Long Duration Heating Tests of Silver Release at Intermediate Temperatures

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Introduction

- Motivation for Long Duration and Intermediate Temperature Testing
 - As-irradiated Silver Release Observations
 - Silver Release from Safety Testing Observations
- Individual Particle Thermal Exposure Testing



Importance of Fission Product Release

- "...the limiting criterion in a given reactor design is derived from the accessibility and maintainability of boilers/circulators/reformer tubes/inspection chambers."^[1]
- ^{110m}Ag is of particular interest due to relatively rapid release and limited understanding of the release mechanism.
- **Goal:** understand release behavior and kinetics to provide data to fuel performance models and improve operation and safety

[1] H. Nabielek, P.E., Brown, P. Offermann, "Silver release from coated particle fuel," Nucl. Technol., 35, 483-493 (1977).



Top down approach to fission product release analysis

"The evaluation of irradiation performance of the AGR-1 fuel focused primarily on assessing the level of fission product release from the fuel and examining the kernel and coating morphology evolution during irradiation." – Demkowicz et al., "AGR-1 Post Irradiation Examination Final Report^[1]

- 1. Analysis of the capsule components
- 2. Gamma Scanning of Individual Compacts
 - Safety Testing of Individual Compacts
- 3. Deconsolidation Leach-Burn-Leach Analysis
- 4. Gamma Scanning of Individual Particles
- 5. Microanalysis of Select Fuel Particles



- Analysis spans ~7 orders of magnitude (~1x10⁻¹ to ~1x10⁻⁸ m) in length scale providing significant insight into fission product behavior.
- Silver was a major interest for the PIE effort, however, the experiment was not designed to fundamentally understand "Ag release"; as such, questions still exist concerning its release behavior and kinetics.



Silver compact retention is influenced by multiple factors



Inflection at 1096°C, Retained ^{110m}Ag fraction as a function of time-average, volume average compact temperature, reproduced from Demkowicz (2017)^[1]



Daily temperature compared to PARFUME-calculated silver production for Compacts 4-4-1 and 4-3-2, reproduced from Collin et al. (2015)^[2]

- Primary influence is temperature: Inversion in retention behavior at 1096°C
- Weak inverse relationship with burnup: indirect temperature effect as lower burnup compacts are "hotter" later in the irradiation.

Retention performance varies particle-to-particle



FP activity measured by gamma spectrometry, at ORNL the Irradiated Microsphere Gamma Analyzer (IMGA)

| Measured versus Calculated (M/C) = | | | | | | | |
|--|--|--|--|--|--|--|--|
| $A_i(^{110m}Ag)$ | | | | | | | |
| $A_{calc}(^{110m}Ag) \frac{A_i(^{137}Cs)}{\sum_{i=1}^n (\frac{1}{n}) A_i(^{137}Cs)}$ | | | | | | | |

| Compact | Fuel Type | TAVA (°C) | TA MAX (°C) | TA Min (°C) | Burnup (%FIMA) | Fast Fluence (10 ²⁵ n/m ²) |
|---------|-----------|-----------|----------------|----------------|-------------------|---|
| 3-2-1 | Baseline | 1051 | 1143 | 897 | 19.1 | 4.21 |
| 5-2-3 | Variant 1 | 1059 | 1141 | 933 | 17.43 | 3.77 |
| 4-4-2 | Variant 3 | 1024 | 1139 | 866 | 16.6 | 3.59 |

Data reproduced from Ref. [1]

- ^{110m}Ag demonstrates broad particle-to-particle retention variation compared to other select FPs^[1]
- Temperature is expected to be the primary factor contributing to particle-to-particle variation of ^{110m}Ag retention
 - Temperature effects (ΔT greater than 300°C exist across a single compact)^[2]
 - SiC microstructural features influence fission product accommodation



Demkowicz et al., "AGR-1 post irradiation examination final report," INL/EXT-15-36407 rev0, (2015).
 G.L. Hawkes, "AGR-1 daily as-run thermal analyses," ECAR-968, Rev. 2, Idaho National Laboratory (2013).

Safety Testing: Controlled thermal exposures to understand performance beyond accident conditions (1600-1800°C)



Compact 6-2-1, 1600°C 300 hour exposure showing fraction release of select fission products, reproduced from Ref. [1]

- For 1600-1700 °C, 300 hour, safety testing shows ^{110m}Ag "burst" release upon heat up with no release through the SiC layer verified – unable to determine kinetic information.
 - Release is believed to be dominated by FPs outside of the SiC layer.

