

APPLICATIONS OF X-RAY FLUORESCENCE AND FISSION PRODUCT CORRELATIONS FOR NUCLEAR FORENSICS

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ABSTRACT

X-ray fluorescence (XRF) and broad range fission product gamma-ray measurements are two promising nondestructive analysis (NDA) techniques for rapid attribution for mixtures of uranium, plutonium, and fission products, including spent fuel, reprocessing waste solutions, and dirty weapon materials. The XRF technique measures self-induced x-ray fluorescence from uranium and plutonium and compares pulse heights of uranium and plutonium peaks to quantify elemental uranium and plutonium. If unknown nuclear material needed to be identified rapidly, XRF could be used as a relatively portable measurement technique to obtain initial information about a sample, which could drastically reduce identification time by narrowing the range of further tests to be performed. Analysis of the presence of various fission products and their ratios can provide valuable information about a number of parameters for SNF or material extracted from it, such as age, burnup, initial enrichment, reactor type, etc. This paper investigates applications of XRF and broad range fission product measurements for nuclear forensics. A variety of data sets were collected during several measurement campaigns at Oak Ridge National Laboratory. Spent fuel rods measured cover a large spectrum of age (one to thirty two years), burn-up (18 to 67 GWd/tU), and plutonium content (0.3% to 5%). This data will be used to develop nuclear forensics algorithms for identification of material origins, fissile contents and historical data associated with it.

1. INTRODUCTION

X-ray fluorescence (XRF) and broad range gamma-ray measurements are two promising nondestructive analysis (NDA) techniques for rapid attribution of mixtures of uranium, plutonium, and fission products. This includes solid spent fuel, reprocessing waste solutions, and dirty weapon materials. XRF measurements are one of the traditional forensics measurements when performed on dissolved solution, but have not been studied extensively for solid spent fuel until recently [1-4]. Performing gamma-ray measurements optimized for low-energy photons provides the possibility of measuring uranium and plutonium x-rays as well as fission products with low-energy gamma-rays which are not visible in typical spent fuel gamma-ray measurements.

The goal of this research is to develop an approach to take low-energy and/or broad-range photon measurements along with dimensional characteristics (such as pin diameter) and use these measurements to rapidly determine the possible reactor(s) the fuel came from by providing information about fuel parameters such as burnup, initial enrichment, cooling time, power history, and reactor type. Providing rapid forensics data and attribution is crucial in facilitating the overall forensics process.

The measurements being considered for this work involve the use of high-resolution gamma-ray spectroscopy using HPGe detector systems based on currently available technology. The instruments would measure the passive radiation emitted from solid spent fuel without any preparation of the sample material. It is conceivable that the instruments used for this approach could be portable and could be rapidly deployed.

Two main pathways for determining the source of a spent fuel sample from measured signatures are being investigated: a database-search method and a deterministic inverse approach. The database search method

involves simulating a wide range of fuel parameters to create a database of expected isotope concentrations. Measurements from an unknown sample would then be compared to this database to select cases which are adequately similar to the sample measurements. These parameters could then be used to look for reactors which fit this description or narrow down which further forensics tests to perform. If spent fuel were found and dimensional characteristics strongly narrowed down the list of possible reactors, this approach could be simplified by selecting only fuels which fit the dimensional characteristics to simulate. Alternatively, a deterministic approach is being investigated such that given a set of sample measurements, fuel parameters could be calculated based on developed correlations. Both of these methods, of course, are limited by the scope of initial parameters considered. They could generate false results if a possibly clandestine reactor were run in an unusual way to try to misguide attribution attempts. To attempt to avoid these attempts at misdirection, either approach should consider as many indicators as possible when determining any fuel parameter.

2. THEORY

X-ray fluorescence occurs when an incident photon interacts with a tightly bound electron and ejects it from the electron cloud. An electron from a higher energy shell falls into the ejected electron's vacancy, emitting an x-ray. A simplified diagram of this process is shown in Figure 1.

