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The direct assay of filter media by gamma spectrometry following DEOX testing has distinct advantages over analytical chemistry. Prior to using gamma spectrometry for the quantification of cesium (Cs-137), a calibration must be established with known sources since gamma spectrometry yields relative results. Quantitative analytical chemistry, in particular ICP-MS, has been performed on the filter media for comparison to the gamma spectrometry data. The correlation of gamma spectrometry to ICP-MS data is presented to justify the continued use of gamma spectrometry for filter media.

I. INTRODUCTION

A head-end processing step, termed DEOX for its emphasis on decladding via oxidation, is being developed for the treatment of spent oxide fuel by pyroprocessing techniques.¹⁻² The head-end step employs high temperatures to oxidize UO_2 to U_3O_8 resulting in the separation of fuel from cladding and the removal of volatile fission products. Development of the head-end step is being performed in collaboration with the Korean Atomic Energy Research Institute (KAERI) through an International Nuclear Energy Research Initiative.

Following the initial experimentation for the removal of volatile fission products, an off-gas treatment system was designed in conjunction with KAERI to collect specific fission gases. The primary volatile species targeted for trapping were iodine, ruthenium/technetium, and cesium. Each species is intended to be collected in distinct zones of the off-gas system and within those zones, on individual filters.

Considering the potential importance of cesium to repository loading³, its removal and collection during pyroprocessing is particularly significant to the head-end processing step. Previous DEOX testing has shown that as much as 99% of the cesium can be removed by applying high temperatures under vacuum conditions.¹ The trapping of cesium is one of the key aspects to

current testing and as such, requires a sampling and analyses program for its quantification.

An alternative to the effort intensive chemical analyses of filters for cesium is a direct assay of the filters by gamma-ray spectrometry. A gamma spectrometer is available in the same facility where DEOX testing is being performed and it would eliminate the need for the transfer of the sample to the analytical chemistry laboratory for analyses. Since gamma spectrometry is a semi-quantitative technique providing relative concentrations, either a calibration process using identical geometries and known cesium quantities or a correlation with analytical chemistry results must be performed. The purpose of this paper is to present the comparison of chemistry and gamma spectrometry results to establish the validity of direct assaying.

II. EXPERIMENTAL

A brief description of the spent oxide fuel characteristics, the experimental conditions, and the equipment used for the collection and analyses of cesium follows.

II.A. Off-Gas Treatment System

The DEOX furnace and associated off-gas treatment system (OTS) includes four zones; the lowest or Zone 4 for oxidation of the fuel and three other zones for collection of volatile off-gases (Fig. 1). The three upper filter zones were designed to collect specific volatile species following oxidation based on the operating parameters and filter media for each zone. The first zone consists of five stainless steel cartridges containing zeolite based media for the trapping of gaseous iodine species (Fig. 2). The second and third zones consist of disk type filters for the collection of ruthenium/technetium and cesium, respectively (Fig. 2). The disks are aluminosilicate based⁴ and contained within stainless steel cartridges. For Zone 2, there are nine disk cartridges and for Zone 3 there are five.

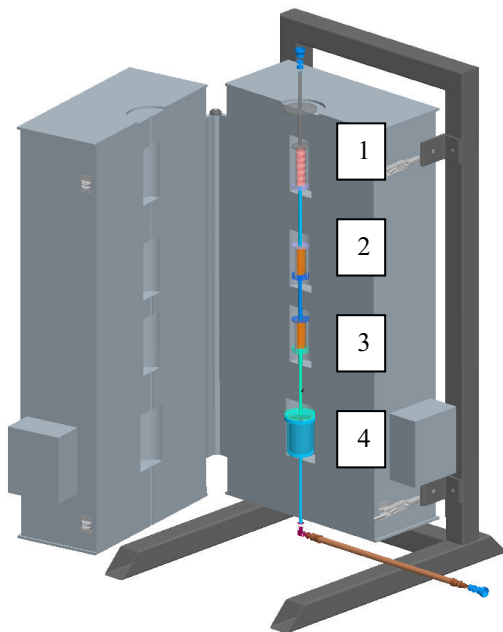


Fig. 1. DEOX furnace and off-gas treatment system



Fig. 2. Filter media for DEOX testing includes zeolite (center) and aluminosilicate (left, right) based materials.