- Observed release is an aggregate of all fuel components difficult to confidently determine source of release
 - Significant effort is made to provide a mass balance across all PIE methods yet uncertainty exists due to inherent error in analysis techniques.



Microstructure influences out-of-pile release behavior at high temperatures



Fractional release measurements of ^{110m}Ag and ¹⁵⁴Eu from AGR-1 Compacts exposed to 1800°C for 300 hours, Compacts 4-4-1 and 4-3-2 were AGR-1 V3, while Compacts 3-2-3 and 5-1-3 were AGR-1 V1 and showed a difference in release behaviors. Reproduced from Morris et al. (2016)^[1]

- Increasing fractional release of ^{110m}Ag and ¹⁵⁴Eu was observed in 1800°C safety tests for Variant 3 compacts, suggesting additional release through the SiC layer of intact particles^[1]
 - Similar behavior was observed for first AGR-2 1800°C Safety Test
- Variation in release behavior for compacts with different microstructures suggests microstructurally-influenced release behavior
- Release of ^{110m}Ag followed behavior expected for diffusional release by grain boundary (GB) driven release mechanism, however, release of ¹⁵⁴Eu was more complex due to likely slow release from matrix and OPyC



Compact 4-4-2 loose particle testing provided additional evidence of ^{110m}Ag release through intact particles





Ratio of measured ^{110m}Ag versus calculated inventory for 75 particles from Compact 4-4-2 loose particle testing, a) as-irradiated and b) after 1800°C heating test, Reproduced from Hunn et al. (2016)^[1]



- Numerous particles had failed TRISO layers (5 of 75) but many particles had TRISO layers that remained fully intact
- Investigation of the individual intact TRISO particles showed evidence of ^{110m}Ag transport through intact SiC layers

[1] Hunn, J. D., R. N. Morris, C. A. Baldwin, F. C. Montgomery, and T. J. Gerczak, 2015, PIE on Safety-Tested Loss Paricle for GE National Laboratory. Oak Ridge, Tennessee, 2015. National Laboratory [2] Demkowicz et al., "AGR-1 post irradiation examination final report," INL/EXT-15-36407 R0, (2015).



Insights from normalized release rates



Normalized inventory release rates of ^{110m}Ag from AGR-1 compacts exposed to 1800°C, Reproduced from Gerczak et al. (2016)^[2]

Estimating effective diffusion coefficient $(\overline{D})^{[1]}$ $\overline{D}(T) \sim \frac{x^2}{_{6t_o}}$ $t_o \sim \text{time to steady-state release}$ $x \sim \text{thickness of SiC layer}$ $\overline{D}_{V3}(1800 \,^{\circ}\text{C}) \sim 3.7E^{-16} \, \frac{m^2}{_{sec}}$ $\overline{D}_{B \& V1}(1800 \,^{\circ}\text{C}) < 1.9E^{-16} \, \frac{m^2}{_{sec}}$

- Release rates were normalized to the ^{110m}Ag release rate after the initial "burst" additional release is observed after an incubation time for V3 compacts allowing for D
 to be estimated.
- Again, indicates microstructure influences out-of-pile release, with V3 demonstrating rapid release compared to Baseline and V1





Influence of SiC microstructure on release



- Based on M-G equation $\overline{D}_{B\&V1}(1800 \text{ °C}) \sim 0.9 1.3E^{-16} m^2/_{sec}$ which is below the upper bounds determined from safety testing for $\overline{D}_{B\&V1}$ implying release would not be expected to be observed.
- Analysis provides validation to microstructurally dependent release mechansim in out-of-pile safety testing at 1800°C
 - Suggests fine-grained SiC is more susceptible to Ag diffuison/release

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Where do the release results fit in comparison with historic data?



- Good agreement with AGR-1 and historic out-of-pile release
- Discrepancy between out-of-pile release and in-pile release^[1,2]

[1] IAEA-TECDOC-978
 [2] R.E. Bullock, J. Nucl. Mater. 125, 304 (1984).



