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1.0 SUMMARY

The feasibility of the Hg Intrusion QC method for measuring SiC coating defects for the MHTGR was conducted as a potential improvement for the Burn/Leach (B/L) QC method currently used. The purpose for evaluating the Hg Intrusion QC method as an alternative method was to determine if B/L QC method underestimated SiC coating defects. Some evidence in work conducted earlier, indicated that TRISO-coated fuel particles with low SiC coating defects measured by the B/L QC method showed higher releases of metallic fission products (Ref. 1). These data indicated that the SiC coating defect fractions were higher than the B/L measured data indicated. Sample sizes used in the current study were too small to conclusively demonstrate that the B/L QC method under estimate SiC coating defects.

However, observations made during this study indicated a need for an additional QC method to the B/L QC method to measure SiC coating defects for the higher quality MHTGR fuels. The B/L QC method is the best method for measuring SiC coating defects with missing SiC layers or broken SiC coatings (gross SiC defects). However, SiC coating defects with microcracks and other SiC defects not detected by the B/L method may contribute to the release of metallic fission products in-service. For these type of SiC coating defects, the Hg Intrusion QC method investigated in this study is feasible, but particle sample size should be increased to a much larger sample size (100,000 particles per test) for the MHTGR.

2.0 INTRODUCTION

The SiC coating is the most important fission product barrier layer for the TRISO-coated fuel particle design for the Modular High-Temperature Gas-Cooled Reactor (MHTGR). Consequently, maintaining the structural integrity of this layer during irradiation is vital. Fuel particles with defective SiC coating layers is a source of metallic fission product release during normal and accident conditions. Detecting SiC coating defects in as-manufactured fuel compacts is necessary in order to predict the long-term behavior of the fuel during irradiation.

The standard Burn/Leach Method has been questioned as to its ability to detect all SiC coating defects which will result in metallic fission product release during irradiation. Several techniques have been studied in the past in attempts to develop an improved Quality Control (QC) method for measuring SiC coating defects in TRISO-coated fuel particles (Refs. 1 and 2). After careful evaluation of the techniques, an approach that was thought to be a theoretically technically sound approach for developing a QC technique was devised. This status report describes the development of a QC method to detect SiC coating defects.

The measurement of SiC coating defects for the MHTGR determines a safety-related feature of the fuel.

3.0 PROGRAM OBJECTIVES AND SCOPE

Historically, the fractions of SiC coating defects in the fresh fuel have been determined by the B/L QC Method. This technique is based on the assumption that all SiC coating defects can be determined by oxidation of the outer and inner carbon layers, followed by a wet acid leach of the burned-back particles. TRISO-coated fuel particles in the batch with missing, cracked or porous SiC layers will allow oxygen to diffuse into the underlying carbon layers. Complete oxidation of these carbon layers in the defective SiC coated particles will expose the kernel material, which is later removed during the acid leach step in the B/L QC method. A problem with this method is that if inner PyC coatings under SiC coatings with defects are not oxidized during the burn-back process, some defective SiC coated fuel particles may go undetected.

The main objective of the SiC coating defect detection QC Method development program was to correlate the metallic fission product release versus the Hg Intrusion technique for measuring SiC coating defects and to develop a draft operating procedure for this QC method. The methodology devised to evaluate this problem included the following components:

1. Conduct high-temperature metallic fission product release experiments on historical fuel particle components which have shown low- and high-metallic fission product release ("good" and "defective" SiC coatings) during irradiation tests.
2. Devise a QC technique to measure the SiC coating defects on the actual samples used in the high-temperature metallic fission release measurements. The objective being to establish a clear correlation between fractional release of metallic fission products and the number of SiC coating defects.

4.0 TECHNICAL BASIS OF PROGRAM

4.1 SiC Coating Defect Types

The release rate of metallic fission products from TRISO coated fuel particles with SiC coating defects is determined by the type of defect present. Three types of SiC coating defects may be present in the as-manufactured fuel which may contribute to the metallic fission product release:

Category 1

Gross SiC defects such as missing SiC and large ($\geq 1 \mu\text{m}$) cracks in the SiC coatings.

Category 2

Small SiC coating defects such as ($\leq 1 \mu\text{m}$) microcracks.

Category 3

SiC defects consisting of closed porosity and Si inclusions.

The existing B/L technique is the best method to detect Category 1 SiC defects. An improved technique is needed to detect Category 2 and 3 defects. A mercury intrusion QC method was thought to have the best chance of detecting Category 2- and 3-type SiC defects. However, substantial calibration data correlating the degree of intrusion versus metallic fission product release must be conducted to verify that the necessary intrusion technique will detect Category 2 and 3 defects.

