix “blanks” and fueled compacts
  - Understand the potential impact of microstructural variation/texture on property analysis from separate effects tests

Accomplishments Since May 2018

- Completed testing in “kinetic regime” and kinetic analysis of AGR-5/6/7 material
- Completed planned accident simulation oxidation tests (empirical tests)
- Initiated microstructural evaluation of oxidation samples and fueled AGR-5/6/7 compacts

Talk Outline

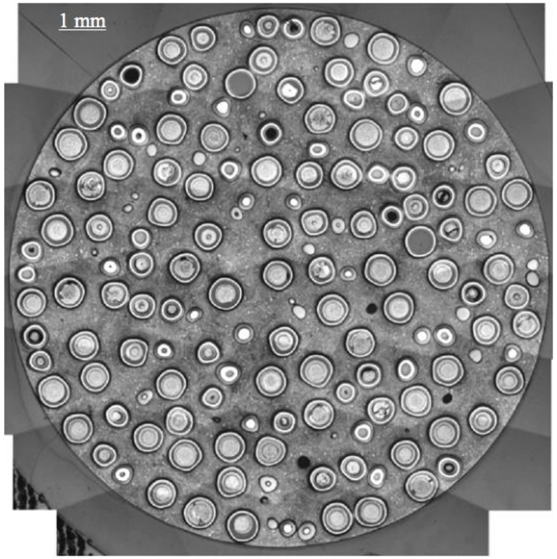
- Background
  - Graphite Oxidation
  - Samples
- Kinetic Analysis
  - System
  - Results
- Accident Scenario Testing
  - System
  - Results
- Microstructural Analysis
- Summary

Motivation: separate effects testing of matrix

- Fuel forms are complex: the matrix material surrounds and protects TRISO fuel in fuel compacts

- The response of each component to oxidizing environments must be known to understand (model) fuel performance in such (improbable) events

- Testing components separately allows for the oxidation behavior of each component to be isolated and measured
  - Ultimately providing input to fuel performance models



Montage of transverse cross section of Compact 3-3-3 after incremental grinding and back-potting [1].

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[1] S.A. Ploger, P.A. Demkowicz, and J.D. Hunn, Ceramographic Examinations of Irradiated AGR-1 Fuel Compacts, INL/EXT-12-25301, Idaho National Laboratory, Idaho Falls, ID (2012).

Current knowledge: oxidation performance of HTGR fuel components

- Matrix oxidation by water (moisture) has not been studied
  - Matrix is a composite material and thus different than nuclear graphite
    - Existing knowledge on steam oxidation of graphite may not apply for matrix
  - Matrix tests in air were performed between 500 and 1600 °C. [1,2]
- Template exists for steam oxidation kinetic analysis
  - Nuclear graphite oxidation tests were performed mostly in the kinetic regime (T < 1000 °C, P_{H_2O} between 0.01 and 3 kPa) [3-5]
  - Accident conditions expected to exceed these conditions but kinetic parameters can be obtained to support modeling efforts
- Oxidation of TRISO SiC in air and moisture was tested on samples not representative of AGR fuel. [6.7]
  - Active-passive oxidation regime has not been explored with TRISO SiC – Focus of recent NEUP call

1. Contescu, C.I., et. al., “Practical aspects for characterizing air oxidation of graphite,” Journal of Nuclear Materials, **381**, (2008) 15-24.
2. Lee, J.J., Ghosh, T.K., and Loyalka, S.K., “Oxidation rate of graphitic matrix material in the kinetic regime for VHTR air ingress accident scenarios,” Journal of Nuclear Materials, **451** (2014) 48-54.
3. Velasquez, C., Hightower, G., and Burnette, R., “The Oxidation of H-451 Graphite by Steam,” GA-A14951 (1978).
4. Overholser, L.G. and Blakely, J. P., “Oxidation of graphite by low concentrations of water vapor and carbon dioxide in helium.” Carbon, **2** (1965) 385-394.
5. Contescu, C. I., Mee, R. W., et al., “Oxidation of PCEA nuclear graphite by low water concentrations in helium,” Journal of Nuclear Materials, **453** (2014) 225-232.
6. Contescu, C.I., Mee, R W et al, “Beyond the classical kinetic model for chronic graphite oxidation by moisture in high temperature gas-cooled reactors” Carbon, **127** (2018) 158-169.
7. Terrani, K. A. and Silva, C. M., “High temperature steam oxidation of SiC coating layer of TRISO fuel particles,” Journal of Nuclear Material, **460** (2015) 160-165.
8. Tang, C. and Liu, Bing, et al., “SiC performance of coated fuel particles under high-temperature atmosphere of air,” Nuclear Engineering and Design **27** (2015) 64-67.

About air and moisture events in HTGR

- Air / Steam ingress
  - Acute corrosive attack and failure of graphitic materials
  - Corrosion of fuel elements and release of fission products from TRISO particles
- Air ingress[2]:
  - Break of primary coolant pipe
  - Reactor coolant system depressurization
  - Air leaking in and natural circulation within system
- Water ingress[2]:
  - Initiated by moderate-sized break of steam generator line
  - Steam leakage into primary system
  - Depressurization of primary system

[2] Preliminary Safety Information Document for the Standard MHTGR, Vol. 1, HTGR-86-024 (1986).

Air and water ingress conditions

- Air ingress:

Maximum Fuel Temperature (°C)	1600 +
Total air pressure (kPa)	101.3
O_2 partial pressure (kPa)	~ 0 to 21
Total Duration (hours)	100 +

- Water ingress

Range of Fuel Temperatures (°C)	1000 to 1630
H_2O partial pressure (kPa)	≤ 2 (for tens of hours) ≤ 400 (for up to several hours)
Total Duration (hours)	100 +

These conditions form basis for experimental test matrix

Two types of testing were performed on AGR-5/6/7 matrix blanks

Oxidation kinetics testing:

- Low pressures $3 < P_{H2O}$ (Pa) < 600

  $3 < P_{H2}$ (Pa) < 90
- Low temperatures $800 < T$ (°C) < 1200
- Continuous rate measurements during oxidation at preset conditions
- 184 data points: Rate = $f(P_{H2O}\, P_{H2}\, T)$
- Measure oxidation rates and fit existing models: Langmuir-Hinshelwood (LH) & Boltzmann-modified Langmuir-Hinshelwood (BLH)

Accident condition testing:

- Live oxidation tests in high temperature furnace
- High steam pressures $10 < P_{H2O}$ (kPa) < 48

  no H_2, residual $30 < P_{O2}$ (Pa) < 50
- High temperatures $1200 < T$ (°C) < 1500
- Rates estimated from final weight differences
- Limited number of data points

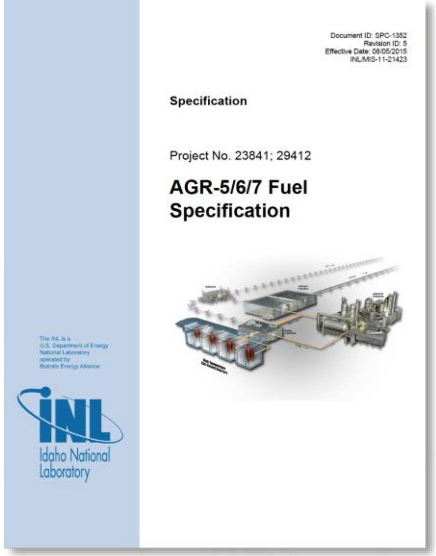
Oxidation Testing Samples

Matrix oxidation specimens

- Specimens fabricated to meet AGR-5/6/7 specifications for fuel matrix carbon as defined by the AGR program completed prior to FY19

- Disk geometry – minimizes density variations across the thickness
  - Over 300 samples were fabricated to meet the needs of the planned test matrix

- Targeted 1:1.1 surface area to volume ratio to minimize volume effects[3]



Document ID: SPC-1352
Revision ID: 5
Effective Date: 08/05/2015
INL/MIS-11-21423

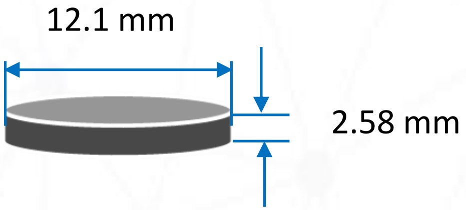
Specification

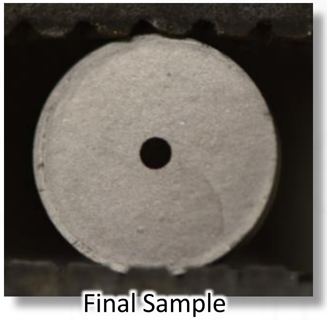
Project No. 23841; 29412

AGR-5/6/7 Fuel Specification

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance

Idaho National Laboratory





Final Sample

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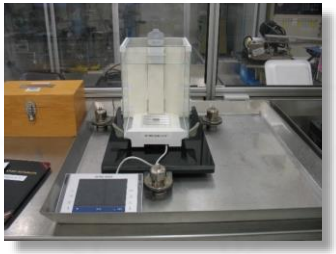
[3] Contescu, C.I., et. al., "Practical aspects for characterizing air oxidation of graphite," Journal of Nuclear Materials, **381**, (2008) 15-24.