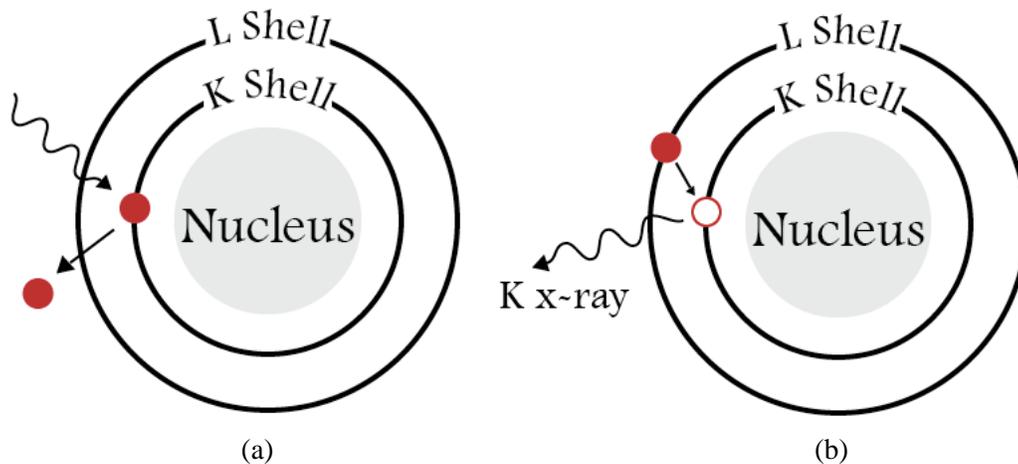


Figure 1. Schematic of x-ray fluorescence showing (a) a photon knocks an electron out of the K-shell and (b) an L-shell electron falls into the K-shell vacancy, emitting an x-ray photon.

The emitted x-rays have an energy equal to the difference in binding energy between the two shells, which is characteristic to each element. Most uranium and plutonium x-rays have energies between 94 and 120 keV. In spent fuel, photons with energies this low have a very small mean free path, around 50 μm , so only the outer layer of fuel is being measured. Since spent fuel is mostly uranium, the uranium x-rays are intense enough to be commonly seen in typical gamma-ray measurements. However, there is not enough plutonium in spent LWR fuel to create a large enough plutonium x-ray peak to be detectable above background in the coaxial detectors commonly used to measure spent fuel.

3. MEASUREMENTS

Several measurements of solid spent nuclear fuel were recently taken at ORNL, which cover a range of burnups, cooling times, and fuel types. The first measurements investigated in this paper were performed on North Anna fuel in July 2008. This fuel pin had an initial enrichment of 4.199 wt% U-235, cooling time of 4.2 years, and burnup values from 35 to 67 GWd/t. In January 2009, another measurement campaign looked at a fuel pin from the Three Mile Island unit 1 reactor. This fuel pin had an initial enrichment of 4.0 wt% U-

235, cooling time of 13.3 years, and a burnup range of 27 to 59 GWd/t. In September 2009, a fuel pin from Catawba with MOX fuel was measured. This fuel had been produced with weapons-derived plutonium. The original fuel was 4.4% plutonium (5.25% heavy metal was plutonium) and depleted uranium with 0.27% U-235. The MOX fuel had a cooling time of 9 months and burnups from 18 to 52 GWd/t. In October 2009, measurements were taken on a fuel pin from Calvert Cliffs. This pin had an initial enrichment of 3.038%, a cooling time of 27.5 years and an estimated burnup of 37 GWd/t. Altogether, these measurements cover cooling times from 9 months to 27.5 years, burnups of 18 to 67 GWd/t, and both uranium dioxide and mixed oxide fuel.

Two sets of measurements were performed for each fuel. Measurements with a coaxial HPGe ORTEC PopTop detector using ORTEC Maestro software were used to acquire a broad-energy spectrum. Also, measurements were taken with a Canberra Low Energy Germanium (LEGe) planar detector specialized to measure energies between 30 and 300keV. With the exception of the January 2009 measurements, the coax detector recorded information between 30 keV and 2040 keV, and the planar detector recorded information between 3 keV and 300 keV. During the January 2009 measurement series, the coax detector spanned from 30 keV to 1830 keV and the planar detector spanned from 3 keV to 190 keV. All count times reported are live time. For more information on the measurement setup, see Ref. 5. For these measurements long planar detector count times were used to provide good resolution of the 103.7 keV Pu X-ray peak while using a very long and thin collimator (resulting in a microscopic beam spot). This detector setup is likely not practical for field use and could possibly be replaced with a segmented HPGe planar detector (using up to 800 miniature HPGe crystal segments in one detector) with a specialized small collimator array.

With these measurements, only dependence on burnup can be determined since for most measurements series, there are multiple burnups with the same initial enrichment, cooling time, and power history, but there are no measurements for something like the same initial enrichment, burnup and multiple cooling times. In the future, simulations will be run on a wider range of initial parameters and power histories to attempt to derive calculations for as many fuel characteristics as possible.