Some SiC coating defect detection work was conducted in the early 1980s (Ref. 1). In this work, the three types of SiC coating defects were categorized as shown in Fig. 1. Defective SiC coatings were categorized according to the following features:

1. A partial or completely missing SiC layer or fissure through the SiC $\geq 1 \mu\text{m}$ wide.
2. A microcrack or fissure $< 1 \mu\text{m}$ wide which extends through more than one-half of the nominal SiC coating thickness.

Fig. 1 Schematic of TRISO-coated Particle Depicting Different Types of SiC Coating Defects (Taken From Ref. 1)

3. Microstructural flaws in the SiC coating such as excessive silicon or a large degree grain-boundary disorder that renders the SiC permeable to metallic fission product release.

However, in the earlier intrusion work the SiC defect fractions detected were not correlated to the release or retention of metallic fission products with a measure of SiC flaws. A low metallic fission product release observed must show a low SiC coating defect fraction and a particle sample showing high SiC defect must show high metallic product release.

4.2 SiC Defect Detection QC Methods

4.2.1. Standard Burn/Leach

The release of metallic fission products is expected to be considerably different for the different types of SiC coating defects (Categories 1, 2 and 3). Therefore, the correlation between release of metallic fission products and fraction of SiC coating defects may be very different for samples with different amounts of each category of SiC defects.

In the standard B/L SiC coating defect measurement method, the oxidation of the outer and inner PyC carbon is followed by acid leaching of the exposed kernels in the defective SiC-coated particles (Ref. 3).

The standard B/L detection technique is insensitive if temperatures reached in QC work are $> 750^{\circ}\text{C}$. Silicon carbide forms a protective, thin layer of SiO_2 on the surfaces of burned-back TRISO-coated fuel particles which inhibits further oxidation of the SiC coating layers. At high temperatures ($> 750^{\circ}\text{C}$) the SiO_2 film can become mobile on the surfaces of SiC coatings which may migrate into SiC coating defects sealing off these defects. Further oxidation of the underlying carbon coatings is, therefore, inhibited by the SiO_2 blockage and these defective SiC-coated fuel particles go undetected in the leaching step of the QC analysis.

4.2.2. Intrusion

Several intrusion-type improved QC methods have been studied to reduce the problems with the B/L method to detect SiC coating defects at GA over the past years (Refs. 1 and 2). Attempts were made to determine if silica blockage of some of the SiC coating

defects does occur during the high-temperature burn-back process and if additional SiC coating defects were present after the standard B/L method. The first method was a mercury intrusion technique followed by x-ray examination of the particles to detect defective SiC coated fuel particles that mercury had intruded through the SiC coating defects during a high pressure mercury exposure. Several other fluids were tested in place of mercury, which included low surface tension liquids (methylene iodide and methylene bromide), dye penetrants such as "Zyglo" and "Spot Check" and fluids containing radioactive trace elements. In all of these QC methods the detection of SiC coating defects was dependent on the penetration of the fluid through the SiC coating defect with detection of the penetrated fluid either by x-ray examination or auto-radiography.

Silicon coating defective fractions estimated with the QC intrusion-type methods have shown SiC coating defect levels several orders of magnitude higher than defect fraction determined by the standard B/L QC measurement data. There was evidence that SiC coating defects were as-manufactured defects that would lead to higher metallic fission product release from the fuel in service. The in-pile release of Cs-137 was relatively high from the particles with high SiC coating defects as measured by the Hg Intrusion Method. These results suggested a correlation between Hg intrusion and fission product release (Ref. 1). The low diffusivity of cesium in PyC required that the annealing experiments had to be conducted at 1600°C and 1800°C for up to 600 hours. This length of time at high temperature may have induced SiC coating failure leading to cesium fission product release. Using Ba-140 or Ce-144, which have much higher diffusivity, is a better choice of tracer isotope because the diffusion rate in PyC is higher. A much lower temperature for shorter times would achieve the same release through defects with less potential for thermally-induced SiC coating failure.

4.3 Quantitative Modeling of the SiC Coating Defect Detection

A quantitative modeling evaluation of the various SiC coating defect detection QC methods was conducted (Ref. 4). The major conclusions of this study were as presented below:

1. The SiC defects in TRISO-coated fuel particles are composed of a population of cracks or holes of a distribution of effective pore radii. The majority of these pores fall in the 5 to 15 nanometer size range { (1 nanometer = 0.003 μ m or 10 angstrom; (See Figure 2) }. SiC coating defects of this size are large enough to allow metallic fission product atoms to escape.

Fig. 2 Additional Information From Application of the Intrusion Method Using Nonwetting Fluids: the Cumulative and Differential Defect Fraction-Pore Radii Distribution Curves.

3. The Hg and Liquid Intrusion methods used previous were found to detect SiC coating defects in the pore size range of 40 to 1300 nanometers (0.04 to 1.3 μm). The Mercury Intrusion Technique has the capability to detect pores down to the 7 nanometer (0.007 μm) size range at 30,000 psig (see Fig. 3).