Fabrication of fuel matrix carbon specimens

- AGR-5/6/7 matrix production recipe (raw material supplied by BWXT):
  - Natural graphite – for compressibility
  - Synthetic graphite – for toughness
  - Thermosetting resin – for bonding TRISO particles and compacting
  - Hardening agent

Press → Carbonization → High temperature → Inspection



Balance for measuring matrix 0.580 g material

Die for pressing sample

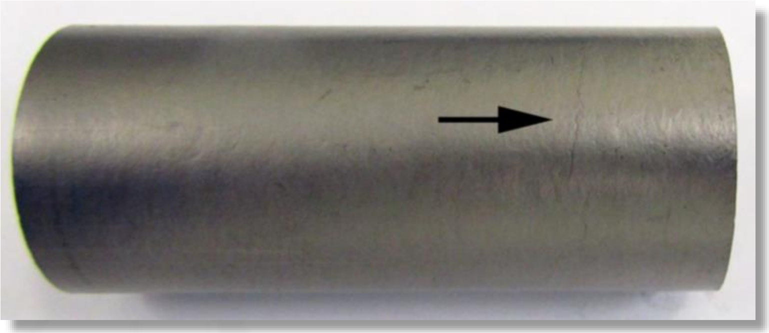
Promess servo press 155 ºC and 1.3 kN

Carbonization furnace 0.5 h @ 900 ºC

High temperature vacuum furnace 1 h @ 1800 ºC

Variability observed among samples; required acceptance criteria

Examples of surface fissures prompting rejection



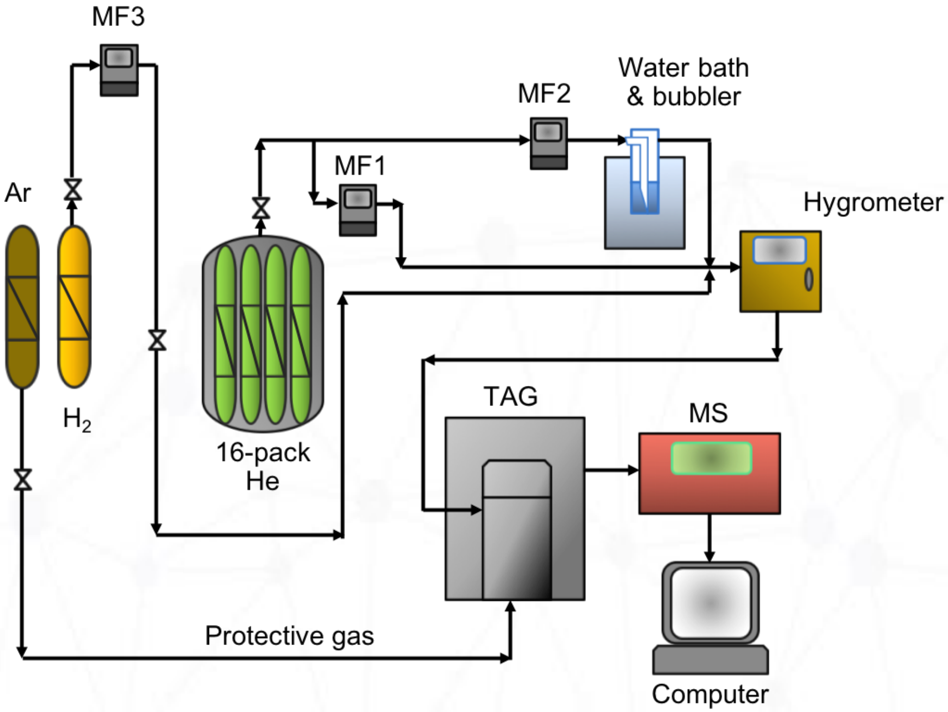
Fissure in ARB-B1 ring blank[2]

- Specimens were visually inspected for surface irregularities
  - Specimens with fissures or other gross surface defects were rejected
- Target density for acceptance ≥ 1.65 g/cm^3
  - Accepted specimen yield was low (~ 30 %) which was expected based on historical experience with AGR-5/6/7 blend. [1]

1. Trammell, M.P. and Jolly, B.C., “AGC-4 Compact Fabrication Study,” Oak Ridge National Laboratory (2014).
2. Hunn, J.D., et al., ORNL/TM-2011/272, (2012).

Oxidation Kinetics Testing

ORNL system for accelerated oxidation tests



The system was designed and used for oxidation kinetic measurements of nuclear graphite[1]

Data collected:
MF1
MF2
MF3
MS
TG
Hygrometer
Water Bath T
Room P, T

Conditions:
Kinetic regime
800 < T(°C) < 1200
$3 < P_{H_2O}$ (Pa) < 1000
$0 < P_{H_2}$ (Pa) < 100
Total flow: 1.5 L/min

1. Contescu et al., Beyond the Classical Kinetic Model for Graphite Oxidation by Moisture in High Temperature Gas-Cooled Reactors, Carbon 127 (2018) 158-169.

Kinetic analysis: Langmuir-Hinshelwood (LH) model

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$$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_2{}_{(g)}$$

H_2O and H_2 compete for surface sites

$$C_f + H_2O_{(g)} \underset{j_1}{\overset{i_1}{\leftrightarrows}} C(H_2O)$$

$$C(H_2O) \overset{j_3}{\rightarrow} CO_{(g)} + H_2{}_{(g)}$$

$$C_f + H_2{}_{(g)} \underset{j_2}{\overset{i_2}{\leftrightarrows}} C(H_2)$$

Gadsby (1946)

Surface sites blocked by atomic H

$$C_f + H_2O_{(g)} \overset{i_1}{\rightarrow} C(O) + H_2{}_{(g)}$$

$$C(O) \overset{i_3}{\rightarrow} CO_{(g)} + C_f$$

$$C_f + \tfrac{1}{2} H_2{}_{(g)} \underset{j_2}{\overset{i_2}{\leftrightarrows}} C(H)$$

Giberson and Walker (1966)

$$\boldsymbol{Rate}_{LH} = \frac{\boxed{k_1}\, P_{H2O}}{1 + \boxed{k_2}\,(P_{H2})^n + \boxed{k_3}\, P_{H2O}}$$

$$\boldsymbol{Rate}_{LH} = \frac{\boxed{k_1}\, P_{H2O}}{1 + \boxed{k_2}\,(P_{H2})^{1/2} + \boxed{k_3}\, P_{H2O}}$$

LANGMUIR-HINSHELWOOD RATE EQUATION

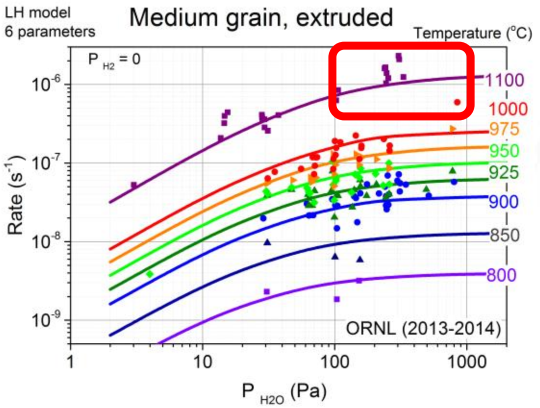
Kinetic analysis: Limitations of LH model for fine grain graphite

Chronic oxidation by moisture of several grades of nuclear graphite has been studied by Contescu et al.

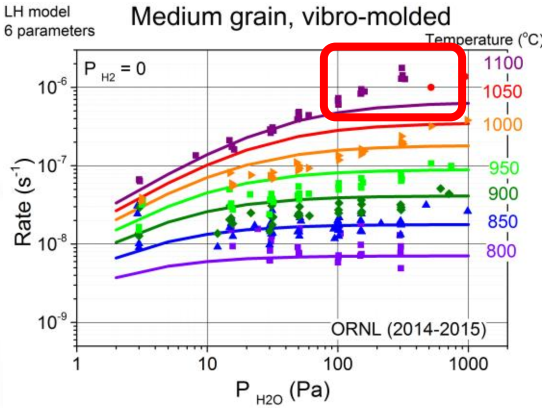
Results showed differences in behavior between medium grain and fine grain graphite.

At T > 1000 °C oxidation rates of fine grain graphite increase faster with P_{H2O} than what the LH model predicted.

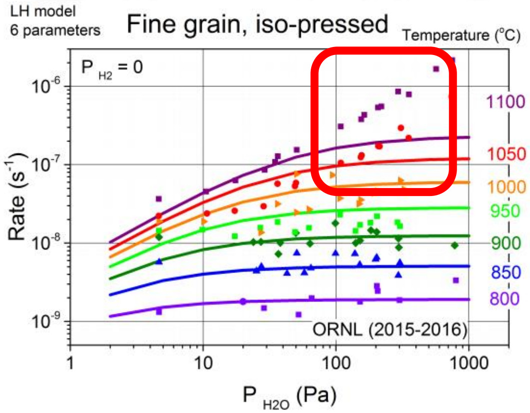
Apparently, more reactive sites on graphite surface activate as the temperature increases.



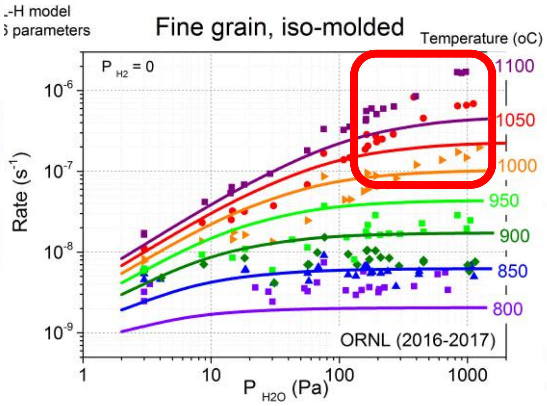
Medium grain, extruded



Medium grain, vibro-molded



Fine grain, iso-pressed



Fine grain, iso-molded

Kinetic analysis: Boltzmann-modified LH model (BLH)

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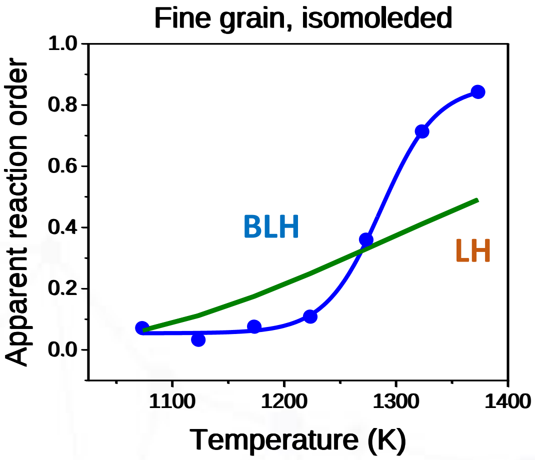
$C + m\, H_2O \rightarrow C + CO + H_2$



$$m(T) = m_{max} + \frac{m_{min} - m_{max}}{1 + exp\left(\frac{T - T_0}{\theta}\right)}$$

