GAS-COOLED REACTOR
ADVANCED REACTOR TECHNOLOGIES PROGRAM

AGR Fuel Oxidation Testing Summary and Plans

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ART AGR TRISO FUEL Post-Irradiation Technical Lead

Purpose of Irradiated TRISO Fuels Testing in Air and Moisture

- Safety testing of AGR fuel compacts has only been under helium (FACS/CCCTF)
- A major objective under AGR-5/6/7 PIE is to “perform oxidation testing to characterize fuel behavior during exposure to air or moisture at nominal and accident temperatures”
- Evaluate fuel performance when exposed to air or steam at high temperatures:
  - Oxidation of matrix and OPyC may mobilize fission products
  - Exposed kernels (from as-fabricated defects or in-pile failures) vulnerable to hydrolysis
  - SiC generally resistant to but will slowly oxidize as well
  - Estimate particle failure rates
  - Measure fission product releases as a function of time
  - Relate fission product releases to fuel irradiation history, test conditions, and extent of fuel oxidation
- Use collected data for:
  - Fuel qualification and licensing
  - Input to and comparisons with predictive models and simulations
  - Reactor accident source term analysis (design-basis and/or beyond-design-basis)

Approach to TRISO Fuels Oxidation Testing

1. Separate effects testing of graphitic matrix at ORNL
2. Testing of loose irradiated particles in the Furnace for Irradiated TRISO (FITT) at ORNL
3. Integrated testing of irradiated TRISO fuel compacts and “fuel bodies” in the Air/Moisture Ingress Experiment (AMIX) at INL

The Oxidation Test Plan Issued in 2019 has not been Altered Since

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INL/MIS-17-43986

Plan

Project No. 29412, 23841

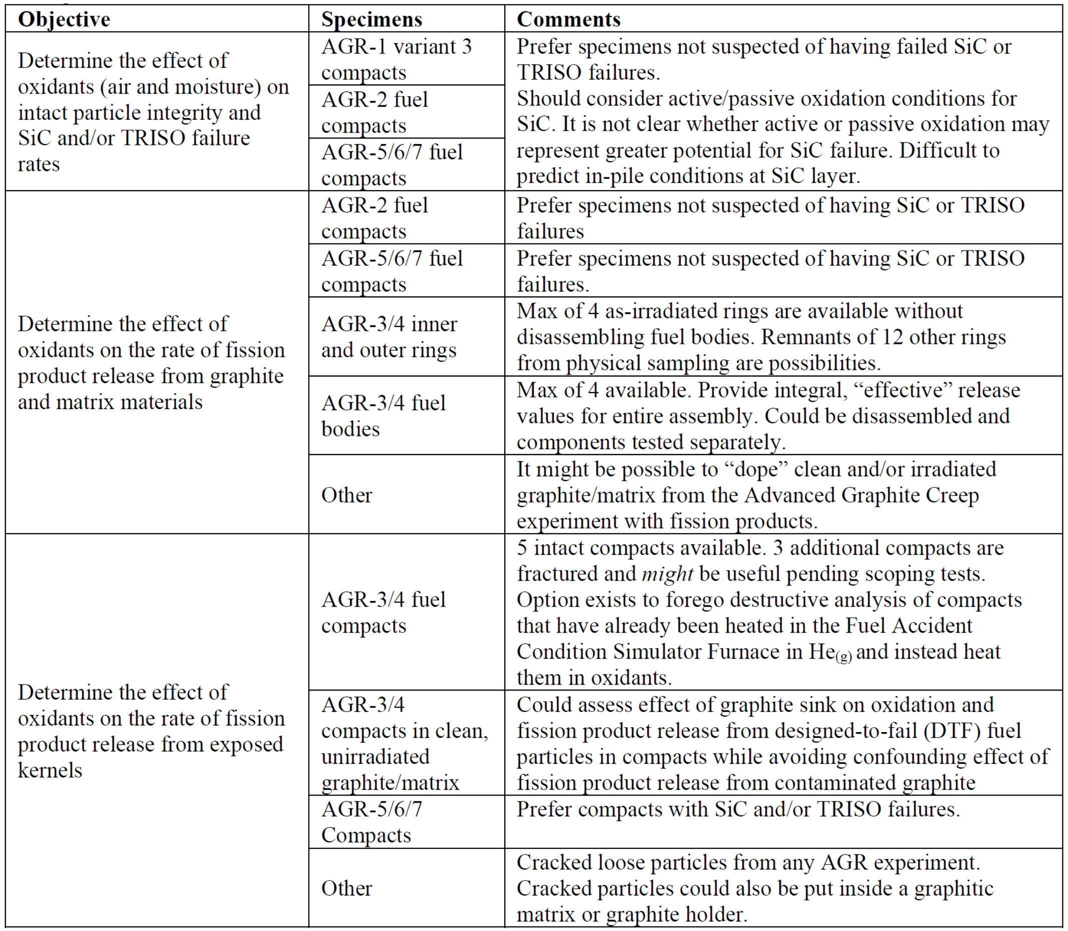
AGR Irradiated Specimen Air/Moisture Heating Test Plan