3.1 July 2008 – North Anna

The July 2008 measurement campaign collected a total of 45 coax measurements and 7 planar measurements from North Anna fuel. The measurements were all from a single rod which had been cut into several pieces and placed inside a shipping tube for transport to ORNL. Most planar measurements included coax measurements at the exact same location; however, there were a few locations where the coax measurements were from a nearby point on the rod. The planar measurement count times ranged from 3,600 s to 44,000 s. The coax measurements count times were each for 120 s. The coax measurement times were chosen based on acquiring good counting statistics for the Cs-137 and Cs-134 main peaks. However, longer count times would have resulted in more peaks being visible.

3.2 January 2009 – Three Mile Island

In January 2009 seven sets of coax and planar measurements were taken along a single section of one Three Mile Island fuel rod such that each measurement point had both coax and planar measurements. After a burnup analysis was done, five of these points with a range of burnups were selected for further analysis. The planar measurements had count times between 6,200 s and 56,000 s, and the coax measurements each had a count time of 600 s.

3.3 September 2009 – MOX

In September 2009, MOX fuel from Catawba was measured with coax and planar detectors at 12 points along a single fuel rod. Eight of these measurement sets from a range of burnups were chosen for further analysis after burnup calculations. Planar measurements had count times between 11,000 s and 200,000 s. Errors in the planar detector setup resulted in high energy tails on most peaks. Coax measurements had count

times between 600 s and 3,000 s, and an error in the detector setup resulted in low energy tails on most peaks. The peak tails on both groups of measurements resulted in asymmetrical peaks, which made peak fitting difficult for overlapping peaks.

3.4 October 2009 – Calvert Cliffs

One fuel rod from Calvert Cliffs was measured at ORNL in October 2009. Only two sets of planar and coax measurements were taken, but one of the coax measurements was corrupted, so there were two planar measurements and one coax measurement available for analysis. While trends could not very well be seen, this was useful to see what is visible in typical fuel after 30 years cooling time. The planar measurement count times were about 63,000 s and the coax measurement count time was 15,000 s.

4. ANALYSIS

The collected spectra were analyzed using GENIE 2000 software to determine photopeak energies and net peak areas as well as identifying specific isotope activities. These activities were used in various ratios to observe correlations between measured isotope ratios and fuel parameters of interest.

4.1 Spectrum analysis software

Canberra's spectrum analysis program, GENIE 2000, was used to analyze the spectra collected from the various measurement campaigns. In order to ensure that GENIE calculated peak areas correctly and consistently for each spectra, an interactive peak fit tool was utilized to visually identify how well GENIE's automated analysis fit the measured data. This involved ensuring that the background was fit well and looking for overlapping peaks. A screenshot from this interactive peak fit program is shown in Figure 3. This shows the impact of the interactive peak fit software for a small portion of a complicated spectra. The figure displays the individual data points for each channel, the GENIE peak fit, the calculated background, and the residual (or difference between the measurement and GENIE's fit for that point). Ideally, the residual would be small and randomly scattered, as in Figure 3b. The definite curve visible in the residual of Figure 3a indicates that a second peak is present in the measurement but not accounted for in GENIE's automated fit.