Insight from PARFUME efforts: Confirmation of contradiction between in-pile and out-of-pile



Compact release data (corrected from particle data) compared to predicted PARFUME release calculations, figure reproduced from Collin et al. (2015) ref. [1]

Safety tested release behavior Matrix-corrected Ag Release Fraction Intact Particles



Fractional release data from safety tested compacts compared to predicted PARFUME release calculations, blue indicates 1600°C and green 1700°C, Figure reproduced from Collin et al. (2016) ref. [2]

- PARFUME does a good job of estimating in-pile release, however estimation of safety testing data is overestimated by orders of magnitude ^[2]
- Suggests disconnect with \overline{D} used to simulate in-pile performance and \overline{D} responsible for release in out-of-pile safety testing



Compact 4-2-2, variable temperature ST: "Goldilocks" zone



Fraction of collected of silver on deposition cups from Compact 4-2-2 thermal exposure test, varied collection efficiencies vary with temperature data does not directly scale with compact release fraction. Figure reproduced from ref. [1,2]



Collection rate of silver from Compact 4-2-2 thermal exposure test, Figure reproduced from ref. [1,2]

- Peak in ^{110m}Ag release rate observed at 1150°C in contrast to release rates at 1000°C and 1300°C.
 - The release rate is not equivalent to the fractional release rate due to ^{110m}Ag collection efficiency issues on the cups at all temperatures, however, the difference in relative magnitudes is correct in indicating a variation in release behaviors.
- Elevated release rates were observed relatively rapidly with appreciable release rates noted after ~30 hours.
 - The fractional release rate at 1150°C was 1.58-3.84x10⁻⁵ (1/hr), while the maximum observed fractional release rate of 6.51x10⁻⁶ (1/hr) was observed from 1400-1600°C and was likely due to primarily matrix release.
- The decrease in ^{110m}Ag release rate above 1150°C and release at 1800°C suggests a bimodal distribution in release rates, indicating two
 different active transport mechanisms related to out-of-pile vs. in-pile disconnect?

 [1] Hunn, J. D., R. N. Morris, C. A. Baldwin, F. C. Montgomery, T. J. Gerczak, 2015b, PIE on Safety-Tested AGR-1 Compact 4-2-2, ORNL/TM-2015/033, Rev. 0, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 2015.
 [2] Demkowicz et al., "AGR-1 post irradiation examination final report," INL/EXT-15-36407 R0, (2015).



Summary of what we know concerning Ag release

- Established that microstructure play a role in accommodating fission products and diffusive release during safety testing
- GB diffusion appears to dominate at 1800°C, fine-grain SiC less retentive
- Disconnect between in-pile and out-of-pile results is GB diffusion dominant inpile?
 - GB diffusion is likely at high temperature ST (thermally dominated diffusion), what is the diffusion mechanism in-pile, "goldilocks"?
 - Is there a transition in diffusion mechanisms? Explore "goldilocks zone"
 - Decouple influence of radiation enhanced diffusion on release.



Goals of individual particle testing

- **Confirm** the elevated release behavior in the "goldilocks" regime
 - The uncertainty present in the Compact 4-2-2 time dependent release measurements due to collection efficiency and deposition of ^{110m}Ag on furnace internals is a primary motivation for the direct-measurement, loose particle test. Individual particle testing aims to mitigate these effects and provide additional validation.
- Better understand the nature of the silver diffusion mechanisms.
- ^{110m}Ag release from particles has not been resolved in CCCTF testing below 1800°C. Need to conduct longer thermal exposures to resolve thermally dependent release (estimate D(T)) for AGR fuel.
- Release from intact particles needs to be decoupled from matrix release, which can be of the same magnitude or greater.

16



Collection rate of silver from Compact 4-2-2 thermal exposure test, Figure reproduced from ref. [1,2]



Fractional release measurements of ^{110m}Ag from AGR-1 Compacts exposed to 1800°C for 300 hours, Reproduced from Morris et al. (2016)^[3]

[1] Hunn, J. D., R. N. Morris, C. A. Baldwin, F. C. Montgomery, T. J. Gerczak, 2015b, PIE on Safety-Tested AGR-1 Compact 4-2-2, ORNL/TN-2016/033, Ke Poloa Rilege National Laboratory, Oak Ridge, Tennessee, 2015.

[2] Demkowicz et al., "AGR-1 post irradiation examination final report," INL/EXT-15-36407 R0, (2015).

[3] R.N. Morris et al., "Performance of AGR-1 high-temperature reactor fuel during post-irradiation heating tests," Nucl. Eng. Des., 306, 24-35 (2016).