In addition to the Hg Intrusion Method being able to detect extremely small size pores, ORNL pointed out that the driving force for this method is the high pressure of the non-wetting fluid. A relatively short time is required for liquid to penetrate all pores which can be filled at a given pressure. Other SiC defect detection methods rely on gas or liquid penetration of defects at one atmosphere pressure. For gas or liquid diffusion through a small pore in the SiC coating at one atmosphere measure, the driving force is very small. Therefore, the times required for penetration of the small diameter pores are excessively long.

Based on the previous evaluation, it was determined that only the Hg Intrusion Method for detecting SiC coating defects in the 5 to 15 nanometers (0.005 to 0.015 μm) size range is feasible. However, several key issues had to be resolved as presented below:

1. Calibration of the Hg Intrusion QC technique versus the release of metallic fission from low and high defective SiC coatings in TRISO-coated fuel particles.
2. Minimize the formation of the SiO_2 during OPyC removal by conducting carbon oxidation at low temperature. This can be accomplished in a activated oxygen system or removal of the SiO_2 by reduction in activated hydrogen or HF acid leaching.

4.3.3. Issues to be Resolved

Some areas of concern for the intrusion-type QC method to measure defective SiC-coated fuel particles are apparent upon technical evaluation. Presented below were the most important of these concerns:

1. The required pressure to force a liquid through a small pore (connected pipe) in the SiC coating may be excessive, causing damage to intact SiC coating layers. For mercury, the pore size penetrated is defined by the following equation of Allen (Ref. 5):

Fig. 3 Comparison of the Defect Fraction-Applied Pressure Curves for Intrusion by Mercury and by a Radioactive Cesium Solution for Particles From Batch 6155-02-020.

$$D = \frac{-4q \cos \theta}{P}$$

Where :

D = diameter pore
 q = surface tension of mercury
 θ = contact angle of mercury
 P = pressure on mercury

Solving this equation based on the data of Allen where $q = 480$ dynes/cm and $\theta = 140^\circ$ at 30,000 psia, results in a pore diameter of 0.00713 μm or 71.3 angstroms. The diameters of metallic fission product atoms are estimated to be a factor of 10 times smaller. Using a gas to penetrate the pore would be more representative of the metallic fission product species, but unlike Hg intrusion, no feasible method exists to measure the amount intruded.. Similar concerns for other liquid penetrating the SiC coating pore can be expressed.

2. Measuring the defective particle fraction by detecting a discrete penetration of the liquid in an individual particle in a sample of 100,000 good particles can be subjective and prone to large errors. The human interpretation required and the problem of removing all the intrusion liquid from the surfaces of the particles prior to x-ray measurement add to the error.
3. There was no clear relationship established between the fraction of SiC coating defects detected and the rate of release of metallic fission products.

5. EXPERIMENTAL WORK

Based on the information presented above, a detailed technical program was developed earlier to evaluate the accuracy of the Hg intrusion QC method to measure SiC coating defects (Ref. 6). The logical approach used with the required methodology to resolve the question of whether the B/L method did or did not underestimate the SiC coating defects in the TRISO-coated fuel components is presented in Figure 4.

5.1 TRISO Coated Fuel Particles Selected for Testing

Four TRISO coated fuel particle batches were selected for testing as presented above. Two of the test batches (Nos. 8876-66 and 8876-70) produced for the HRB-21 Capsule were expected to have low SiC coating defect fractions (Good SiC). The other two batches (Nos. 6157-11-010 and 6155-00-010) selected were from earlier coating production. These batches had shown high cesium releases in capsule irradiation tests which indicated lower quality SiC (defective SiC).

The physical dimensions along with the B/L defective SiC coating data for the four coated particle samples used are presented in Table 1 below.

5.2 Metallic Fission Product Release Experiments

Post irradiation heat treatment experiments at 1400 and 1600°C were conducted on duplicate particle samples from the four test batches to determine the fractional releases of Ba-140, Te-132 and Cs-137. Particles from Batch No. 8876-66 were laser drilled through the SiC coatings to the IPyC layers in one case and through the buffer layers to the kernels in the second case (See Figure 5). The laser drilled particles were irradiated and annealed along with the undrilled particles to determine the release rates for the metallic fission products from the bare kernel and from particles with known holes through the SiC coating layers. These laser drilled calibration data were required to translate the metallic fission product release fractions measured from the anneal data into fractions of SiC coating defects present.