Boltzmann distribution function

$$Rate(P_{H2O}, P_{H2}, T) = \frac{A_1\, exp\left(-\frac{E_1}{RT}\right)(P_{H2O})^m}{1 + A_2 exp\left(-\frac{E_2}{RT}\right)(P_{H2})^n + A_3 exp\left(-\frac{E_3}{RT}\right)(P_{H2O})^m}$$

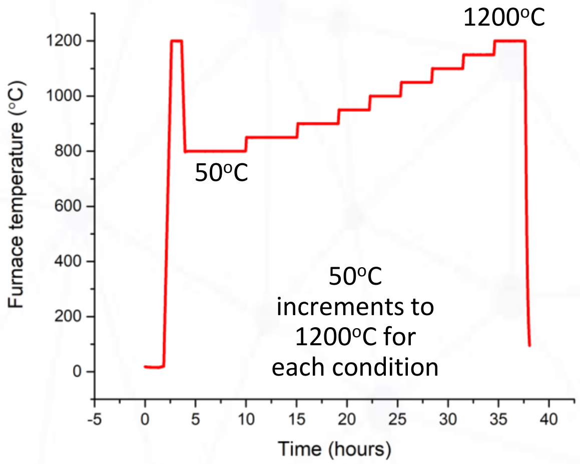
- The LH model was observed to be limited at higher temperatures and partial pressures[1]
- Boltzmann-enhanced Langmuir-Hinshelwood (BLH) model developed to better predicts oxidation rates over large ranges of temperatures, and partial pressures of water and hydrogen
  - BLH model is based on empirically measured reaction order (m) which follows the integral Boltzmann distribution function

1. Contescu et al., Beyond the Classical Kinetic Model for Graphite Oxidation by Moisture in High Temperature Gas-Cooled Reactors, Carbon 127 (2018) 158-169.

Test matrix and status of testing

Gas Compositions	P H_2O (Pa)	5	20	50	100	150	200	250	300	500	1000
P H_2 (Pa)	0 (2x)		x		x		x		x	x	x
	25		x		x		x		x	x	
	100		x		x		x		x	x	

- Conditions provide scope to determine kinetic parameters for oxidation of matrix in moisture environments – skewed toward higher P H_2O to reflect accident conditions
  - Follow well developed test matrix for nuclear grade graphite oxidation[1]
- Include P H_2 to account for competition for surface sites
- >1000 °C conditions added to link to high temperature steam tests (not typical in prior analysis)[1]



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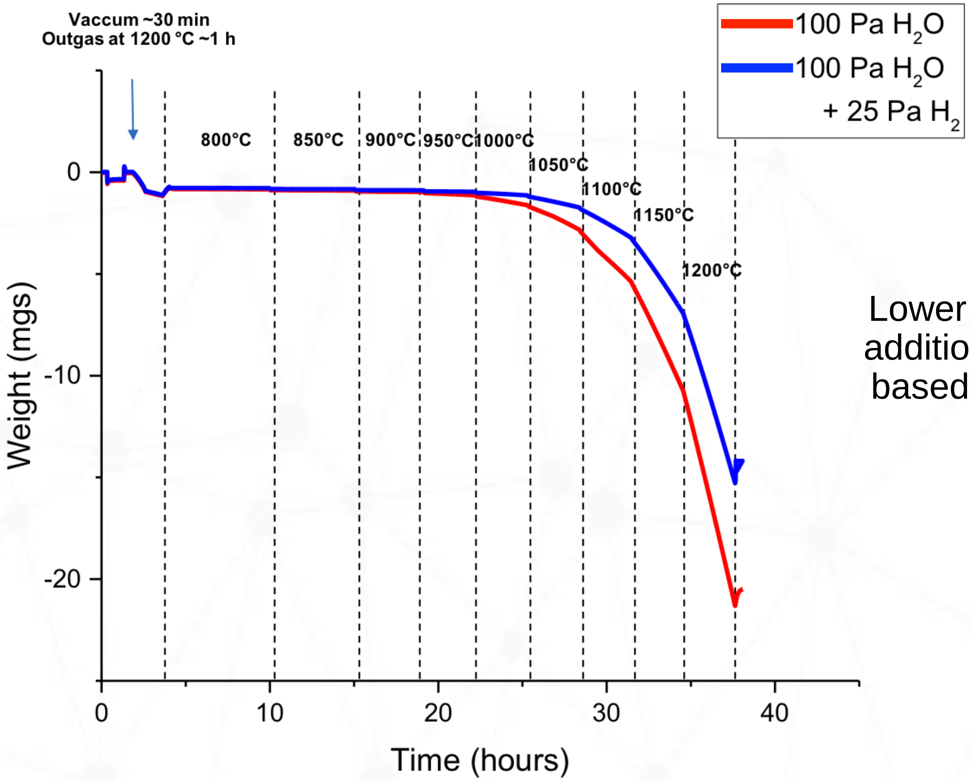
[1] Contescu, C. I., Mee, R. W., et al., "Oxidation of PCEA nuclear graphite by low water concentrations in helium," Journal of Nuclear Materials, **453** (2014) 225-232.

Demonstration that H_2 suppresses oxidation of matrix material

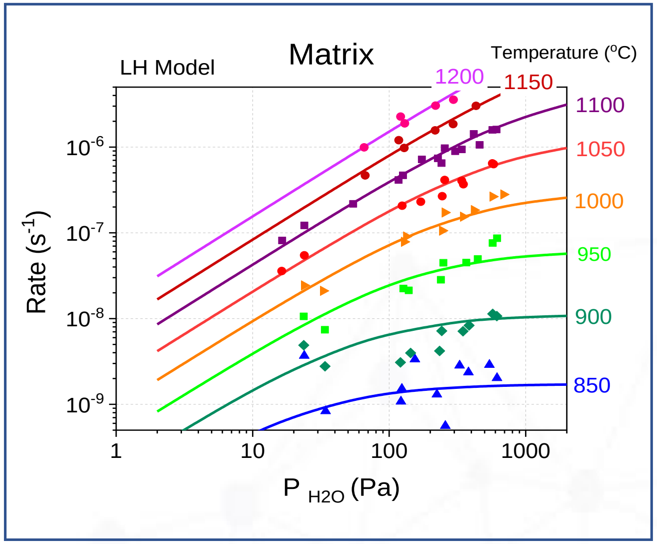
ADVANCED REACTOR TECHNOLOGIES

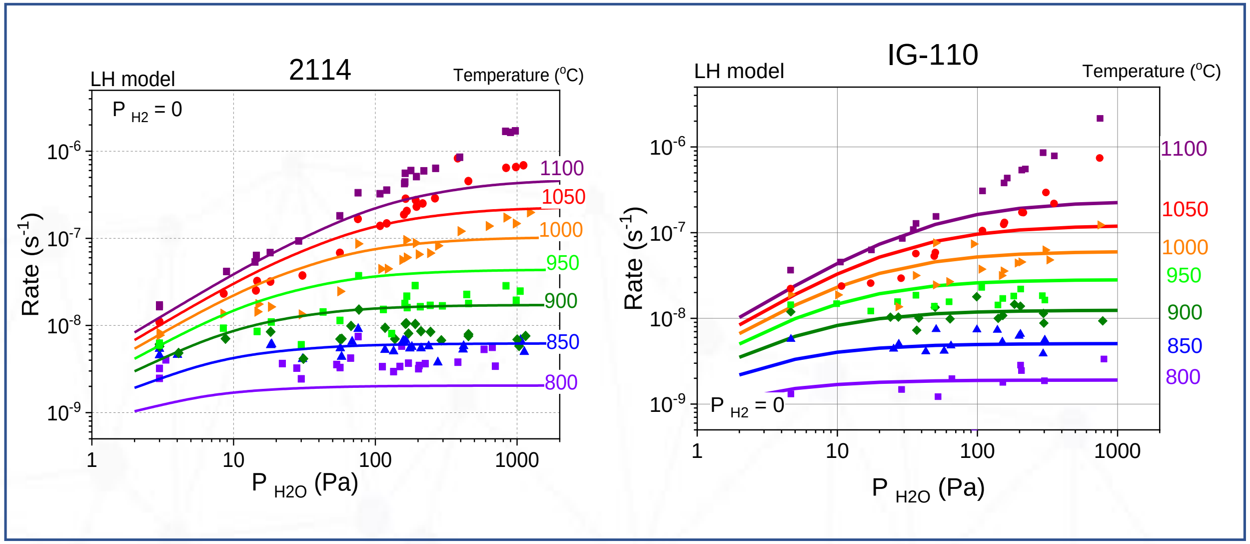


Lower oxidation rate with addition of H_2 is expected based on global reaction

Matrix performs similar to nuclear grade graphite

This work

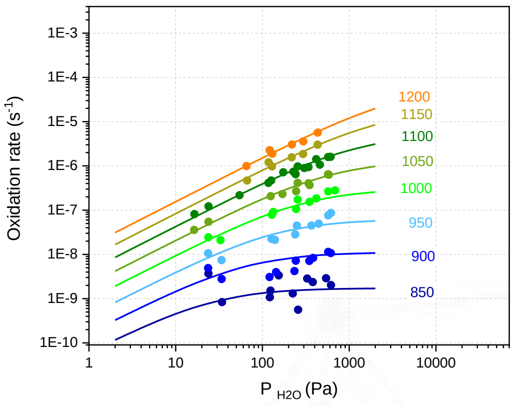


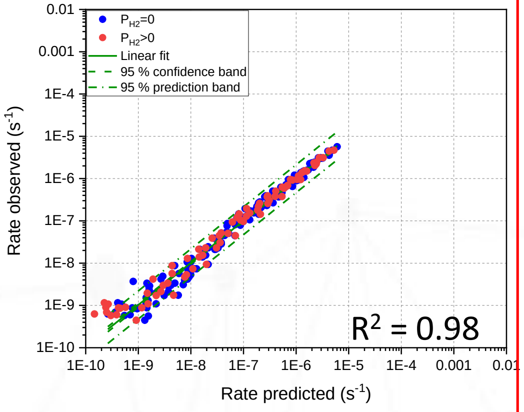


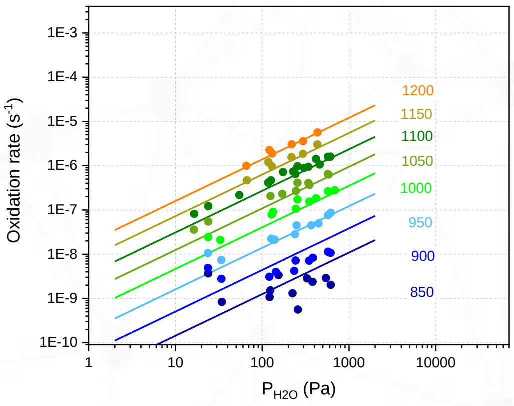
- Similar rates and trends between matrix and nuclear grade graphite
  - Even with significant structural differences between nuclear graphite and matrix (natural versus synthetic, carbonized resin binder, etc.)
- Observation provides confidence in testing approach