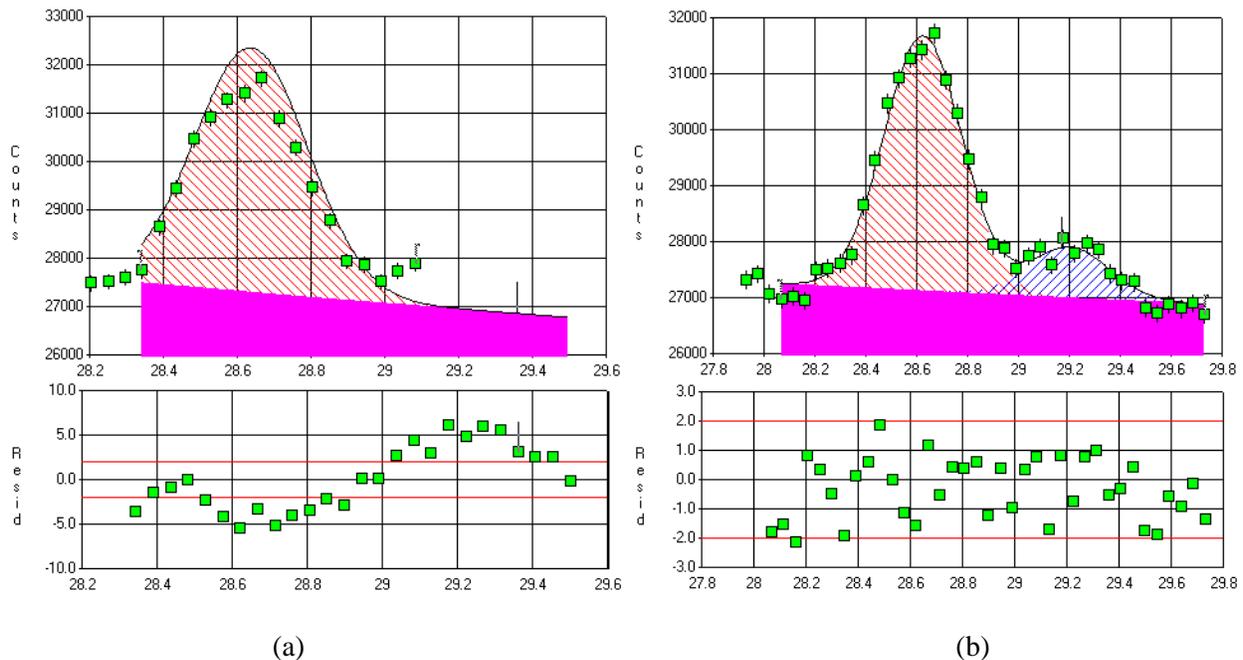


Figure 3. Interactive peak fit showing (a) fit directly from GENIE 2000 automated fit and (b) fit after manual correction with additional peaks.

4.2 Visible Nuclides

The first stage of measurement analysis was to identify which nuclides were visible for each group of measurements. Isotopes with a half life greater than ten days along with decay products of these isotopes were added to a library of fission products for use with GENIE 2000. This library was used to identify the nuclides visible in each spectra. Table I lists the presence of each isotope identified in the measured fuels. Figures 4-6 show some examples of the measured spectra. Figure 4 shows a close up of the x-ray region for one of the low burnup MOX measurements (with a 10 hours count time). Figure 5 shows the extent to which Cs-134 is still visible in the Calvert Cliffs fuel after 30 years cooling time. The strongest Cs-134 604 keV peak is almost washed out by Compton from the Cs-137 661 keV peak, but the Cs-134 795 keV peak is still clearly visible, with a net peak area uncertainty of 2.9% after a 4.2 hour (live time) count. Figure 6 displays the visibility of short-lived isotopes Ag-110M and Ru-106 in relation to the strongest Cs-137 and Cs-134 peaks in the MOX fuel. This measurement was the highest burnup along the rod, at 52.5 GWd/t, but the peaks are clearly visible at lower burnups as well.

TABLE I
Measurable nuclide presence in the four fuels measured.

Nuclide	NA	TMI	CC	MOX
Cs-137	All Coax	All Coax	All Coax	All
Cs-134	All Coax	All Coax	All Coax	All
Eu-154	All	All	All Coax	All
Ce-144*	High BU Coax	None	None	All
Sb-125	High BU coax	All Coax	None	All
Ag-110M	High BU Coax	None	None	All Coax
Rh-106	All Coax	None	None	All Coax
Co-60	All Coax	All Coax	All Coax	All Coax
Bi-214	All Coax	All Coax	All Coax	All Coax
U x-ray	All	All	All Coax	All
Pu x-ray	All Planar	All Planar	All Planar	All
Eu-155	All Planar	All Planar	All Planar	All
Am-241	None	All Planar	All	Low BU Planar

*While Ce-144 is one of the commonly used isotopes for measuring cooling time, this usually takes advantage of the low background around Ce-144's 2185 keV peak. None of these measurements extended to this high of an energy.