The heat treatment furnace equipment used for these experiments was that previously used for core heat up simulation experiment (Ref. 7). The irradiated particles were loaded into graphite crucibles to trap

Fig. 4 SiC Coating Defect QC Method Development Logic

Table 1
Particle Characteristics

Sample No.	Kern. Dia. μm	Kern. Den. ₃ Mg/m^3	Buffer Thck μm	Buffer Den. ₃ Mg/m^3	IPyC Thck μm	IPyC Den. ₃ Mg/m^3	SiC Thck μm	SiC Den. ₃ Mg/m^3	OPyC Thck μm	OPyC Den. ₃ Mg/m^3	PPyC Thck μm	PPyC Den. ₃ Mg/m^3	Burn/ Leach Frac
8876-66	348	10.70	105.5	1.04	50.0	1.88	35.2	3.22	41.8	1.93	--	--	5.0E-6
8876-70	351	10.65	105.0	0.97	52.8	1.90	32.6	3.22	46.8	1.95	46.4	1.00	2.5E-5
6157-11 -010	353	11.07	115.3	0.97	35.6	1.88	35.6	3.22	47.8	1.90	--	--	3.5E-4
6155-00 -010	403	9.70	80.5	1.22	32.5	1.88	32.3	3.22	36.1	1.78	--	--	4.7E-4

*All samples are UCO kernel except 6155-00-010, which is $(\text{Th,U})\text{O}_2$.

(a)

(b)

Fig. 5 Photographs of Laser Drilled TRISO-Coated Fuel Particles From Batch 8876-66 OPyC: a) Drilled to the Kernel; b) Drilled Through the SiC Layer

the Ba-140 release, a mullite Cs-137 collection tube was loaded down stream of the heated sample. The crucibles were heated in a tantalum (Ta) diffusion barrier tube. At the end of each heating cycle the furnace was cooled to ambient temperature, the particles were unloaded and the graphite and the mullite tube were removed and gamma counted to measure metallic fission products. The particles were reloaded in fresh graphite crucibles with new mullite tubes, loaded back into the Ta furnace tube and annealed for the next time interval. At the end of the annealing test the particles were gamma counted to determine total fission product inventory. The fractional release of the metallic fission product was calculated from the amount released to the collectors divided by the total produced.

5.3 Mercury Intrusion Testing

After the irradiated particles had been annealed the OPyC coatings were removed by low temperature oxidation (750°C) and the SiO₂ film was removed by leaching in hot hydrofluoric (HF) acid. These samples were loaded into the High Pressure Hg Porosimeter and injected with Hg to 30,000 psig. The Hg intruded particles were cleaned of surface Hg, x-rayed to detect Hg intrusion and microscopically examined for Hg intruded particles. The fraction of defective SiC coated particles present was calculated from the number Hg intruded divided by the total number in the sample.

6.0 DISCUSSION OF EXPERIMENTAL RESULTS

6.1 Metallic Fission Product Calibration Data

The first series of metallic fission product anneal tests were conducted with the laser drilled particles from Batch No 8876-66. These experiments were conducted to calibrate the metallic fission product from particles with holes through the total coating to the kernels (direct kernel release), with through the SiC coating to the IPyC layer (IPyC delay release) and fully coated particles (diffusion release through intact SiC coatings).

Metallic fission product anneal runs were conducted on duplicate samples from TRISO coated UCO particles (Batch No. 8876-66) laser drilled to the kernel and laser drilled to the IPyC layer. After laser drilling the particles were irradiated in TRIGA to $\sim 8 \times 10^{12}$ fissions/sample to produce an inventory of metallic fission products. The samples were gamma counted and loaded into graphite collector crucible and annealed for various time intervals at 1400°C and 1600°C . After each anneal interval the particles were transferred to a fresh crucible and the spent crucible was submitted for gamma counting. Mullite tubes were located in furnace as cesium collectors for some of the experiments.

The fractional releases of Ba-140, Cs-137 and Te-132 as a function of time at temperature were determined. The release data for these samples are presented in Tables 2 and 3.

A discussion of the data generated and some conclusions reached from data evaluation in these experiments are presented in summary below:

6.2.1 Release of Fission Products for Particles Drilled to the Kernel

6.2.1.1 Ba-140 release

Ba-140 showed essentially zero release at 1400°C for 25 hours. After raising the temperature to 1600°C , there was a short time delay then the drilled particles released 25 and 30 % respectively for the two samples annealed for an additional 120 hours at 1600°C .

At the 25 to 30% release level the Ba-140 must be diffusing from the kernels. An estimation of the diffusion

Table 2
Metallic Fission Product Release From Particles
Drilled to the Kernel (Batch No. 8876-66 OPyC)