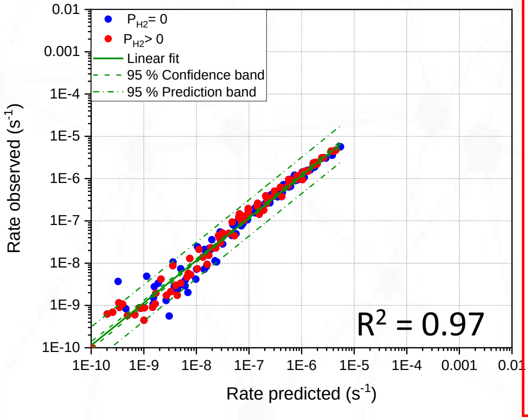
Analysis of matrix carbon oxidation data (low P_{H2O} and T)

ADVANCED REACTOR TECHNOLOGIES


LH Model


LH Model


BLH Model


BLH Model

LH model

A_1	2.8E-02	$(Pa.s)^{-1}$
A_2	4.0E-10	$(Pa)^{-0.5}$
A_3	2.1E-16	$(Pa)^{-1}$
E_1	181	kJ/mol
E_2	-223	kJ/mol
E_3	-318	kJ/mol

End Goal!

$$Rate\ (P_{H2O}\ P_{H2}\ T) = \frac{A_1 exp\left(-\frac{E_1}{RT}\right) P_{H2O}}{1 + A_2 exp\left(-\frac{E_2}{RT}\right)(P_{H2})^{0.5} + A_3 exp\left(-\frac{E_3}{RT}\right) P_{H2O}}$$

BLH model

A_1	1.1E+02	$(Pa.s)^{-m}$	m_{max}	0.94	
A_2	6.6E-05	$(Pa)^{-0.5}$	m_{min}	0.11	
A_3	3.4E-04	$(Pa)^{-m}$	To	1146	K
E_1	276	kJ/mol	θ	75	K
E_2	-87	kJ/mol	n	0.5	
E_3	42	kJ/mol			

$$Rate\ (P_{H2O}, P_{H2}, T) = \frac{A_1 exp\left(-\frac{E_1}{RT}\right)(P_{H2O})^{\left[m_{max}+\frac{m_{min}-m_{max}}{1+exp\left(-\frac{T-T_o}{\theta}\right)}\right]}}{1 + A_2 exp\left(-\frac{E_2}{RT}\right)(P_{H2})^{n} + A_3 exp\left(-\frac{E_3}{RT}\right)(P_{H2O})^{\left[m_{max}+\frac{m_{min}-m_{max}}{1+exp\left(-\frac{T-T_o}{\theta}\right)}\right]}}$$

- Both LH and BLH models can reasonably fit observed oxidation rates

Tests simulating water ingress accident

Testing acute oxidation at high temperature and pressure

- Had a living test matrix – aggressive tests result in a need to adjust test conditions based on feasibility assessment from initial runs
- Conditions: 1200–1500 °C*, 10–48 kPa $H_2O_{(g)}$ steam to provide empirical oxidation rates for AGR-5/6/7 matrix samples in steam ingress accident conditions
  - *Initial maximum temperature target was 1600 °C
  - Tested bounding conditions at 1200 °C (48 kPa) and 10 kPa (1500 °C)
- Testing in HT module of the SATS furnace
  - Flowing UHP-He carrier gas (0.5 L/min)
  - Measure mass loss associated with residual pO_2 (<300 ppm)
- Measure $\Delta w(T,t,pH_2O)$; require 4+ exposure times for each test condition (temperature and pH_2O) to determine oxidation rate

High Temperature Furnace Module

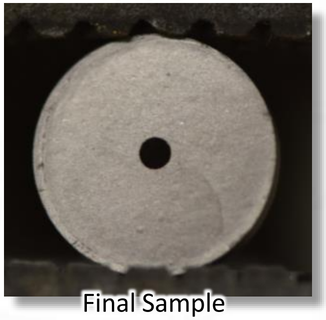
Final Test Matrix

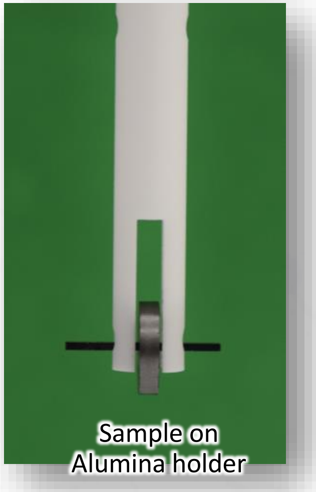
Steam/Temperature		1200ºC	1300ºC	1400ºC	1500ºC
P H_2O (kPa)	10	x	x	x	x
	20	x	x	x	
	30	x	x	x	
	48	x			
	0*	x	x	x	x

* Baseline to account for residual oxygen in system

Mass loss measurements after each run

- A central hole (1/16” dia.) was drilled to suspend sample during testing
- Samples were conditioned according to ASTM standard D7542-09[1]
  - 130°C, 3 hours in air with samples stored in a desiccator after conditioning
- Exposed samples were placed directly into pre-weighed aluminum pans due to fragile nature of exposed samples to limit sample loss during handling
  - Samples were soft after oxidation
  - Exposed samples were stored in desiccator after exposure
  - Select samples were cross-sectioned after exposure for optical microscopy


Final Sample


Sample on Alumina holder


As-Fabricated


1400 °C, 20 kPa H_2O, 1 hour

Results of accident simulation testing

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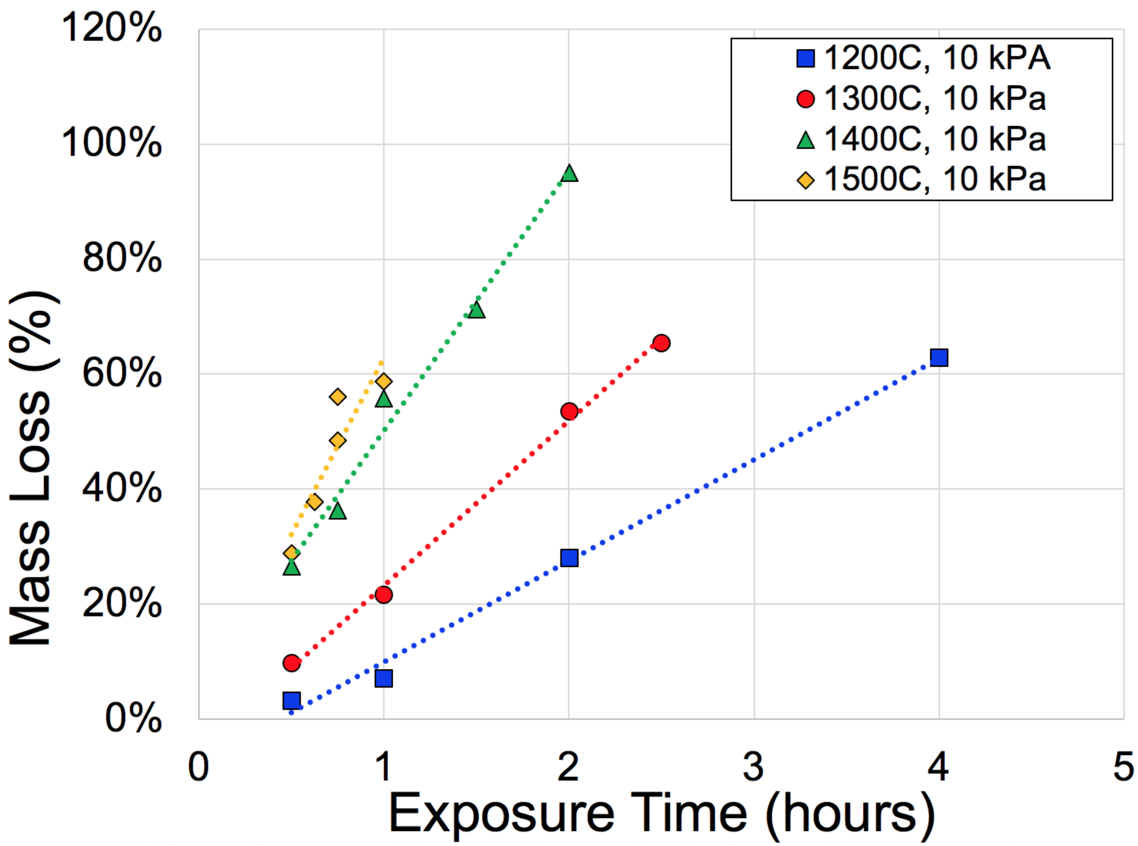
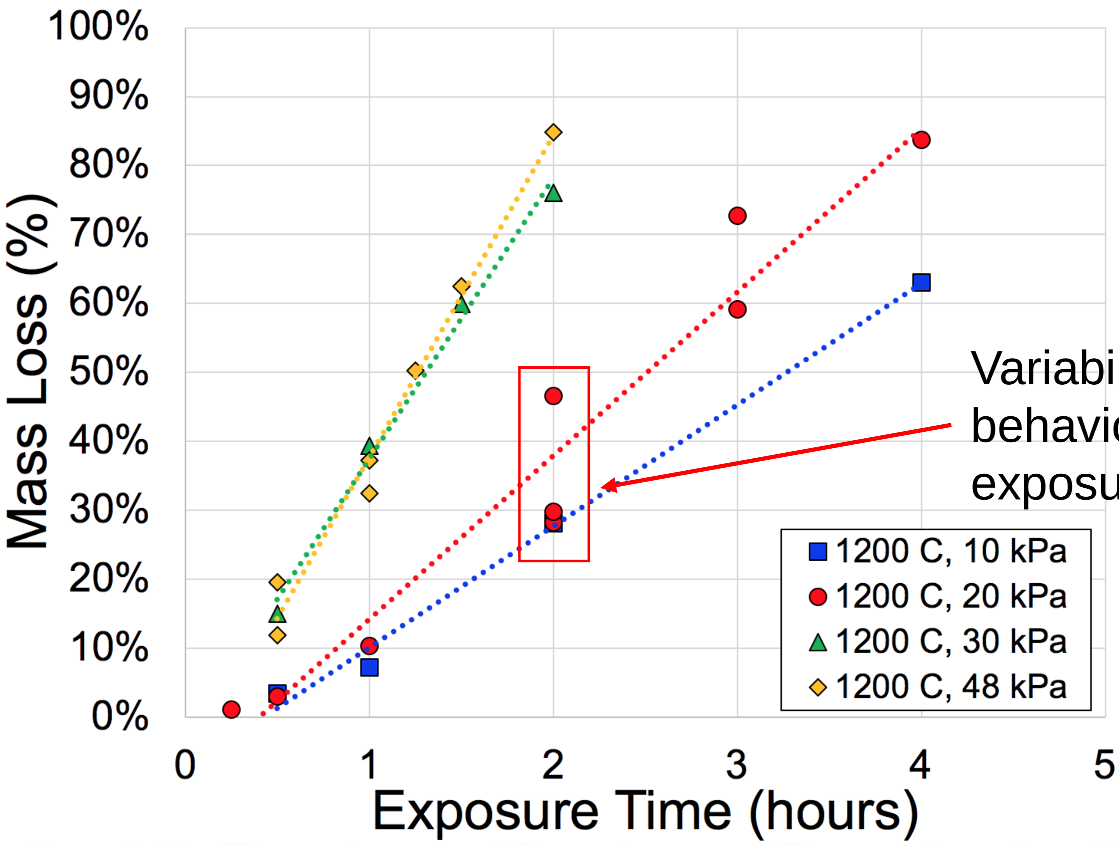