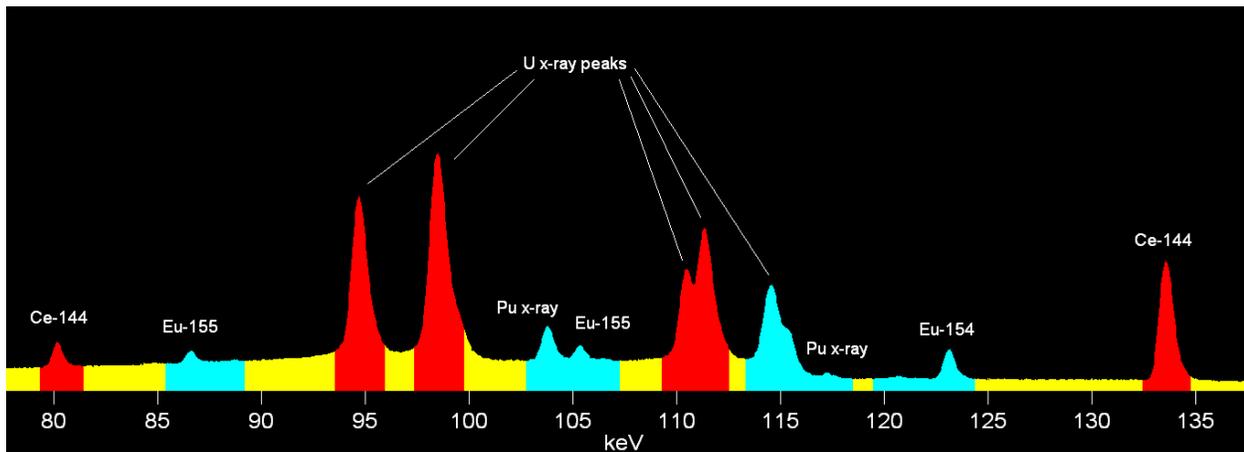


Figure 4. x-ray region of MOX fuel at position 1965.

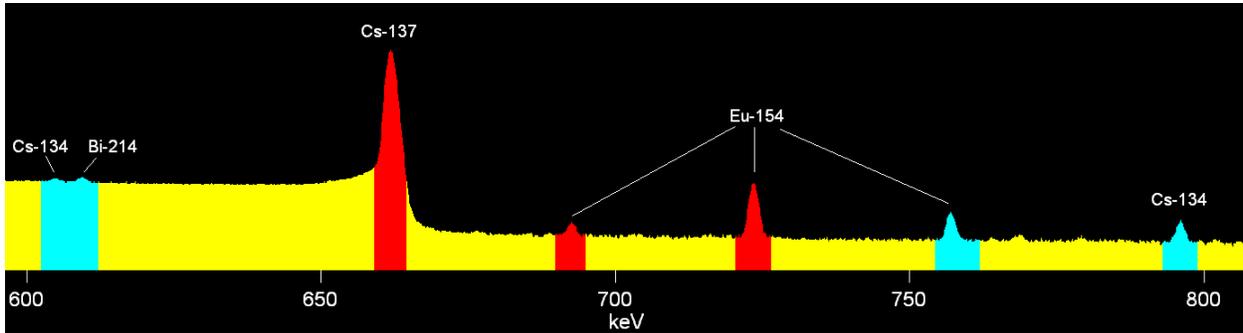


Figure 5. 600 keV to 800 keV region from Calvert Cliffs coax measurement.

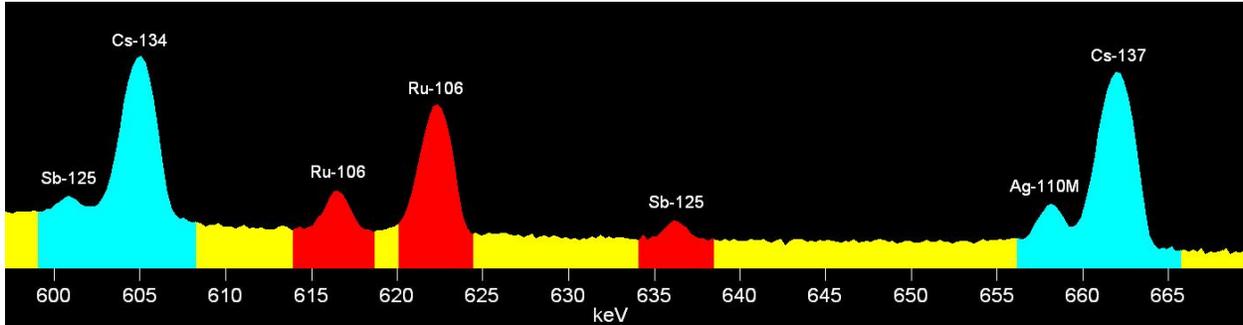


Figure 6. 600 keV to 670 keV region from MOX fuel at position 1865.

4.3 Nuclide Production

The nuclides visible in the spectra consist of (1) fission products generated during reactor operation, (2) activation products produced from absorption reactions in the cladding or other fuel support structures, and (3) actinides and their decay products. The buildup of fission products depends on burn up and possibly initial enrichment, depending on the relative fission yields from uranium and plutonium. Table II shows the thermal neutron fission yields of each nuclide from Table I and other nuclides relevant to their production (yield data from Ref. 6).