Benefits of individual particle testing over compact safety testing

- In the individual particle analysis the FP inventory is known for each particle and release can be tracked directly by measuring changes in the particle activity using IMGA.
 - In the compact heating tests the distribution of fission products is unknown, this leads to difficulty in confirming if FPs collected on deposition cups are being evolved from the compact matrix, OPyC layers, through failed TRISO layers, or through intact SiC layers. These challenges make it difficult to confirm that the FPs released from a compact during safety testing are due to diffusion of FPs across intact SiC layers.
 - Better understand the influence of initial conditions on fission product release variation in starting M/C.
- The individual particle tests represent a controlled experiment where the number of variables contributing to release are reduced.
 - Considering the testing of burn-back particles to provide a direct observation of FP release through SiC.
 - Test conditions and exposure system are simplified to focus on confirming release through intact SiC and the nature of FP retention behavior after long term exposure - confirmatory.
 - In the individual particle test the FP inventory of unique particles will be tracked after each exposure time to determine the change in FP inventory as a function of time and temperature and allow resolution of individual particle behavior.



Estimating observable release in "goldilocks" regime based on release rates from Compact 4-2-2 safety test



Estimated avg. compact fractional release as a function of exposure time for the low temperature regime of interest, showing the high and low estimate from CCCTF testing of Compact 4-2-2.

- A 5% fractional release from an individual particle is expected to be the lower limit for detection using IMGA.
- The minimum aggregate fractional release to produce particles with measurable ^{110m}Ag release is expected to be 2-3%, based on the particleto-particle behavior observed in AGR-1 safety tests and historically observations from the work by Bullock^[6].
 - In the Bullock work, a 2-3% average fractional release resulted in 30% of the total particles investigated with ^{110m}Ag fractional releases above the detection limits of 5%^[6].
- Based on the previously measured release rates from Compact 4-2-2, a minimum exposure time of 500-1000 hours at 1150°C is necessary to detect ^{110m}Ag release, while at 1300°C a minimum exposure time of 1000-2000 hours would be necessary.



Estimating observable release in the high temperature regime



Estimated break-through time as a function of temperature based on 1800°C safety test results

- The break-through times at T < 1800°C can be estimated from previously reported results from the 1800°C exposures and the observation that ~100% of the ^{110m}Ag inventory was released after 600 hours at 1800°C in AGR-1 4-4-2.
 - The break-through times are extrapolated assuming a diffusion dependent process, where the D follows an Arrhenius relationship, $D = D_o exp(-Q/kT)$.
 - Based on the observed release rates at 1800°C from the loose particle tests, measureable ^{110m}Ag release would be expected 10 to 100 hours after breakthrough.
- From this analysis, break-through times of ~8000 hours at 1500°C, ~2000 hours at 1600°C, and ~500 hours at 1700°C are expected (Assuming Bullock's Q^[6]). The break-through times and observable release would be expected to be accelerated if the Q from literature^[7] reflects the diffusion of Ag in SiC.



Furnace for Irradiated TRISO Testing: FITT



- CM Furnace capable of operating up to 1700 °C, intentionally simple and operates in fume hood
- Slight positive pressure (+3-5 psi), low flow (5-15 ml/min) under UHP Ar to reduce O_2 ingress
- Have run graphite and TRISO surrogates to demonstrate operation



Testing status: FITT

- FITT has been mocked up and surrogate particles have been tested
- Moved furnace to Irradiated Fuels Examination Laboratory (IFEL, 3525)
 - Awaiting rewiring of power cables and radiological control technician walk through
- Approvals granted to conduct work in IFEL fume hood
 - Approvals includes work assessment in non-reactor nuclear facility, research safety assessment, operating procedure
- Targeting operational FITT in hood in early August