Increase in rate as a function of temperature

Results of accident simulation testing

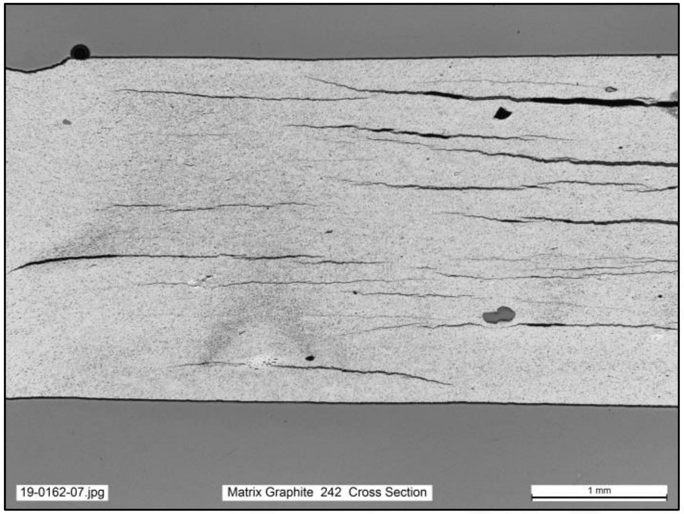


Variability in oxidation behavior at identical exposure conditions

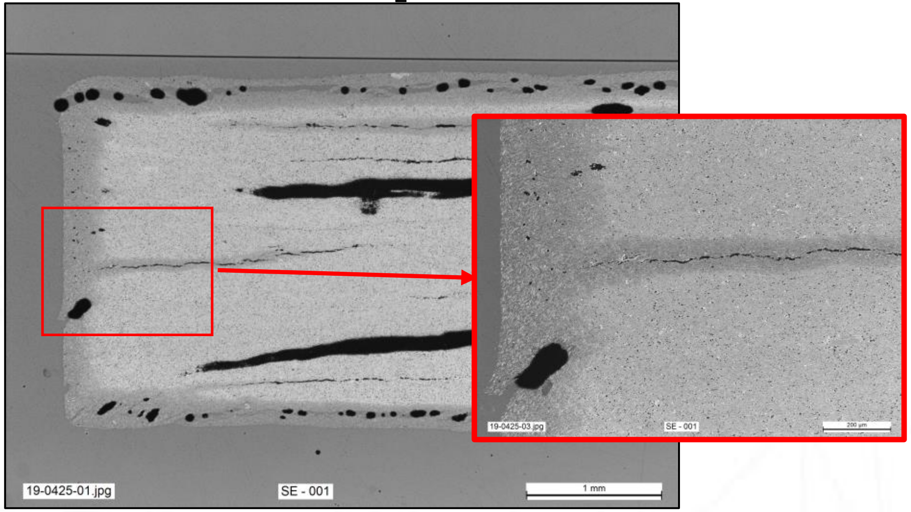
Increase in rate as a function of P H_2O 10–30 kPa, with apparent saturation above 30 kPa as similar mass loss (ML) is observed

Impact of Microstructure on Oxidation?

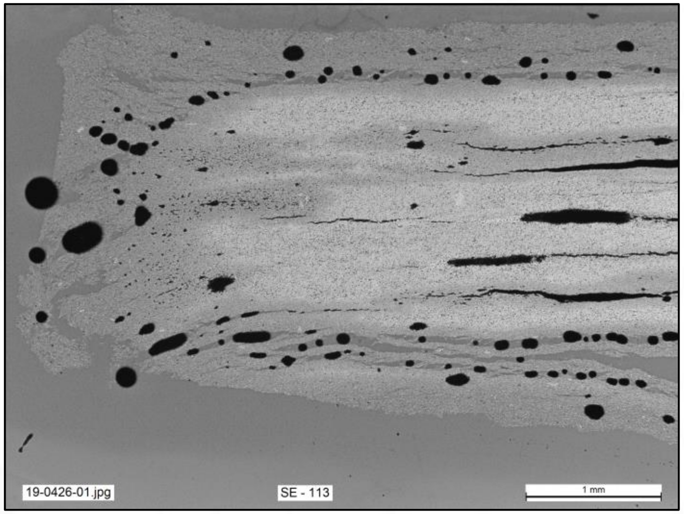
As-fabricated



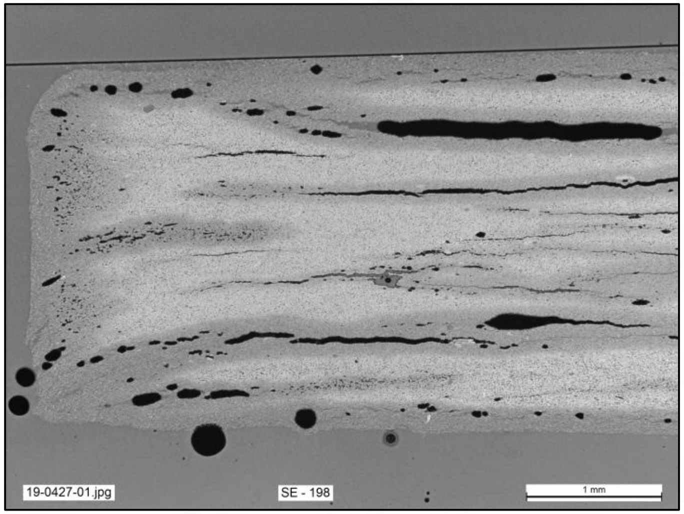
1200 °C, 1h, 20 kPa H_2O (10% ML)



1200 °C, 1h, 30 kPa H_2O (39% ML)

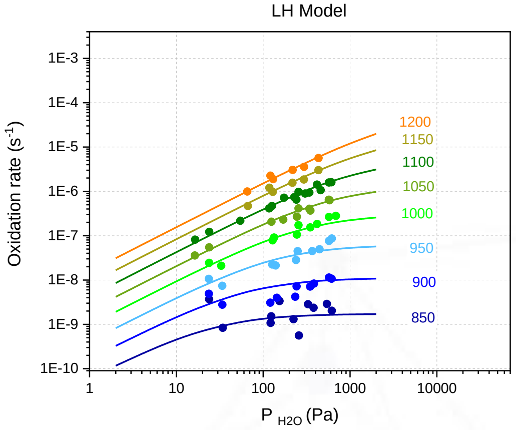


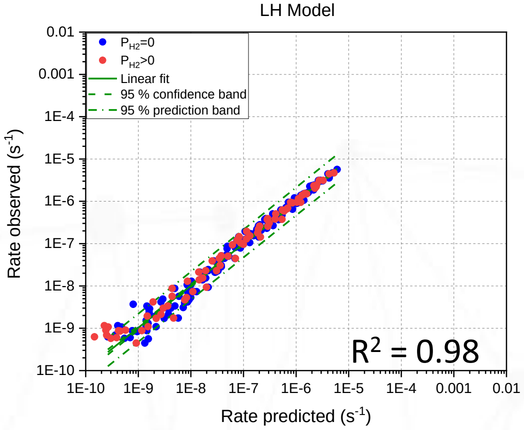
1200 °C, 1h, 50 kPa H_2O (37% ML)



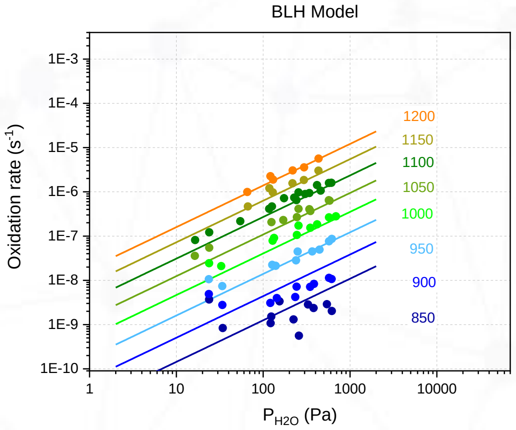
- Considerable internal fissuring is a likely cause of rate variation
- Beyond kinetic regime – oxidation is non-uniform and surface dependent