Run Temperature °C	Time Cum. hrs.	Fractional Ba-140	Release Te-132	(Cumulative) Cs-137
Sample 1				
1306	1.5	0	0	1.15E-2
1398	7.5	0	2.14E-4	1.01E-1
1411	25.5	3.00E-5	9.75E-4	1.94E-1
1626	27.0	2.22E-4	2.04E-3	2.42E-1
1608	33.0	1.58E-3	2.02E-2	4.78E-1
1624	51.0	1.70E-2	2.60E-2	6.35E-1
1619	71.0	8.54E-2	2.91E-2	6.78E-1
1620	91.0	1.55E-1	3.02E-2	6.78E-1
1616	111.0	2.08E-1	3.02E-2	6.78E-1
1592	131.0	2.49E-1	3.02E-2	6.78E-1
1600	151.0	2.93E-1	3.02E-2	6.78E-1
Sample 2				
1306	1.5	0	2.69E-4	2.33E-2
1398	7.5	0	1.24E-3	2.16E-1
1411	25.5	1.56E-5	1.72E-3	4.15E-1
1626	27.0	1.63E-4	2.06E-3	4.42E-1
1608	33.0	1.16E-3	1.95E-2	6.21E-1
1624	51.0	9.86E-3	2.49E-2	7.59E-1
1619	71.0	4.88E-2	2.74E-2	7.81E-1
1620	91.0	9.38E-2	2.84E-2	8.96E-1
1616	111.0	1.56E-1	2.84E-2	8.96E-1
1592	131.0	1.89E-1	2.84E-2	8.96E-1
1600	151.0	2.45E-1	2.84E-2	8.96E-1

Table 3
Metallic Fission Product Release from Particles
Drilled to the IPyC (Batch No. 8876-66 OPyC)

Run Temperature °C	Time Cum. Hrs.	Fractional Ba-140	Release Te-132	(Cumulative) Cs-137
Sample 1				
1306	1.5	0	1.60E-4	1.91E-2
1398	7.5	0	4.84E-4	2.58E-1
1411	25.5	0	1.33E-3	2.87E-1
1626	27.0	1.94E-5	2.17E-3	3.07E-1
1608	33.0	7.00E-4	4.04E-2	3.33E-1
1624	51.0	6.94E-3	5.80E-2	5.24E-1
1619	71.0	4.58E-2	6.38E-2	6.27E-1
1620	91.0	7.84E-2	6.62E-2	6.26E-1
1616	111.0	1.19E-1	6.62E-2	6.26E-1
1592	131.0	1.49E-1	6.62E-2	6.62E-1
1600	151.0	1.87E-1	6.62E-2	6.62E-1
Sample 2				
1306	1.5	0	9.16E-5	2.10E-2
1398	7.5	0	6.16E-4	2.78E-1
1411	25.5	0	1.08E-3	3.29E-1
1626	27.0	3.48E-5	1.85E-3	5.22E-1
1608	33.0	3.52E-4	4.04E-2	5.56E-1
1624	51.0	7.76E-3	5.88E-2	7.33E-1
1619	71.0	1.75E-2	6.43E-2	8.04E-1
1620	91.0	3.83E-2	6.43E-2	8.04E-1
1616	111.0	9.72E-2	6.65E-2	8.04E-1
1592	131.0	1.19E-1	6.64E-2	8.45E-1
1600	151.0	1.48E-1	6.64E-2	8.45E-1

coefficient in the kernel at 1600°C was made using the "Slider Code" approach. Plotting the fractional release versus the square root of the annealing time a delay time (time lag) is experienced initially followed by straight portion of the curve. For a coated particle the time lag (t_1) is attributed to the fission product diffusing through the coating. Approximations of the diffusion coefficients in the coating and in the kernel can be calculated from the following equations.

Equation 1

$$d_c = \frac{x^2}{6 t_1}$$

where

d_c = diffusion coefficient in the coating.

x^c = coating thickness.

t_1 = time delay through the coating.

Equation 2

$$d_k = \frac{f^2 \times r^2 \times \pi}{36 t'}$$

Where:

d_k = diffusion coefficient in the kernel.

f^k = fractional release (release must be less than 30 %).

r = radius of the kernel.

t' = total anneal time minus the lag time.

Plots of the Ba-140 releases versus the square root of time for the particles drilled to the kernel were made. At 1600°C there were 21 and 31 hours delays followed by a straight section in the plot to releases of 30% and 25% for the two samples tested. These time delays were attributed to the Ba-140 saturation of the IPyC before migrating out of the hole through the SiC (for bare kernels no time delay would be expected). Using the methodology in Equation 2 and the straight parts of the curves the Ba-140 diffusion coefficients in the UCO kernels were calculated to be:

$$\begin{array}{ll} \text{Sample 1} & d_k = 6.45\text{E-}12 \text{ cm}^2/\text{sec at } 1600^\circ\text{C} \\ \text{Sample 2} & d_k = 4.83\text{E-}12 \text{ cm}^2/\text{sec at } 1600^\circ\text{C} \end{array}$$

These data appear consistent with solid state diffusion of Ba-140 in the particles.

6.2.1.2 Cesium Release

Cesium showed essentially unity release from the laser

drilled particles to the kernel in both samples after a total of 70 to 90 hours (the first 25 at hours 1400°C) Twenty and forty percent of the cesium was released at 1400°C for the two samples in only 25 hours. At 1600°C for only 1.5 hours the accumulative releases were over 40%. These data show a high release rate initially followed by a decreasing rate at 1400°C. Upon raising the samples to 1600°C the remaining cesium was rapidly released.