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

Idaho National Laboratory

The Plan Identified Three Objectives

- Determine the effect of oxidants on intact particle integrity and SiC and/or TRISO failure rates → initiated with FITT testing.
- Determine the effect of oxidants on the rate of fission product release from graphite and matrix materials
- Determine the effect of oxidants on the rate of fission product release from exposed kernels



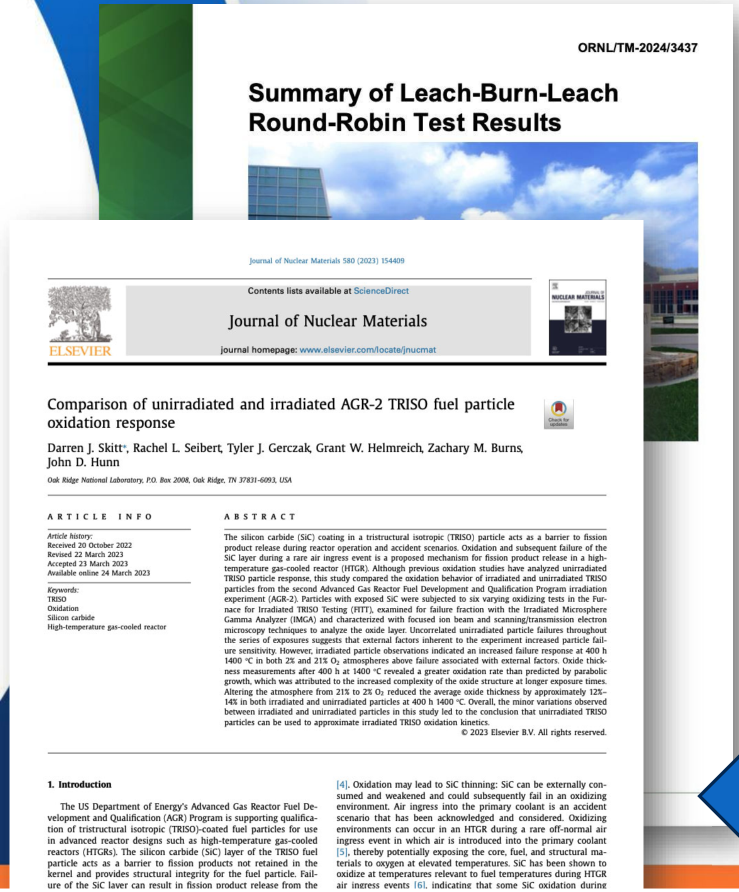
Objective	**Specimens**	**Comments**
Determine the effect of oxidants (air and moisture) on intact particle integrity and SiC and/or TRISO failure rates	AGR-1 variant 3 compacts	Prefer specimens not suspected of having failed SiC or TRISO failures. Should consider active/passive oxidation conditions for SiC. It is not clear whether active or passive oxidation may represent greater potential for SiC failure. Difficult to predict in-pile conditions at SiC layer.
	AGR-2 fuel compacts	
	AGR-5/6/7 fuel compacts	
Determine the effect of oxidants on the rate of fission product release from graphite and matrix materials	AGR-2 fuel compacts	Prefer specimens not suspected of having SiC or TRISO failures
	AGR-5/6/7 fuel compacts	Prefer specimens not suspected of having SiC or TRISO failures.
	AGR-3/4 inner and outer rings	Max of 4 as-irradiated rings are available without disassembling fuel bodies. Remnants of 12 other rings from physical sampling are possibilities.
	AGR-3/4 fuel bodies	Max of 4 available. Provide integral, "effective" release values for entire assembly. Could be disassembled and components tested separately.
	Other	It might be possible to "dope" clean and/or irradiated graphite/matrix from the Advanced Graphite Creep experiment with fission products.
Determine the effect of oxidants on the rate of fission product release from exposed kernels	AGR-3/4 fuel compacts	5 intact compacts available. 3 additional compacts are fractured and *might* be useful pending scoping tests. Option exists to forego destructive analysis of compacts that have already been heated in the Fuel Accident Condition Simulator Furnace in $He_{(g)}$ and instead heat them in oxidants.
	AGR-3/4 compacts in clean, unirradiated graphite/matrix	Could assess effect of graphite sink on oxidation and fission product release from designed-to-fail (DTF) fuel particles in compacts while avoiding confounding effect of fission product release from contaminated graphite
	AGR-5/6/7 Compacts	Prefer compacts with SiC and/or TRISO failures.
	Other	Cracked loose particles from any AGR experiment. Cracked particles could also be put inside a graphitic matrix or graphite holder.