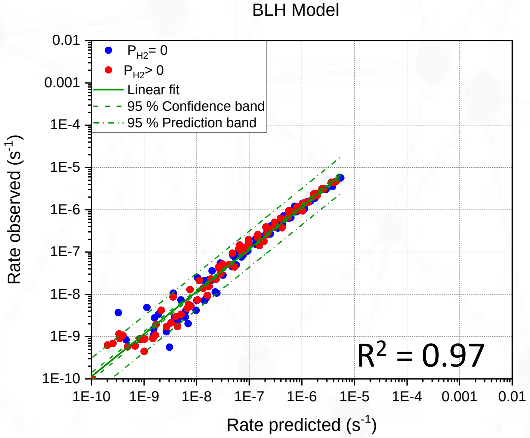
Analysis of matrix carbon oxidation data (low P_{H2O} and T)


LH Model


LH Model

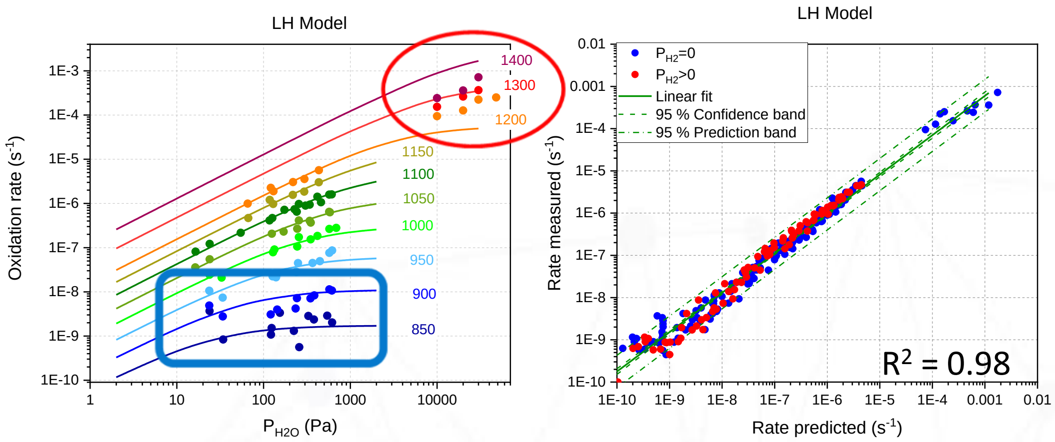
$R^2 = 0.98$


BLH Model


BLH Model

$R^2 = 0.97$

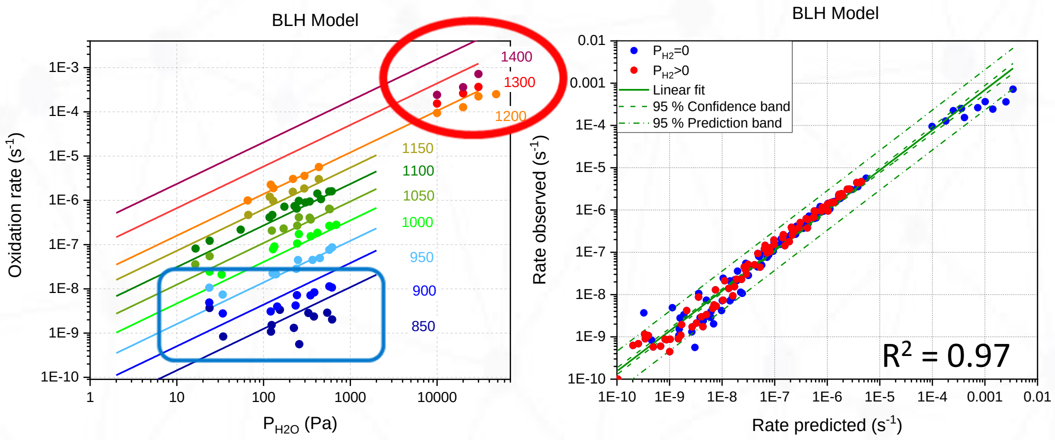
Analysis of matrix carbon oxidation data (low P_{H2O} and T)



BLH model fits remarkably well all rate data at 1200 ºC.

Both models overpredict the rates at 1300 and 1400 ºC.

- *Oxidation is no longer in kinetic regime at these temperatures*

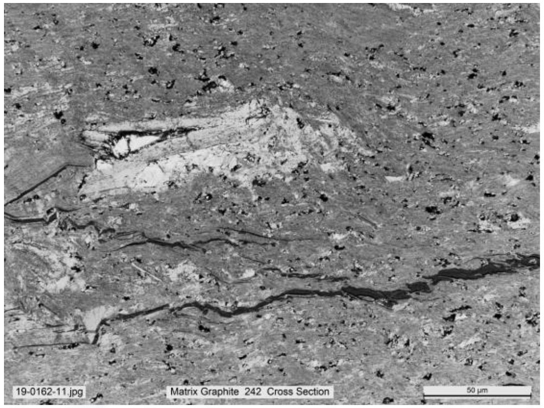


LH model appears to better predict rate data at 850-900 ºC

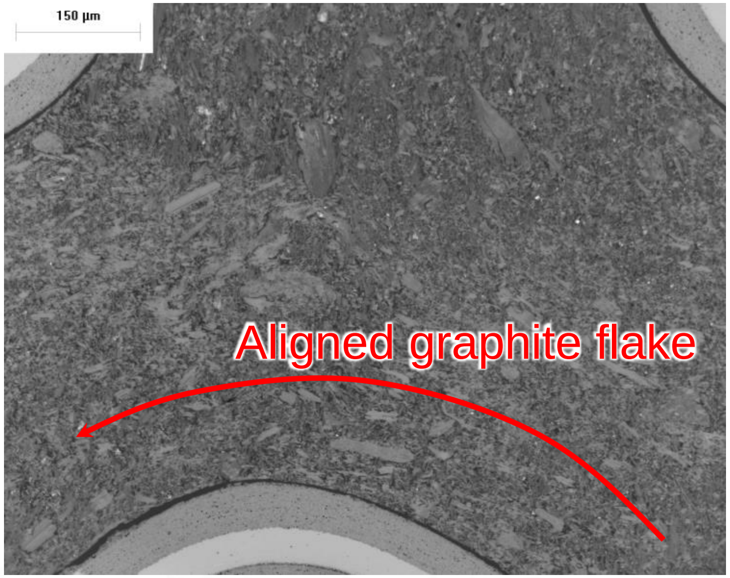
- *At these temperatures oxidation is in the kinetic regime.*

Microstructural analysis of AGR-5/6/7 materials

Microstructural variation between matrix “blanks” and compacts



Optical image of AGR-5/6/7 matrix blank cross-section

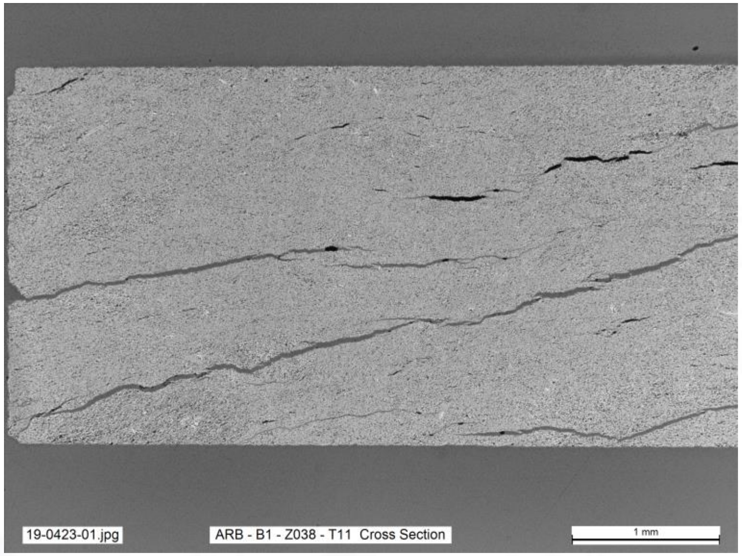


Optical image of AGR-2 compact cross-section[1]

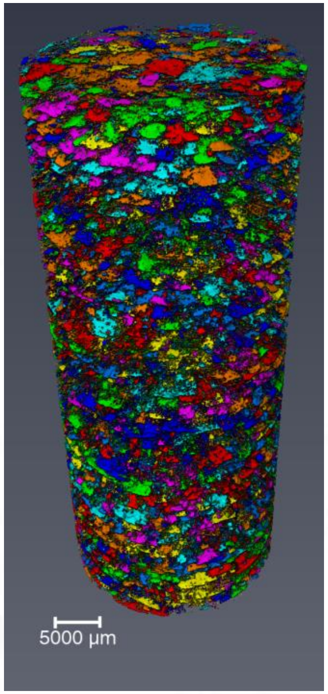
- Matrix blank samples show “fissures” and apparent alignment of graphite flake which varies from compacts
- Striving toward a quantitative measurement to capture texture variation between sample types
  - Graphite is highly anisotropic – properties and performance of graphite are relatively well-known but we’re not studying graphite
  - Matrix is a composite (graphite in carbonized resin binder) where preferential alignment of graphite flake in blanks will influence property evaluation (oxidation, thermal conductivity, diffusion, etc.)
  - **Primary effort:** Use 2-MGEM to measure the degree of texture variation between compacts and unfueled “blanks” - important as matrix blanks are being analyzed for many separate effects tests (AGR and NEUP)

[1] Hunn, J.D., et al., ORNL/TM-2012/295-R0 (2012).