These data were consistent with the Cs-137 release from kernels exposed by laser drilling mode to be one of vapor transport.

6.2.1.3 Tellurium Release

Te-132 showed 3 to 6 % release after the total annealing time at 1400 and 1600°C. These data indicated that only the Te-132 recoiling into the coatings during irradiation is released.

6.2.2 Fission Product Release from Particles Drilled to the IPyC Layers

The releases of Ba-140, Cs-137 and Te-132 from particles drilled to the IPyC layers and drilled to the kernel were for the most part similar.

6.2.2.1 Ba-140 Release

Total Ba-140 release through the IPyC layer was similar to that drilled to the kernel. However, the total fractional releases were less being 18.5 and 15% for the two sample aliquots tested. Diffusion coefficients in the kernels calculated were $2.64\text{E-}12$ and $1.74\text{E-}12$ cm²/sec, respectively.

6.2.2.2 Cs-137 Release

Essentially unity Cs-137 release with no delay time was observed (Same as with particles drilled to the kernels).

6.2.2.3 Te-132 Release

The Te-132 release was the same as with particles drilled to the kernel.

6.2.2.4 Release Constant Data for Drilled Particles

The release constants for Ba-140 and Cs-137 from the laser drilled particle data were determined from these results. At 1600°C for 150 hours the fractional releases of Ba-140 for the two sample aliquots drilled to the IPyC layer averaged 16.7 % released and the Cs-137 averaged 75.4 % released.

The SiC coating defect fractions estimated from the release data are as follows:

$$\text{Fraction of defective SiC} = \frac{\text{Fraction of Ba-140 released}}{\text{0.167}}$$

$$\text{Fraction of defective SiC} = \frac{\text{Fraction of Cs-137 released}}{\text{0.754}}$$

6.3.0 Metallic Fission Product Release from Non-laser Drilled Particles

The release of metallic fission products through intact SiC coatings was expected to be low for the TRISO coated UCO particles used in these annealing tests. The purpose of this experiment was to determine the integrity of the SiC layers by the migration of metallic fission product through the SiC coating and use these same to calibrate the Hg intrusion QC method.

The metallic fission product release data for the intact TRISO coated fuel particles are presented in Tables 4, 5, 6 and 7 below.

6.3.1 Ba-140 Release

The Ba-140 releases for Batch Nos. 8876-66 and 8876-70 were essentially zero ($< 1.0\text{E-}6$ fractions) For the Batch Nos. 6157-11-010 and 6155-00-010 the average Ba-140 releases for the two samples tested were $4.8\text{E-}5$ and $2.1\text{E-}3$ respectively. These data showed that the SiC coatings for the "Good SiC" was intact and that a relative large fraction for the "Bad" SiC was defective.

6.3.2 Cs-137 release

The cesium release data were much less accurate than that measured for the Ba-140 because of the low inventory in the irradiated particles ($2.6\text{e}+5$ dpm per sample). With this small amount of Cs-137 present the detection limit for Cs-137 release was at $5\text{E-}4$ fraction. For the sample size of 450 particles if 1 defective SiC particle released all of its Cs-137 the fractional release of $2.2\text{E-}3$ would be observed. Therefore, using these Cs-137 data to estimate SiC coating defects were very uncertain.

The observed Cs-137 release from Batch No. 8876-66 which expected to be a high quality SiC coating was approximately a

Table 4
Metallic Fission Product Release from Particles
As-coated (Batch No. 8876-66 OPyC, Non-drilled)

Run Temperature °C	Time Cum. hrs.	Fractional Ba-140	Release Te-132	(Cumulative) Cs-137
Sample 1				
1306	1.5	0	0	4.49E-3
1398	7.5	0	0	4.37E-2
1411	25.5	0	0	4.76E-2
1626	27.0	0	0	4.98E-2
1608	33.0	1.49E-7	1.43E-7	5.43E-2
1624	51.0	"	"	6.12E-2
1619	71.0	"	"	6.97E-2
1620	91.0	"	"	7.26E-2
1616	111.0	"	"	7.53E-2
1598	131.0	"	"	7.72E-2
1600	151.0	"	"	7.82E-2
Sample 2				
1306	1.5	0	0	3.27E-3
1398	7.5	0	0	5.20E-3
1411	25.5	0	0	1.03E-2
1626	27.0	0	0	1.38E-2
1608	33.0	0	0	2.29E-2
1624	51.0	0	0	3.91E-2
1619	71.0	0	0	4.33E-2
1620	91.0	0	0	5.26E-2
1616	111.0	1.11E-4 ^a	0	5.69E-2
1592	131.0	4.93E-4	0	5.91E-2
1600	151.0	8.26E-4	0	6.13E-2

^a = particle broken during crucible loading.