Goal 1: Particle Oxidation Performance

- Conditions aim to straddle active and passive SiC oxidation regimes
- At a minimum, two test of irradiated compacts in air and two in moisture are planned

	Temperature (°C)	Oxidant Partial Pressure (atm)
SiC active moisture	1300-1650	H_2O, 5.4E-4
SiC passive moisture	1300 [a]	H_2O, 0.5
SiC active oxygen	1300-1650	O_2, 5E-6+
SiC passive oxygen	1300 [a]	O_2, 0.1
[a] Test temperature could be reduced to < 1300°C to ensure passive oxidation.		

Loose particle tests in oxygen at ORNL



ORNL/TM-2024/3437

Summary of Leach-Burn-Leach Round-Robin Test Results

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Comparison of unirradiated and irradiated AGR-2 TRISO fuel particle oxidation response

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A R T I C L E I N F O

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A B S T R A C T

The silicon carbide (SiC) coating in a tristructural isotropic (TRISO) particle acts as a barrier to fission product release during reactor operation and accident scenarios. Oxidation and subsequent failure of the SiC layer during a rare air ingress event is a proposed mechanism for fission product release in a high-temperature gas-cooled reactor (HTGR). Although previous oxidation studies have analyzed unirradiated TRISO particle response, this study compared the oxidation behavior of irradiated and unirradiated TRISO particles from the second Advanced Gas Reactor Fuel Development and Qualification Program irradiation experiment (AGR-2). Particles with exposed SiC were subjected to six varying oxidizing tests in the Furnace for Irradiated TRISO Testing (FITT), examined for failure fraction with the Irradiated Microsphere Gamma Analyzer (IMGA) and characterized with focused ion beam and scanning/transmission electron microscopy techniques to analyze the oxide layer. Uncorrelated unirradiated particle failures throughout the series of exposures suggests that external factors inherent to the experiment increased particle failure sensitivity. However, irradiated particle observations indicated an increased failure response at 400 h 1400 °C in both 2% and 21% O_2 atmospheres above failure associated with external factors. Oxide thickness measurements after 400 h at 1400 °C revealed a greater oxidation rate than predicted by parabolic growth, which was attributed to the increased complexity of the oxide structure at longer exposure times. Altering the atmosphere from 21% to 2% O_2 reduced the average oxide thickness by approximately 12%–14% in both irradiated and unirradiated particles at 400 h 1400 °C. Overall, the minor variations observed between irradiated and unirradiated particles in this study led to the conclusion that unirradiated TRISO particles can be used to approximate irradiated TRISO oxidation kinetics.