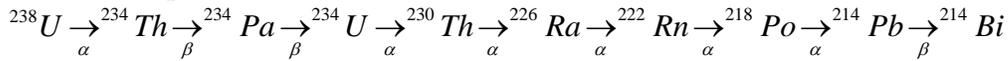
TABLE II
Cumulative fission yields.

Nuclide	²³⁵ U fission yield	²³⁹ Pu fission yield	²³⁹ Pu/ ²³⁵ U yield ratio	Half-life
Cs-137	6.19E-2	6.61E-2	1.07	30.04 y
Cs-134*	3.85E-8	3.35E-6	86.9	2.06 y
Cs-133	6.7E-2	7.02E-2	1.05	Stable
Eu-154*	9.7E-10	1.4E-7	144	8.59 y
Eu-153	1.58E-3	3.61E-3	2.28	Stable
Eu-155	3.21E-4	1.66E-3	5.15	4.76 y
Co-60	0	0	n/a	5.27 y
Bi-214	0	0	n/a	19.9 m
Sb-125	3.40E-4	1.12E-3	3.28	2.76 y
Ru-106	4.02E-3	4.35E-2	10.83	373 d
Ce-144	5.5E-2	3.74E-2	.68	284 d
Ag-110M*	2.28E-14	0	n/a	249 d
Ag-109	3.12E-4	1.48E-2	47.34	Stable
Am-241	0	0	n/a	432.2 y

*This nuclide is shielded by a stable isotope, thus individual fission yields are shown rather than cumulative.

Buildup information for many of these isotopes is well covered in literature. For more information on Cs-137, Cs-134, and Eu-154 production see Ref 7. For more information on Ag-110M, Rh-106, Ce-144, and Sb-125, see Ref 8. Brief descriptions of the production of these other isotopes is given below:

1. Co-60 is not a fission product, but is formed as an activation product in the cladding and structural materials surrounding the fuel when iron and nickel are irradiated.
2. Bi-214 is a decay product of U-238 which is created as follows:



Many Bi-214 peaks are visible in the Calvert Cliffs fuel, since after 30 years from reactor discharge, the background radiation has gone down significantly. In the other fuels, Bi-214 is measurable because one of its strongest gamma lines is at 1764 keV, where there is less background than at lower energies. When there is strong activity from Rh-106, the Bi-214 1764 keV peak can be covered up by the Rh-106 1766 keV peak. However, in the measurements here, they were easily separated with Genie's interactive peak fitting program. While Bi-214 should not provide any information about cooling time, burnup, initial enrichment, or power history, it has the possibility of indicating the time since the uranium was chemically processed.

3. Eu-155 is a fission product which is not practically measurable through typical coax measurements, but is clearly visible in all of the planar measurements taken. It is produced and removed from nuclear fuel in a similarly complicated process. It has a reasonably large cumulative fission yield and is created through neutron capture in Eu-154, but also has a large capture cross section of 19,311 barns. It is of particular interest to measure in relation to neutron measurements due to its large neutron absorption cross section and the fact that its stable daughter product, Gd-155, is also a common neutron absorber in spent nuclear fuel.
4. Am-241 is formed in nuclear fuel from Pu-241 decay, and thus grows with cooling time and burnup. Am-241 has a large absorption cross-section, and thus the Am-241 measured in spent fuel is almost entirely from plutonium decay once fuel has been removed from the reactor, making it a promising cooling time indicator. The capability of measuring Am-241 provided by low-energy gamma-ray measurements is of particular interest to neutron measurements attempting to quantify Pu mass because of its large neutron absorption cross section.
5. The uranium and plutonium x-ray peaks scale heavily with background radiation, since they are created when fission product gamma rays knock electrons from uranium and plutonium atoms. The relative intensities of the uranium and plutonium peaks trend with the relative quantities of uranium and plutonium on the outer edge of the fuel. While gamma peaks have a natural Gaussian shape, x-ray peaks have a natural Laurentian shape. Genie does not fit these peaks well, so manual measurement regions were placed around the uranium 98 keV x-ray peak – which was well isolated – to compute the net peak area. The plutonium 103 keV x-ray peak is too close to the Eu-155 105 keV peak to fit in this method, so it was assumed that Genie fit this peak in the same manner for each spectra.