Testing with spent oxide fuel is performed in the Hot Fuel Examination Facility (HFEF) located at the Idaho National Laboratory. The HFEF is an inert shielded hot cell requiring remote-handled operations. The spent oxide fuel used for testing originated from the Belgium

Reactor-3 (BR-3), a pressurized water reactor located in Mol, Belgium. The BR-3 fuel has a typical burnup of ~37 GWd/t with a 25 year decay time and zircaloy-4 type cladding. Segments of approximately 2.5 cm in length are sectioned from a BR-3 spent oxide fuel rod and loaded into a stand that keeps the segments vertical while processing. The stand is then placed into a crucible and loaded into the outer containment vessel of Zone 4. The nominal batch size is 100 g of fuel and cladding per test.

Oxidation of the spent fuel commences with either oxygen or air supplied as the furnace heats at approximately 10°C/min to 500°C. At 500°C, the temperature in Zone 4 is held for 3 hrs under the flow (0.5 L/min) of oxidative gas. Following the oxidation cycle, the system is evacuated (<1 Torr) and heating continues at approximately 10°C/min to 1200°C. Zones 1, 2, and 3 are maintained at constant temperature throughout the entire sequence given. Zone 1 is at 150°C, Zone 2 is at 600°C, and Zone 3 is at 800-1000°C. Following a test, the entire OTS assembly is scanned by the gamma spectrometer located in HFEF. Samples are then taken of the oxidized fuel and individual filters so that chemical analyses can be performed in the analytical laboratory.

II.B. Gamma-Spectrometry and Inductively Coupled Plasma Mass Spectrometry

The gamma spectrometer in HFEF has historically been utilized in the non-destructive examination of irradiated fuel elements. As such, a handling stage exists for positioning the item of interest in front of a collimator which extends through the hot cell wall to the detector. The rectangular-shaped collimator can be positioned both vertically and horizontally and varied in one dimension for slit width. The detector is a solid germanium crystal surrounded by a sodium-iodide crystal for the removal of background interferences. Gamma-scanning of the OTS following a test is performed by raising the assembly past the collimator at set increments and time intervals. A slit width of 0.25 cm at 0.25 cm increments for 120 seconds yields a scan of over 13 hours for the ~100 cm length OTS. Since individual energies can be discerned with gamma spectrometry, specific isotopes can be identified. The isotope Cs-137 has been chosen to represent elemental cesium so that a comparison with the analytical chemistry results can be performed. Due to the age of the BR-3 fuel, no other significant isotopes are present for comparison.

Following the sampling of individual filters in HFEF and their transfer to the analytical chemistry laboratory, the filters are weighed, dissolved/leached, and the resultant solutions are analyzed by inductively coupled plasma mass spectrometry (ICP-MS). It should be noted that the transfer and subsequent analyses are all

performed remotely due to the radioactivity of the samples and solutions. The analyses are performed using a VG Elemental PQ3 nuclide ICP-MS. This nuclide instrument is different from most commercial ICP-MS instruments in that it utilizes a glovebox to limit personnel exposure to the high field irradiated samples. A Cetac (Omaha, NB) ASX-100 autosampler is used to introduce samples to the ICP-MS for analysis. All samples are analyzed using the peak hopping mode of the instrument software. Quantitative isotopic data on Cs-133 and Cs-135 are determined from ICP-MS using a NIST traceable standard and a slope integrated count per second calculation, respectively. The Cs-133 and Cs-135 data are then used to calculate Cs-137 content based on known ratios in the BR-3 spent fuel. Quantitative gamma spectrometry has also been performed in the analytical laboratory on solutions but only for verification of the calculated Cs-137 data from ICP-MS.

III. RESULTS AND DISCUSSION

Three DEOX tests have been performed in HFEF with the BR-3 fuel for the collection of volatile fission products by the filter media of the off-gas treatment system. Following these tests, both gamma spectrometry in HFEF and analysis in the chemistry laboratory have been performed.