Table 5
Metallic Fission Product Release from Particles
As-coated (Batch No. 8876-70 O/Buffer, Non-drilled)

Run Temperature °C	Time Cum. Hrs.	Fractional Ba-140	Release Te-132	(Cumulative) Cs-137
Sample 1				
1600	1.5	0	0	1.14E-3
1600	6.0	0	0	1.33E-3
1600	25.0	0	0	1.40E-3
1600	75.0	0	0	"
1600	125.0	0	0	"
1600	150.0	0	0	1.40E-3
Sample 2				
1600	1.5	0	0	8.67E-4
1600	6.0	0	0	1.12E-3
1600	25.0	0	0	1.27E-3
1600	75.0	0	0	1.39E-4
1600	125.0	0	0	"
1600	150.0	0	0	1.39E-3

Table 6
Metallic Fission Product Release from Particles
As-coated (Batch No. 6157-11-010, Non-drilled)

Run Temperature °C	Time Cum. Hrs.	Fractional Release (Cumulative)		
		Ba-140	Te-132	Cs-137
Sample 1				
1611	1.5	0	0	1.46E-4
1604	6.0	2.68E-6	0	1.78E-4
1629	25.0	4.10E-6	0	6.94E-4
1608	75.0	6.25E-6	0	9.25E-4
1618	125.0	6.25E-6	0	2.60E-3
1615	150.0	6.25E-6	0	3.81E-3
Sample 2				
1611	1.5	0	0	1.07E-3
1604	6.0	0	0	1.16E-3
1629	25.0	3.80E-6	0	1.37E-3
1608	75.0	1.80E-5	0	1.52E-3
1618	125.0	4.87E-5	0	1.63E-3
1615	150.0	8.93E-5	0	2.37E-3

Table 7
Metallic Fission Product Release From Particles
As-coated (Batch No. 6155-00-010, Non-drilled)

Run Temperature C	Cum. Time hrs.	Fractional Release Ba-140	(Cumulative) Te-132	Cs-137
Sample 1				
1602	1.5	9.60E-5	0	1.33E-4
1590	6.0	3.75E-4	0	2.45E-4
1611	25.0	7.54E-4	0	3.34E-4
1610	75.0	2.26E-3	0	6.84E-4
1613	125.0	3.27E-3	0	1.17E-3
1606	150.0	3.92E-3	0	1.28E-3
Sample 2				
1602	1.5	4.03E-6	0	1.15E-4
1590	6.0	2.63E-5	0	2.63E-4
1611	25.0	1.10E-4	0	2.96E-4
1610	75.0	3.66E-4	0	4.78E-4
1613	125.0	7.08E-4	0	1.45E-3
1606	175.0	9.03E-4	0	1.69E-3

factor of ten higher than the release observed the two lower quality SiC coated particle samples. These data were apparently in error based on the Ba-140 release data and the Hg intrusion results presented below in Sec. 6.4.0 below.

6.4.0 Mercury Intrusion Data for Irradiated Annealed Particles and As Coated Particles

After oxidation of the outer carbon layers from the annealed test particles and from as-coated particles from the same coating batches, Hg intrusion at 30,000 psig were conducted. The results of these tests are presented in Table 8 below.

Examination of these Hg intrusion data clearly showed that the "Good SiC" particles showed zero SiC defects while the "defective" SiC particles showed a substantial number of SiC coating defects.

Silicon carbide defect fractions measured by the three QC methods were compared and they are presented in Table 9 below.

The conclusions reached from these data were not totally defensible. For the "Good SiC" samples all SiC defects measured were low as expected. The SiC defects measured by B/L and the Ba-140 release methods for Batch No. 8876-66 were both low. However, the sample sizes for the Hg intrusion was only 2037 particles and that for the Ba-140 release measurement was based on 900 particles total. One defective SiC coated particle in each of these samples would result in a Hg intruded fraction of $4.5E-4$ and a Ba-140 of $1.1E-3$. The same conclusions were reached for the sample from Batch No. 8876-70 O/Buffer.