1. Introduction

The US Department of Energy's Advanced Gas Reactor Fuel Development and Qualification (AGR) Program is supporting qualification of tristructural isotropic (TRISO)-coated fuel particles for use in advanced reactor designs such as high-temperature gas-cooled reactors (HTGRs). The silicon carbide (SiC) layer of the TRISO fuel particle acts as a barrier to fission products not retained in the kernel and provides structural integrity for the fuel particle. Failure of the SiC layer can result in fission product release from the

[4]. Oxidation may lead to SiC thinning: SiC can be externally consumed and weakened and could subsequently fail in an oxidizing environment. Air ingress into the primary coolant is an accident scenario that has been acknowledged and considered. Oxidizing environments can occur in an HTGR during a rare off-normal air ingress event in which air is introduced into the primary coolant [5], thereby potentially exposing the core, fuel, and structural materials to oxygen at elevated temperatures. SiC has been shown to oxidize at temperatures relevant to fuel temperatures during HTGR air ingress events [6], indicating that some SiC oxidation during

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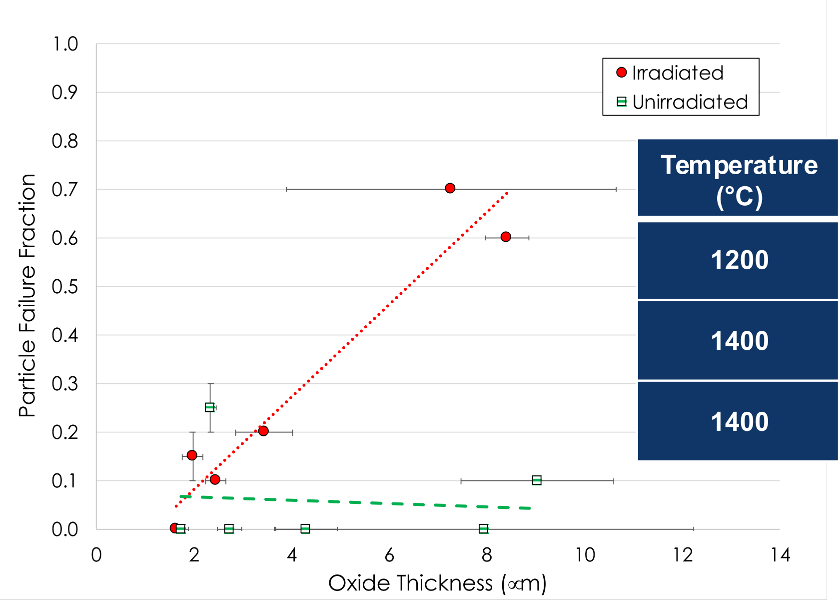

Temperature (°C)	Atmosphere	Exposure Times (h)
1200	21% O_2 (balance N_2)	400
1400	21% O_2 (balance N_2)	10, 100, 400
1400	2% O_2 (balance He)	10

- Initial tests conducted on burnback AGR-2 TRISO fuel particles from Compact 5-4-2 show increased particle failure with increased oxide thickness
- Irradiated particles are more susceptible to failure than unirradiated particles, but oxidation kinetics are similar

Next steps of loose particle testing at ORNL

- Completed analysis to full-TRISO AGR-5/6/7 Compact 2-2-1 particles
  - Testing full TRISO particles from AGR-2
  - Initial testing on AGR-5/6/7 Compact 2-2-1 showed limited particle failure compared to AGR-2 Compact 5-4-2 but large variations in oxide thickness
- Extending analysis to full-TRISO AGR-5/6/7 Compact 3-6-3
  - Implementing **SiC recession analysis** versus oxide thickness measurement which supports model interpretation
- Expand testing envelope if needed to refine AMIX test matrix if possible

AGR-5/6/7 Compact 2-2-1 Test Matrix

Temperature (°C)	Atmosphere	Exposure Times (h)
1400	21% O_2 (balance N_2)	10, 100, 400
1400	2% O_2 (balance He)	10, 100*

AGR-5/6/7 Compact 3-6-3 Test Matrix

Temperature (°C)	Atmosphere	Exposure Times (h)
1200	21% O_2 (balance N_2)	400
1400	21% O_2 (balance N_2)	100, 200 400*
1400	2% O_2 (balance He)	100

*will include AGR-2 Full TRISO comparison

Goal 2: Fission Product Release from Graphitic Matrix

- Compacts with intact particles and significant matrix inventory preferred. A minimum of four compact tests planned. Also considering tests of graphite/graphitic materials from AGR-3/4
- Test in kinetic regime and diffusion-controlled regime. Lower temps should prevent/minimize particle degradation that would make matrix performance harder to distinguish
- Tests may also double to give more info on compact/particle performance
- Need to be sure all particles are intact or at lease account for failures. (Option to screen fuel by heating in helium could help identify compacts with SiC and/or TRISO defects.)