The gamma-scans for all three tests included the entire off-gas filter assembly under identical scan conditions (Figs. 3-5). Figs. 3-5 depict the counts of Cs-137 detected by gamma scanning versus the axial z-position along the OTS assembly. Note that the scales of the left y-axes are the same for all three figures. Also shown in the figures as circles which correspond to the right y-axis is the maximum temperature obtained during testing of that particular section of the OTS. As can be seen, the filters do not cover the entire length of their zone; spacers are used to complete the length.

Distinctions between the zones as well as between the filters are apparent on the gamma traces for all three tests. Looking at the relative magnitude of the data, very little Cs-137 was collected during Test #1 while a significant amount was trapped by Zone 3 in Test #3.

For Tests #2 and #3, Cs-137 migrated past Zone 2 to the tubing between Zones 1 and 2. The tubing has been sampled so that chemical analyses can be performed and compared to the gamma scan data. Although cesium is intended to be collected primarily in Zone 3, it is apparent that this did not occur for various reasons beyond the context of this paper. The correlation of gamma scanning results to analytical chemistry results is the intent of this study and the migration has provided additional data.

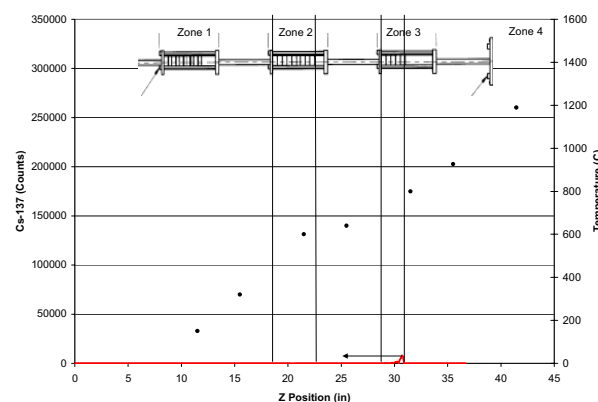


Fig. 3. Cs-137 gamma scan for Test #1 including OTS overlay and zone temperatures.

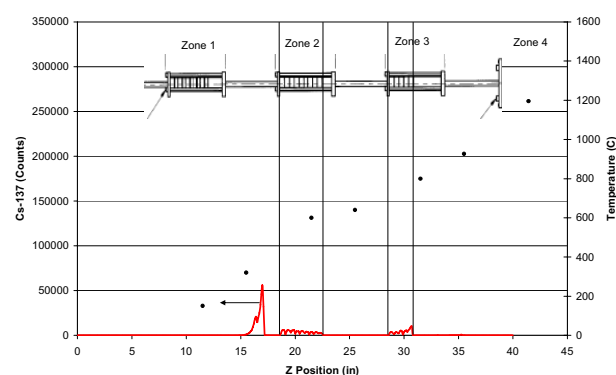


Fig. 4. Cs-137 gamma scan for Test #2 including OTS overlay and zone temperatures

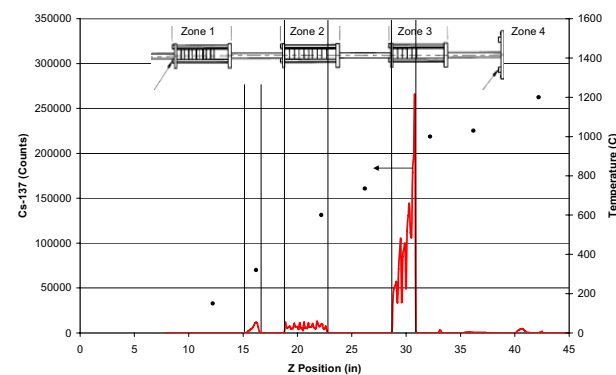


Fig. 5. Cs-137 gamma scan for Test #3 including OTS overlay and zone temperatures

Shown in Table I are Cs-137 data from both gamma scanning in HFEF and analytical chemistry results from

ICP-MS. For the gamma scan data, the counts were summed over the known axial length of the filter cartridges and verified by gaps in the gamma traces. Several filters were omitted from Table I due to either a loss of sample material between gamma scanning and ICP-MS or negligible amounts of Cs-137 detection by gamma scanning and analytical chemistry. The loss of material was identified by the difference in weight measurements taken prior to DEOX testing and dissolution in the analytical laboratory. This loss or removal of material is not surprising given the remote aspects and handling challenges encountered in both HFEF and the analytical laboratory hot cells.