6.5.0 Evaluation of Hg Intrusion as an Improvement for the B/L QC Method for SiC Coating Defect Detection

The evaluation of the feasibility of a Hg Intrusion QC method for measuring SiC coating defects for the MHTGR was conducted as an

TABLE 8
As-coated and Annealed Particle Hg Intrusion
Data at 30,000 psig

Unirradiates Samples				Irradiated Samples			
Sample No.	No. of Part Impreg	No. of Defects	Frac Defect	Cruc No.	No. of Part Impreg	No. of Defects	Frac Defect
8876-66	1137	0	0	21	450	0	0
8876-70	973	0	0	39	450	0	0
8876-70	977	0	0	40	450	0	0
6157-11-010	1100	25	2.3E-2	61	450	4	8.9E-3
6157-11-010	1500	21	1.4E-2	62	450	5	1.1E-2
6155-00-010	1584	135	8.5E-2	63	450	2	4.4E-3
6155-00-010	Sample Lost			64	450	2	4.4E-3

Table 9
Comparison of SiC Coating Defect Measured by
Hg Intrusion, Burn/Leach and Ba-140 Release Methods

Batch No.	Hg Intrusion			B/L	Ba-140	
	No. of Defect	No. of Part.	Fract SiC Defects	Fract SiC Defects	Fract. Rel.	Fract SiC Defects
8876-66	0	2037	0	5.0E-6	1.5E-7	1.0E-6
8876-70	0	2850	0	2.5E-5	<1.0E-7	<1.0E-6
6157-11-010	55	3500	1.57E-2	3.5E-4	4.8E-5	2.9E-4
6155-00-010	139	2484	5.57E-2	4.7E-4	2.4E-3	1.4E-2

improvement for the Burn/Leach QC method currently used. The observations on the validity of the Hg intrusion as a replacement for the B/L method were not totally conclusive from this work as presented below:

The SiC coating defects measured by B/L and the Ba-140 release methods for Batch No. 8876-66 "Good SiC" were both low. However, for the purposes of determining feasibility the sample sizes for the Hg intrusion was only 2037 particles and that for the Ba-140 results was based on 900 particles total in order to keep examination effort within funding constraints. Observation of no defects in such a small sample would be consistent with the MHTGR quality goal of $< 5E-5$ fraction SiC defects, but a larger sample size would be needed to provide statistical verification. One defective SiC coated particle in each of these samples would result in a Hg intruded fraction of $4.5E-4$ and a Ba-140 of $1.1E-3$. The same conclusion was reached for the sample from Batch No. 8876-70. There appeared to be no induced SiC failure from the high pressure (30,000 psig) Hg intrusion with these particles.

It appeared that the "Bad" SiC samples did show a higher defective SiC coating fraction by both the Hg intrusion and the Ba-140 release methods than by the B/L method for 6155-00-010. However, the SiC defects measured by the B/L and the Ba-140 release methods were in better agreement than the Hg intrusion for 6157-11-010. The Hg intrusion data were about 33 times higher.

For earlier manufactured TRISO coated fuel particles (Batch Nos. 6157-11-010 and 6155-00-010) there appears to be an under estimation of the SiC coating defects by the B/L method as indicated by the Ba-140 release data and the Hg intrusion results obtained in this study. However, for the recently produced particles (Batch Nos. 8876-66 and 8876-70) this does not appear to be the case. With recent improvements in coating technology it appears that the quality of the SiC coatings has improved. The levels of SiC coating defects in the 2 and 3 categories have decreased and most defects are of category 1 type (missing SiC, broken SiC during compact fabrication and others). The standard B/L method is required to detect Category 1. However, the improved fuel quality for the MHTGR requires that the Category 2 and 3 SiC defects must be detected and the Hg intrusion QC method is required for these measurements.

The major interest is to measure SiC coating defects for the MHTGR reactor, where very low defect SiC coated fuel particles are required. Gross SiC coating defects must be measured by the B/L QC method. In addition, the other SiC coating defects which may contribute to the fission product release must be measured by the Hg intrusion technique. Therefore, the Hg intrusion QC method for measuring SiC coating defects should be further evaluated at much larger sample sizes (100,000 particles/test or larger) for the MHTGR. Use of the AIA automated system to measure Hg intruded particles will be required at the larger sample size.

7.0 REFERENCES

1. Kovacs, W. J., "Gaseous Fission Product Release Predictions in TRISO HTGR Fuel Particles", Journal of the American Ceramic Society Vol 66 No. 3, March 1982.
2. Kovacs, W. J., "Characterization of Defective SiC Coatings in TRISO HTGR Fuel Particles," GA-A16215, April 1981.
3. Partain, K. E. and Adams, C. C., "Operating Procedures Used to Measure Uranium and Thorium Contamination and Defective SiC Coating Defects In Fuel Particles And Compacts," General Atomics Document No. 910008/NC, September, 1989.
4. Myers, B. F., "An Assessment of Methods For the Determining Defect or Failure Fractions in HTGR Coated Particle Fuels and Their Relationship to Particle Microstructure", ORNL Doc. No. DOE-HTGR-88260, ORNL/TM-10805, April 1989.
5. Allen, T., "Particle Size Measurement," Wiley, New York, 1974.
6. Adams, C. C. "SiC Coating Defect Detection Technique Development", GA Doc. No. DOE-HTGR-88247, Nov. 30, 1988.
7. Goodin, D. T. and Partain, K. E., "FY-83 Core Heatup Test on KFA TRISO Fuel", GA Doc. No. 906886, March 1983.