Oxidant	Test Temp (°C)	Oxidant Partial Pressure (atm)
O_2	800	0.1
	1200	0.1
H_2O	800	0.5
	1200	0.5

Unirradiated AGR-5/6/7 Matrix Tested at ORNL, Unirradiated Graphite with Simulated Fission Products Tested at INL, Various Graphite and Matrix in University-led NEUPs

ORNL/TM-2019/1341

Oxidation of Matrix Material in Helium with Varied Moisture Content

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Robert Mee
Austin Schumacher
John Stempien
Michael Trammell

November 2019

Approved for public release.
Distribution is unlimited.

Oak Ridge National Laboratory

Journal of Nuclear Materials

Catalyzed oxidation of nuclear graphite by simulated fission products Sr, Eu, and I

Junhua Jiang, John Stempien, Yaqiao Wu

Nuclear Materials and Energy

Catalyzed oxidation of IG-110 nuclear graphite by simulated fission products Ag and Pd nanoparticles

Junhua Jiang, John Stempien, Yaqiao Wu

ORIGINAL ARTICLE

Effects of microstructure on the oxidation behavior of A3 matrix-grade graphite

Adam Bratten[1] | Jiaqi Duan[1] | Andrew Hoffman[2] | Haiming Wen[1,2] | Xiaoqing He[3,4] | John D. Stempien[5]

Abstract

The oxidation behavior of matrix-grade graphite in air- or steam-ingress accident scenarios is of great interest for high-temperature gas reactors (HTGRs). In this study, the microstructures of two variants of matrix-grade graphite based on the German A3-3 and A3-27 formulations were characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy, and correlated to oxidation behavior observed through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Through TEM imaging and selected area electron diffraction (SAED), a higher volume fraction of partially graphitized carbon was identified in the A3-3 type graphite than in the A3-27 type. This structure is believed to have contributed to the accelerated oxidation exhibited by A3-3 in the chemical reaction-controlled oxidation regime.

KEYWORDS

matrix graphite, microstructure, oxidation, TEM, TGA/DSC

Carbon

Water vapor oxidation behaviors of nuclear graphite IG-110 for a postulated accident scenario in high temperature gas-cooled reactors

Yi Je Cho, Kathy Lu

Final Report

Milestone Report: NEUP Project 18-15039
Submitted: December 30th, 2021
Revised and resubmitted: March 23, 2022

Prepared for:
U.S. Department of Energy, Nuclear Energy University Programs

Prepared by:
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Composites Part B

Water vapor oxidation of SiC layer in surrogate TRISO fuel particles

Yi Je Cho, Kathy Lu

Graphite/Graphitic Materials Oxidation Testing in AGC

- Acute oxidation in air in kinetic regime:
  - Temperature: 550-750°C
  - Graphites:
    - Unirradiated PCEA, Unpurified PCEA, NBG-18, NBG-17, NBG-25, IG-110, Unpurified IG-110, IG-430, BAN ETU-10, ET-10 (in progress).
    - Irradiated NBG-25, NBG-18, and IG-430.
  - Graphitic matrix from unirradiated pebble (400-700°C).
- Chronic oxidation in kinetic regime in moist helium
  - Temperature range: 550-1200°C
  - At ORNL
  - Graphites: PCEA, NBG-18, IG-110, IG-430
- Graphite residual properties (e.g., strength and oxidation depth) after air oxidation of 2114, IG-110, IG-430, ETU-10, NBG-18, PCEA, planning ET-10

AGC Oxidation Contacts: Will Windes and Rebecca Smith. See agenda for July 17, especially 8 am–10 am. Also see Lu Cai for pebble matrix oxidation work.

Goal 3: Fission Product Release from Exposed Kernels

- Desire to use compacts known to have exposed kernels:
  - Several options from AGR-3/4
  - AGR-5/6/7 options most likely from Capsule 3
- Proposed matrix:
  - At least three moisture tests
  - At least two air tests
- Conditions are chosen to span the kinetic, transition, and diffusion-controlled regimes in graphite

	H_2O Partial Pressure (atm)	Test Temperature (°C)
1	0.3	1300
2	0.3	1000
3	0.3	800