Table I. Gamma scan and analytical chemistry data for filters from Tests #1-3

Test	Filter	Zone	Gamma Cs-137 (counts)	ICP-MS Cs-137 (ug)	Gamma/ICP-MS (counts/ug)
1	F1-1	3	23579	541	44
1	F1-2	3	5733	127	45
2	F2-1	3	34311	506	68
2	F2-2	3	16763	402	42
2	F2-3	3	15877	365	43
2	F2-5	3	12488	278	45
2	C2-1	2	10369	203	51
2	C2-2	2	12095	267	45
2	C2-3	2	11612	249	47
2	C2-4	2	13421	381	35
2	C2-5	2	18908	309	61
2	C2-6	2	16563	360	46
2	C2-7	2	19537	394	50
2	C2-8	2	23246	389	60
2	C2-9	2	21150	483	44
3	F5-1	3	801091	17014	47
3	F5-3	3	320137	8593	37
3	F5-4	3	317266	5623	56
3	F5-5	3	201284	3977	51

The gamma data ranges in counts from a low of 5733 to a high of 801,091. Corresponding ICP-MS data ranges from 127 ug to 17,014 ug. Converted to an exposure rate or dose, the ICP-MS data ranges from 4 to 500 mR/hr at 1 m, respectively, assuming the filters act as a gamma point source. The gamma scan and ICP-MS data have been plotted and are shown in Fig. 6.

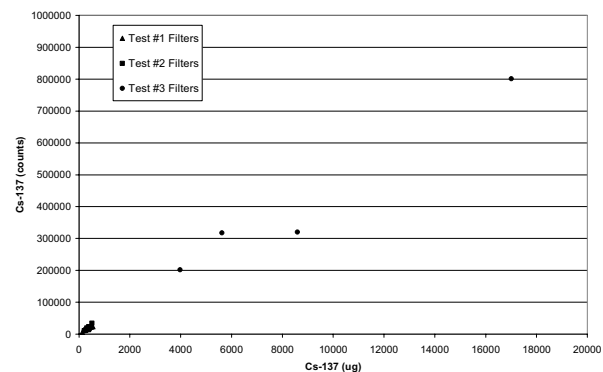


Fig. 6. Comparison of HFEF gamma scan and analytical laboratory ICP-MS data

Data from the filter media in Fig. 6 show quite an extended range with a majority clustered near the base axes of the plot. In general, a linear relationship exists for the data such that a correlation can be established. Given in the last column of Table I are the ratios of gamma to ICP-MS data. An averaged value of 48 counts/ug is determined from these data.

For the tubing between Zones 1 and 2 from Tests #2 and #3, the gamma to ICP-MS ratios were 64 and 77, respectively. Although slightly higher than those for the filters, geometry effects during gamma scanning may be the cause given the diametrical differences and/or the distribution of Cs-137 in the tubing and filters.

IV. CONCLUSIONS

The direct assay of filter media following DEOX testing in the HFEF gamma scanning equipment has several advantages over analytical chemistry. The advantages are addressed in terms of time, effort, sample integrity, and dose:

- In terms of time following a test, the ability to receive gamma scan results in a matter of days compared to the receipt of analytical results in a period of weeks is extremely beneficial for continued testing purposes.
- The personnel effort required to gamma scan an OTS assembly is approximately a factor of five less than that required to analyze filter media in the chemistry laboratory.
- As has already been recognized, loss of filter material is a consequence of the additional handling and sample characteristics and thus,

could be avoided by relying on gamma scanning in HFEF for cesium analyses.

- Less personnel dose is acquired by retaining the filter media in the HFEF hot cell versus handling the samples and solutions for ICP-MS in the analytical laboratory.

In summary, a very good correlation of gamma scan to ICP-MS data has been presented which combined with the advantages of direct assay over analytical chemistry merits the continued use of gamma analyses on DEOX filters in HFEF for cesium content.

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