Microstructural variation between unfueled “blanks” and compacts



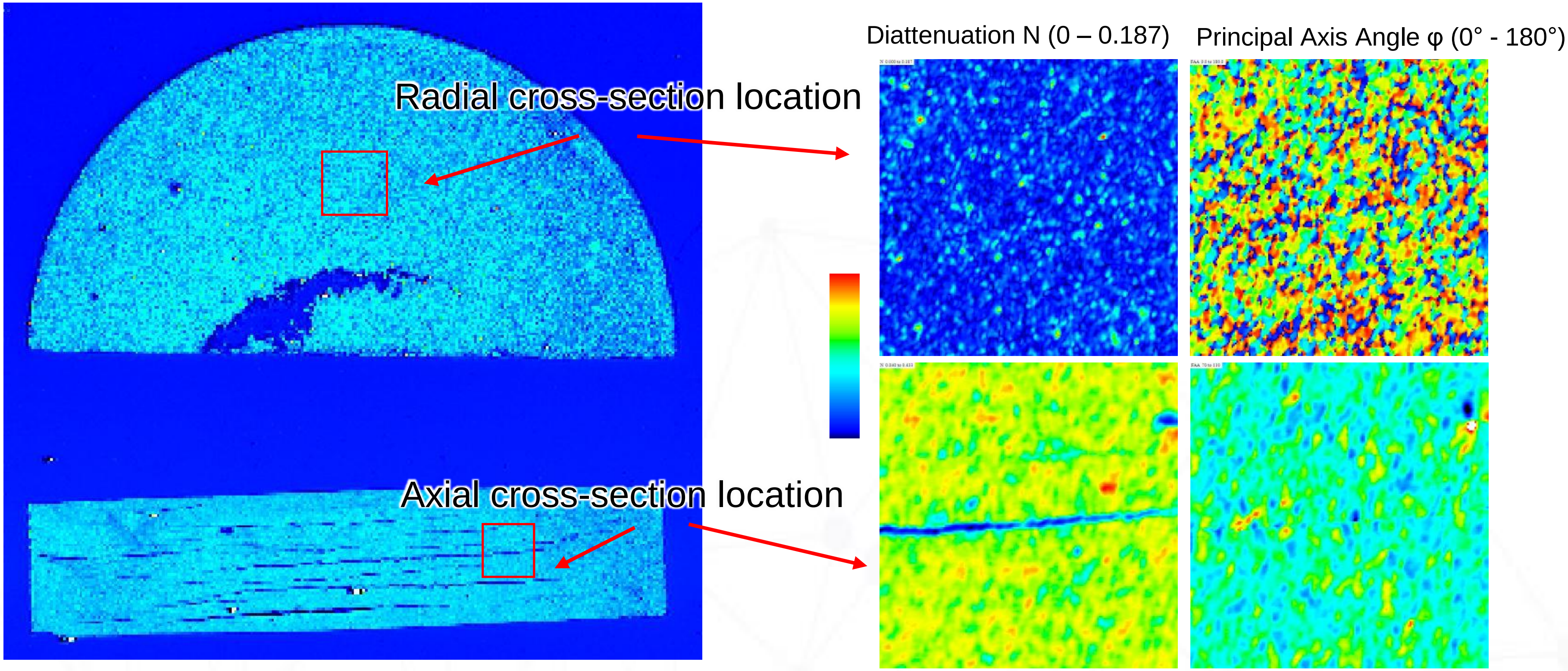
Optical image of AGR-3/4 ring blank (AGB-B1)



Reconstructed fissure/pore structure from X-ray tomography analysis of AGR-3/4 ring blank, Anne Campbell and Grant Helmreich

- Brief commentary – X-ray tomography can be performed to spatially resolve the fissures and pore structure
- Reconstructions demonstrate interconnected pore structure - important for diffusion, vapor transport, permeability, thermal diffusivity, etc.
- Fissure analysis is not a primary focus of the ongoing effort but will be documented

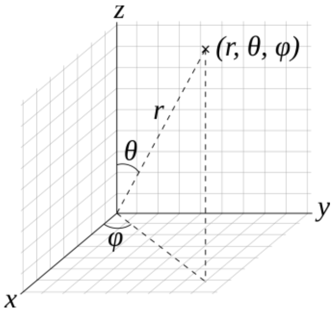
Texture analysis using the 2-MGEM

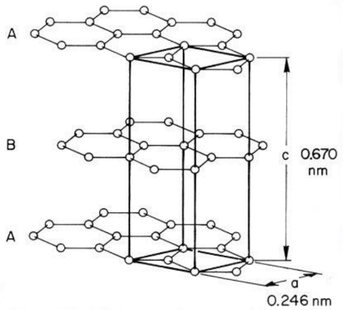


2-MGEM intensity map

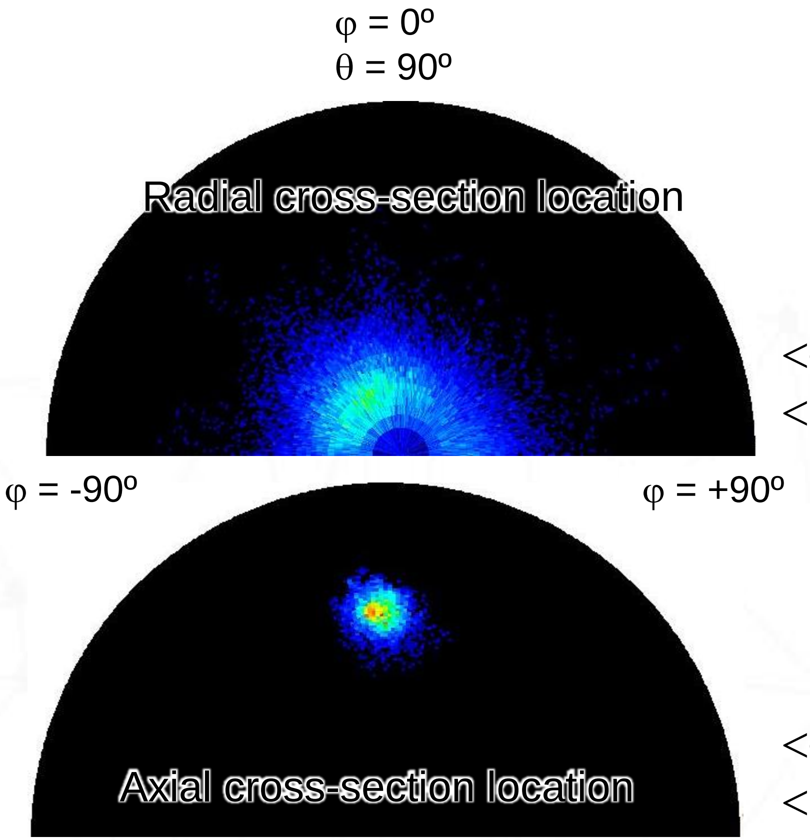
- Pixel to pixel orientation mapping of local areas on axial and radial cross-sections
    - Measure local diattenuation (N) and principal axis angle φ (0° - 180°)
- Produce optical pole figure to demonstrate presence of a preferred orientation of the graphitic components

Current Results: Optical Pole Figures





A. Hawari, et al., Nucl. Sci. Eng. 155(3):449 (2006)



<φ> = -13.6 ± 46.9º
<θ> = 19.9 ± 7.6º

<φ> = 88.7 ± 4.0º
<θ> = 57.0 ± 3.7º

Relationship between diattenuation and θ

$N = N_{max} * \sin^2(\theta)$

$N_{max} \sim 0.187$

- Clear texture observed in matrix blank - technique can provide a direct measurement of texture in matrix composite samples
- Next step is to perform 2-MGEM analysis on cross-sections of AGR-5/6/7 compacts – optical microscopy to be performed as well (fissures)
  - Provide context to possible impact on separate effects tests

Conclusion and future work

- Both LH and BLH models can reasonably fit observed oxidation rates.
  - LH model is more reliable at low P_{H2O} and low T (850-950 ^{o}C)
  - BLH model is more reliable at high P_{H2O} and high T (1000 – 1200 ^{o}C)
  - Oxidation rates measured in the two different systems at 1200 ^{o}C are consistently predicted by the BLH model
    - But BLH model predicts higher rates than those actually measured at 1300 – 1400 ^{o}C in the high temperature furnace, possible a a system difference
- The matrix material's macrostructure (fissures) impacts the high temperature oxidation behavior
- Texture analysis shows strong texture in matrix blanks
- Ongoing work:
  - Summarizing results in ORNL technical report (FY19Q4)
  - Continue texture analysis to provide a comparison to fueled AGR-5/6/7 compacts with both packing fractions
    - Need to ask the question: what is the impact of microstructure/texture on separate effects testing of matrix blanks

Thank you for your attention !!

QUESTIONS ??

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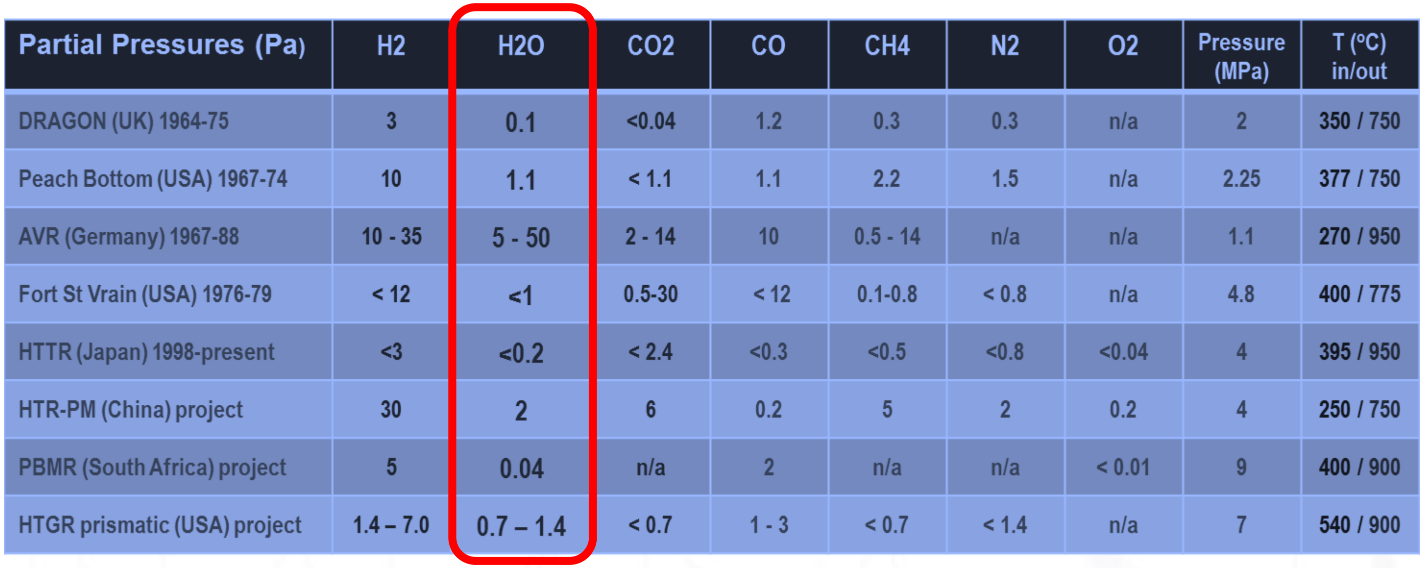
There will always be water in HTGR normal operation