	O_2 Partial Pressure (atm)	Test Temperature (°C)
1	0.1	1300
2	0.1	800

AMIX Update – Qualification Tests and a New Facility Issue

- Atmospheres: **COMPLETE**
  - Helium **COMPLETE**
  - Helium + air **COMPLETE**
  - Helium + water vapor **COMPLETE**
- Furnace **COMPLETE**
- Heat trace **COMPLETE**
- Mass spectrometer **COMPLETE**
- Human-machine interface (e.g., programming and data acquisition) **COMPLETE**
- Gas cleanup (removal of condensable species ahead of cold traps) **COMPLETE**
- Fission gas monitoring system **INCOMPLETE – flow restrictions limit run time. Traps redesigned and ordered.**
- **FCF facility has a new mission that may limit or curtail planned AMIX operations**

Potential In-pile Conditions During Air or Moisture Ingress Vary

The information below was used to specify AMIX capabilities and test matrices. Recent reactor designs may have different peak temperatures, pressures, durations, etc.

- Time-related information:
  - Moderate break: depressurize in 1 min
  - Small break: depressurize in 12 min
  - Small “leak”: depressurize in 10 h
  - Onset of natural circulation following depressurization 3 min or > 100 h
- Temperature:
  - Up to about 1620°C
  - As low as about 500°C
- Oxygen partial pressures:
  - Near 0
  - Up to 21%
- References in oxidation test plan:
  - IAEA 1997; Petti et al. 2002; Oh et al. 2011; Xu et al. 2016; Silady 2010; Oh et al. 2008; Stone & Webster 1986; Schenk and Nabielek 1996; Wei et al. 2016; Huang et al. 2014

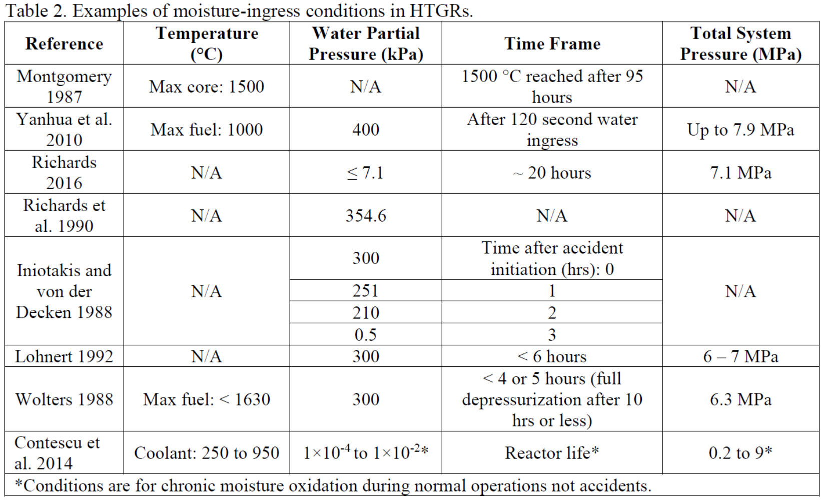

Table 2. Examples of moisture-ingress conditions in HTGRs.

Reference	**Temperature (°C)**	**Water Partial Pressure (kPa)**	**Time Frame**	**Total System Pressure (MPa)**
Montgomery 1987	Max core: 1500	N/A	1500 °C reached after 95 hours	N/A
Yanhua et al. 2010	Max fuel: 1000	400	After 120 second water ingress	Up to 7.9 MPa
Richards 2016	N/A	≤ 7.1	~ 20 hours	7.1 MPa
Richards et al. 1990	N/A	354.6	N/A	N/A
Iniotakis and von der Decken 1988	N/A	300	Time after accident initiation (hrs): 0	N/A
		251	1	
		210	2	
		0.5	3	
Lohnert 1992	N/A	300	< 6 hours	6 – 7 MPa
Wolters 1988	Max fuel: < 1630	300	< 4 or 5 hours (full depressurization after 10 hrs or less)	6.3 MPa
Contescu et al. 2014	Coolant: 250 to 950	1×10^{-4} to 1×10^{-2}*	Reactor life*	0.2 to 9*

*Conditions are for chronic moisture oxidation during normal operations not accidents.

Lingering Questions

- Do any recent reactor designs have estimates for air/moisture ingress accident progression?
- Planning to establish:
    - Particle failure rates: planned to be able to run for ~300 h. That time may be un-realistically long.
    - Fission product release rates
    - May be able to estimate matrix burnoff rate
    - Others?

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Thank you for your attention

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