Proposed test matrix for determining release behavior

| | | Ag Release Measurements (hours) | | | | | | | |
|--------------------|------------------|---------------------------------|------|------|-----|-----|--|--|--|
| | Temperature (°C) | #1 | #2 | #3 | #4 | #5 | | | |
| | 1700 | 100 | 500 | 1000 | TBD | TBD | | | |
| Focus on | 1500 | 100 | 1000 | TBD | TBD | TBD | | | |
| "aoldilocks" first | 1150 | 100 | 1000 | TBD | TBD | TBD | | | |
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- The planned experiment intends to identify the magnitude of FP release in both temperature regimes.
- This test matrix will explore the expected high release rates at 1150 °C to 1700 °C, exploring the two independent release mechanisms.
 - If multiple furnaces are eventually in operation, the use of identical exposure times will be planned to reduce the number of hot-cell days
 required for sample transfers to the IMGA cell for FP inventory measurements by allowing parallel transfers
- "TBD" implies the next exposure time will be selected based on previous measurement observations.
- Ten particles with known FP inventories will be selected for loose particle testing for each temperature of interest.
 - AGR-2 Compact 5-4-2 is a prime candidate for loose particle testing based on it's potential to have particles with remaining ^{110m}Ag inventory (~50% remaining in compact) and it is currently planned for as-irradiated DLBL and IMGA at ORNL.
 - The particles will be selected to reflect the representative FP inventory distribution from Compact 5-4-2 as determined by the distribution of ^{110m}Ag inventories from the planned IMGA measurements.



What will be learned from individual particle testing

- What can be learned from fractional release observations?
 - Understand variation between "low" and "high" temperature silver release
 - Insight into factors contribution to diffusion (Initial/Boundary Conditions)
 - Observe finite Ag release versus continuous release
 - Investigate a large range in T and time compliment safety testing and determine D
- Possible intermittent sampling of particles; variations as a F(T,t)
 - XRT evolution of internal structure
 - FP distributions in the TRISO layers
 - SiC defect structure (recovery, stability defect microstructure)



General Discussion and ????

Thank you for your attention:

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Summary of compact observations and M/C comparisons

- Strong indication that release is dominated by temperature effects
 - Burnup correlation: when the fuel was "hot" complex boundary conditions
 - Particle-to-particle variation may reflect ΔT across compact (300 °C)
- Gradient of fission products in SiC layer and variable distribution based on Ag retention (SEM/TEM) – indicative of a temperature dependent diffusional process
 - Presence of U in low retention particles indicates particle experienced high T
 - No obvious FP transport in SiC below 1700 °C in safety testing
- Influence of microstructure noted: accommodation at GBs
- FPs confirmed intragranularly suggests lattice diffusion is active



Example of complex influences on Ag release behavior

B.P. Collin et al. / Journal of Nuclear Materials 466 (2015) 426-442



Thermal Histories

Daily temperature compared to PARFUME-calculated silver production for Compacts 4-4-1 and 4-3-2, reproduced from Collin et al. (2015)^[1]

TAVA = 1057 °C

Burnup (%FIMA)

- Compact 4-4-1: 18.96%
- Compact 4-3-2: 16.38%

Retained Ag-110m

- Compact 4-4-1: ~96.8%
- Compact 4-3-2: ~57.6%

Weak inverse relationship with burnup: indirect temperature effect.

Variable in-pile conditions evolving with time influence silver release^[1]



Selecting Particles Based on M/C to explore potential cause of distribution



Use SEM/STEM to look for trends in particles to provide insight on exposure conditions and diffusional behavior.

- M/C provides a metric for differentiating particle performance based on retention
- Targeting bounds in M/C to generate an understanding of particle behavior based on Ag retention performance
 - M/C \ge 1 indicates a high probability that a particle retained most of it's silver
 - M/C near zero indicates a particle released most of its silver
 - M/C in intermediate distribution presents ambiguity in silver retention behavior due to uncertainties in retention analysis and neutronics (average value used for analysis)
 - Investigation of bounds aims to observe possible trends which may provide insight on release, cues in the distribution of fission products to learn information that may be relevant to Ag release – not necessarily observing Ag directly

[1] J.W. Sterbentz, "JMOCUP as-run daily depletion calculation for the AGR-1 experiment in ATR B-10 position," ECAR-958 Rev. 2, Idaho National Laboratory (2013) [2] G.L. Hawkes, "AGR-1 daily as-run thermal analyses," ECAR-968, Rev. 2, Idaho National Laboratory (2013)



Particle Distribution After Safety Testing (ST)



Figure 10. Fraction of retained ^{110m}Ag inventory in 56 of the 72 AGR-1 fuel compacts after irradiation. Data are plotted as a function of vertical position in the experiment (top of the experiment at the left) and by the stack number. Figures from Ref. [1]

 No recognizably different M/C variations, unable to suggest release of Ag from intact particles at 1600-1700 °C ST