4.4 Isotope ratios

Measurements of activity of a single nuclide depend heavily on measurement geometry and detector characteristics. Measurements of this type require calibration and repeatable configurations. In a rapid attribution forensics tool, measurements in the field would benefit from not requiring access to calibration standards or prescribed configurations. To obtain spent fuel measurements that are independent of geometry and detector specifications, isotope ratios are a preferred method of quantitatively analyzing gamma spectra.

Cs-134/Cs-137 ratios were used to calculate burnup for each set of measurements. ORIGEN simulations were run for each fuel over the known power history and cooling times, but with varying power levels to simulate the axial power distribution the fuel rod experiences in the reactor. Atom densities for Cs-134 and Cs-137 were pulled from these simulations, and compared to measured Cs-134/Cs-137 ratios. To account for differences in the energies of peaks used, detector efficiency curves were obtained with an Eu-152 source and escape ratios were calculated through MCNP simulations. Differences in peak intensities were also taken into account. For more information on this process, see Ref. 5.

Using the planar detector provided the unique opportunity to measure several uranium x-rays as well as the main plutonium x-ray in spent fuel and to use this as a monitor of burnup without the need for *a priori* knowledge of the fuel history and dimensions. The fact that the half-lives of most uranium and plutonium isotopes are much longer than the age of any spent fuel means that this ratio is relatively independent of cooling time. Since the energies of the uranium and plutonium x-ray peaks differ by only ~5 keV, the detector efficiency and escape ratios are not needed in order to draw meaningful conclusions. This adds to the convenience of using this ratio as a burnup monitor in the field when little information is known about the fuel being measured. TMI and MOX measurements indicate that Pu x-ray/U x-ray ratios scale very well with burnup. Figure 7 shows the Pu/U x-ray ratio for the TMI measurements.

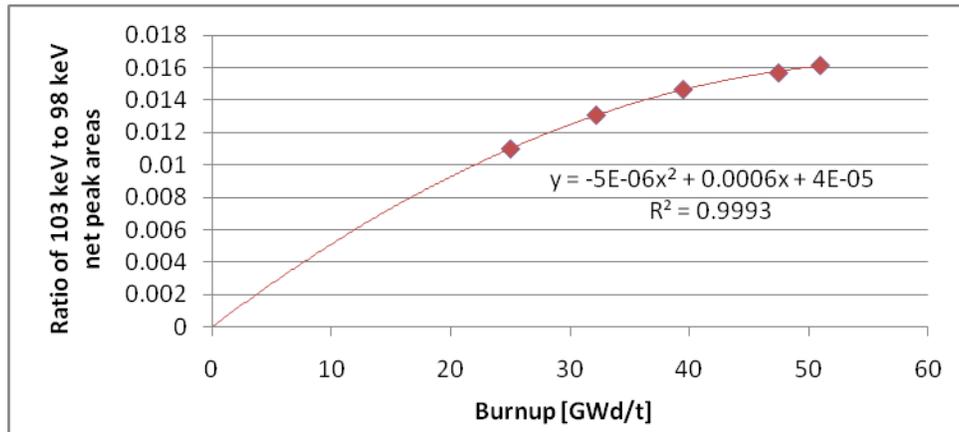


Figure 7. Ratio of Pu 103 keV x-ray to U 98 keV x-ray vs. burnup for TMI fuel.

As expected from normal LWR fuel, this indicates that the plutonium content grows with burnup, but levels off as the plutonium fissions. It is also promising that the y-intercept is almost zero, which is also expected since there is no plutonium in the fuel at zero burnup. Figure 8 shows the Pu/U x-ray ratio for the MOX fuel as a function of burnup. This shows the expected downward trend in plutonium content as the plutonium in the original fuel is burned off even though plutonium is also building up from U-238 neutron absorptions. The y-intercept suggests that the initial plutonium content was 5.35% of the total heavy metal content of the fuel, which has an error of only 2% from the actual value of 5.25%.

The ratio of Eu-155 to a uranium x-ray (shown in Figure 9) is another promising burnup indicator measurable with planar detectors. The ratio of any fission product to a uranium x-ray peak should have a value of zero when extrapolated to the fresh fuel case.