Partial Pressures (Pa)	H2	H2O	CO2	CO	CH4	N2	O2	Pressure (MPa)	T (°C) in/out
DRAGON (UK) 1964-75	3	0.1	<0.04	1.2	0.3	0.3	n/a	2	350 / 750
Peach Bottom (USA) 1967-74	10	1.1	< 1.1	1.1	2.2	1.5	n/a	2.25	377 / 750
AVR (Germany) 1967-88	10 - 35	5 - 50	2 - 14	10	0.5 - 14	n/a	n/a	1.1	270 / 950
Fort St Vrain (USA) 1976-79	< 12	<1	0.5-30	< 12	0.1-0.8	< 0.8	n/a	4.8	400 / 775
HTTR (Japan) 1998-present	<3	<0.2	< 2.4	<0.3	<0.5	<0.8	<0.04	4	395 / 950
HTR-PM (China) project	30	2	6	0.2	5	2	0.2	4	250 / 750
PBMR (South Africa) project	5	0.04	n/a	2	n/a	n/a	< 0.01	9	400 / 900
HTGR prismatic (USA) project	1.4 – 7.0	0.7 – 1.4	< 0.7	1 - 3	< 0.7	< 1.4	n/a	7	540 / 900

Generally accepted design assumptions:

Chronic oxidation rates increase with increasing temperatures

Chronic oxidation will be more pronounced at the bottom of reactor

However, oxidation will be very limited because of limited amounts of oxidant

Oxidized layer will affect only a thin layer at the surface of graphite components

M P Kissane Nucl. Eng Des (2009)
W R Corwin, ORNL/TM-2008/129 (2008)
B Castle, INL/EXT-10-10533 (2010)
Wright, INL/EXT-06-11494 (2006)
M Eto et al, JAERI-M 86-192 (1986)
X Yu, S Yu, Nucl Eng Des (2010)

Environmental effects in HTGR normal operation

- Impurities in He coolant:
  - **O_2** <0.04 ppm, **H_2O** <0.2 ppm, **CO_2** <0.6 ppm, N_2 <0.2 ppm, H_2 <3 ppm
  - H_2 and CO (1…10 Pa); N_2, **CO_2**, CO, **H_2O**, CH_4 at < 1 Pa
- Various impurities (if present) – may catalyze oxidation
  - Ca, Al, Li, Cl, B, S, Fe, Si
- Oxidation resistance increases with the degree of graphitization:
  - Structural graphite
    - Final temperature > 2800-3000 ºC (highly graphitized, inert)
  - Fuel matrix carbon in fuel sticks and pebbles
    - Final temperature ~ 1800 ºC (less inert than graphite)
- Chemistry: $2\,C + O_2 = 2\,CO$ $C + H_2O = CO + H_2$ $C + 2\,H_2 = CH_4$

$C + O_2 = CO_2$

$C + CO_2 = 2\,CO$

$2\,CO + O_2 = 2\,CO_2$

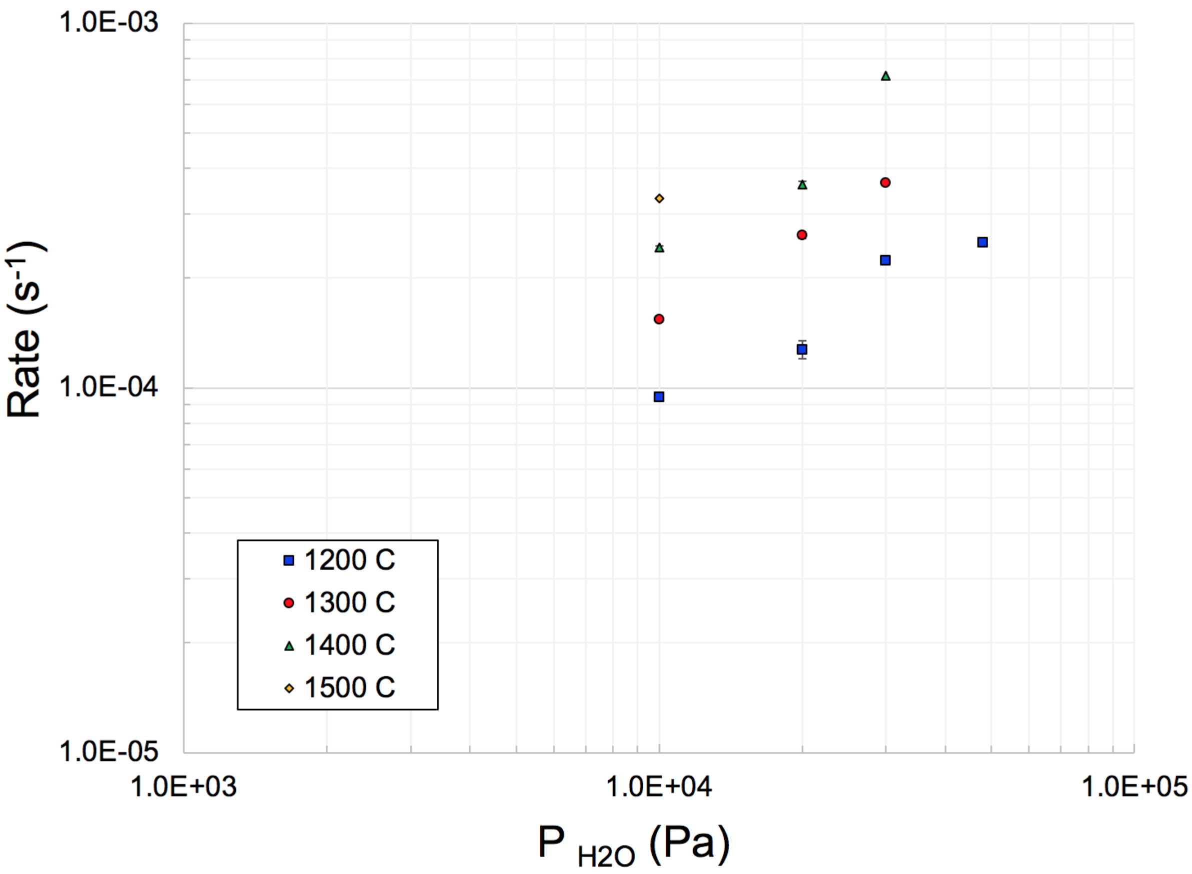
Steady HTGR operation conditions

- Projected coolant composition: H_2 and CO at 1…10 Pa
  N_2, **CO_2**, **O_2**, **H_2O**, CH_4 at < 1 Pa

- Projected temperature: 400 – 500 °C entry; 850 – 950 °C outlet
- Large variation / non-uniformity of local conditions (flow rate, temperature)
- Generally accepted design assumptions:
  - Oxidation rates increase with increase of temperatures
  - Prismatic HTGR: **smaller exposure of matrix** compacts to coolant than of graphite
    - Pebble bed HTGR: **much more matrix in pebbles exposed** to coolant than graphite
  - However, oxidation will be very limited because of limited amounts of oxidant

Wang et al;. Annals Nucl Energy 131 (2019) 483-495
Yu et al, Nuclear Engn. Design, 238 (2008) 2230

Oxidation rate



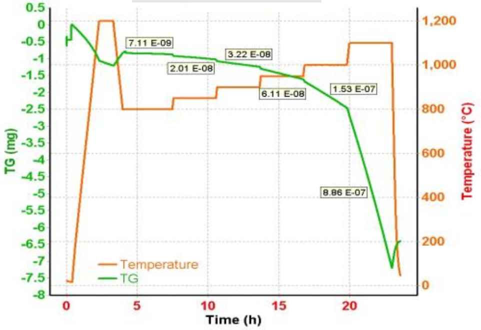
Increasing rate as a function of temperature expected

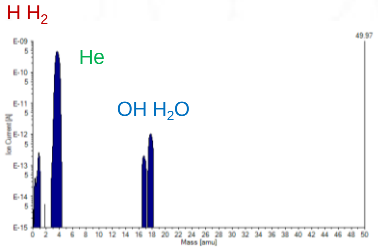
Accurate control of experimental conditions

$C + H_2O \Rightarrow CO + H_2$

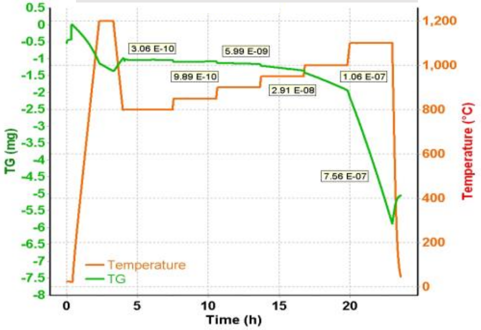
Hydrogen slows down carbon oxidation by water

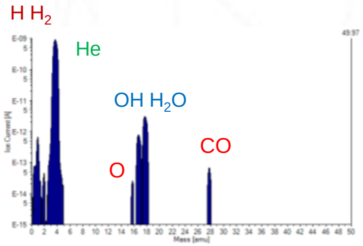
150 Pa H_2O



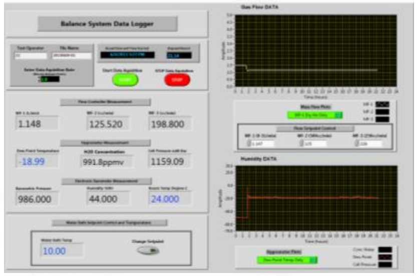


150 Pa H_2O + 28 Pa H_2





Flow and humidity control



Temperature control and continuous weight measurement