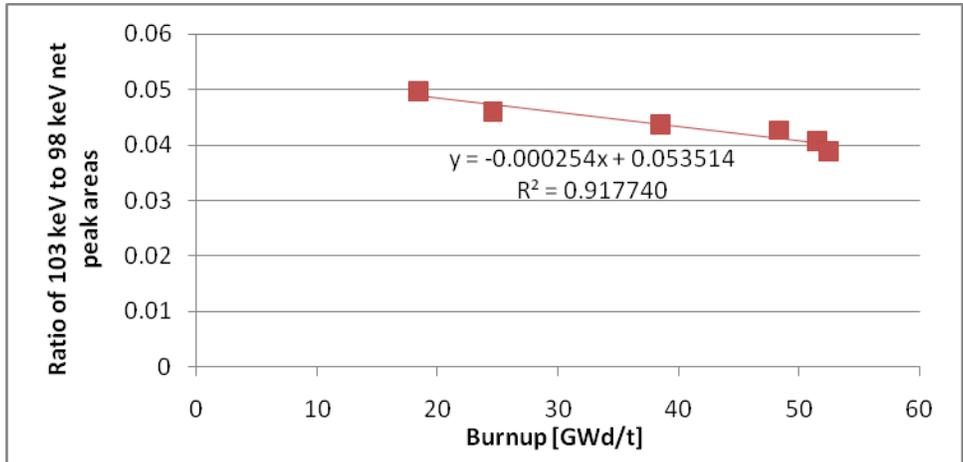


Figure 8. Ratio of Pu 103 keV x-ray to U 98 keV x-ray vs. burnup for MOX fuel.

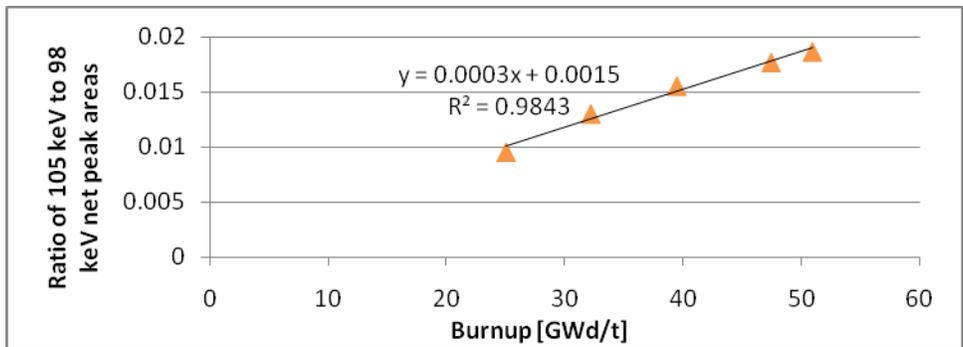


Figure 9. Ratio of Eu-155 105 keV peak to 98 keV U x-ray peak vs. burnup for TMI fuel.

5. FUTURE WORK

Destructive analysis is planned on some of the fuel measured, and results from this analysis should provide insight on how accurate the ORIGEN simulations used to correlate Cs-134 to Cs-137 ratios to burnup were. This will help validate ORIGEN for similar simulations. Since these measurements only really allowed for burnup correlations to be developed, a broader set of fuel parameters will be simulated to investigate isotope ratio dependence on other fuel parameters.

6. CONCLUSION

A set of four fuel pins with a wide range of fuel parameters have been measured with both broad-range and low-energy detectors. The goal of these measurements was to determine which x-ray and gamma-ray peaks are visible in a wide range of fuels in order to determine correlations between these measurements and fuel parameters, which would be useful for forensics purposes as well as spent fuel assay. The collected spectra have been analyzed with Genie 2000 to locate peaks and calculate net peak areas. Visible nuclides and elements have been identified, and peak ratio correlations with burnup have been investigated. Low-energy measurements of a wide range of spent fuel has allowed for an expanded database of photon peaks visible in spent fuel. Measurements of strong neutron absorbers Am-241 and Eu-155 are also of importance for Pu mass quantification in spent fuel for other neutron based techniques.

7. ACKNOWLEDGEMENTS

This material is based upon work supported by the Department of Energy, National Nuclear Security Administration under Grant DE-FG52-06NA27606, entitled “The Nuclear Security Science and Policy Institute: Enhancing the Nuclear Nonproliferation Regime.” Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author and do not necessarily reflect the views of the US Department of Energy, National Nuclear Security Administration. The authors would also like to acknowledge support from the Next Generation Safeguards Initiative of the U.S. Department of Energy. We would also like to thank Alissa Stafford (TAMU), Andrew Hoover (LANL), Daniel Strohmeyer (TAMU), Jessica Feener (TAMU), Grant Ford (TAMU), Steve Saavedra (ORNL), and Angela Lousteau (ORNL) for their help performing the measurements at ORNL.

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