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# The Multi-Isotope Process Monitor Project: FY11 Progress and Accomplishments

CR Orton  
CG Fraga  
JW Hayes  
JM Schwantes  
SE Bender<sup>1</sup>

K Unlu<sup>1</sup>  
KJ Dayman<sup>2</sup>  
SS Schreiber<sup>2</sup>  
S Landsberger<sup>2</sup>

August 2011



**Pacific Northwest**  
NATIONAL LABORATORY

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<sup>1</sup> Pennsylvania State University

<sup>2</sup> University of Texas at Austin

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## Summary

The Multi-Isotope Process (MIP) Monitor represents a potentially new and efficient approach to monitoring process conditions in reprocessing facilities with the high-level goal of aiding in the “...(minimization of) the risks of nuclear proliferation and terrorism” (Office of Technology Assessment 1995). This approach relies on multivariate analysis and gamma spectroscopy of spent fuel product and waste streams to automatically and simultaneously monitor a variety of process conditions (e.g., acid concentrations, burnup, cooling time, etc.) in near real-time (NRT). While the conceptual basis for the MIP Monitor has been shown to be effective in an aqueous reprocessing system, the fundamental approach should also be viable in a pyro-processing recycle system. The MIP Monitor may be calibrated to provide online quantitative information about process variables for process control or domestic safeguards applications; or it can simply monitor, with a built-in information barrier, for off-normal conditions in process streams, making the approach well-suited for applications where it is necessary to respect proprietary information or for international safeguards applications. Proof-of-concept simulations and experiments were performed in previous years demonstrating the validity of this tool in a laboratory setting. This report details follow-on research and development efforts sponsored by the U.S. Department of Energy Fuel Cycle Research and Development (FCR&D) related to the MIP Monitor for fiscal year 2011 (FY11). Specific aspects of research completed in FY11 include

- a simplified bench scale flow loop was constructed, tested, and used to gather spectra from spent fuel solutions prepared in previous years (Milestone Activity);
- spent fuel solutions were maintained to provide continued access to spent fuel solutions for testing of the MIP Monitor;
- gamma spectra were collected and analyzed by a variety of multivariate techniques on samples of the dissolver, raffinate and extract solutions from the processed fuel using high purity germanium (HPGe), cadmium zinc telluride (CZT), lanthanum bromide (LaBr<sub>3</sub>), and sodium iodide (NaI) detectors;
- additional data analysis techniques and approaches were explored;
- subcontracts were setup to support graduate students and their research efforts at Pennsylvania State University and University of Texas at Austin (milestone activity);
- two graduate students finished and published Master’s theses with topics directly relating to MIP Monitor development;
- contact was made on several fronts to engage international partners with the intent to collaborate in order to gain access to large amounts of reprocessing data for further MIP Monitor development;
- several publications and presentations (lists to follow), including several that concerned the MIP Monitor but were funded either internal to the lab or whose funding was shared between DOE programs.

## Publications

Orton, CR, CG Fraga, RN Christensen, and JM Schwantes. 2011. "Proof of Concept Simulations of the Multi-Isotope Process Monitor: An Online, Nondestructive, Near-Real-Time Safeguards Monitor for Nuclear Fuel Reprocessing Facilities." *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 629(1):209-19.

Orton CR, CG Fraga, RN Christensen, and JM Schwantes. Submitted. "Proof of Concept Experiments for the Multi-Isotope Process Monitor: An Online, Nondestructive, Near-Real-Time Monitor for Spent Nuclear Fuel Reprocessing Facilities." *Nuclear Instruments and Methods in Physics Research Section A* (Submitted August 2011, awaiting review).

Orton, CR, SA Bryan, JM Schwantes, TG Levitskaia, CG Fraga, and SM Peper. 2010. Advanced Process Monitoring Techniques for Safeguarding Reprocessing Facilities. In *Proceedings of the Symposium on International Safeguards: Preparing for Future Verification Challenges*, IAEA, Vienna, Austria.

Orton, CR, CE Rutherford, CG Fraga, and JM Schwantes. 2011. The Multi-Isotope Process Monitor: Multivariate Analysis of Gamma Spectra. In *Proceedings of the Institute of Nuclear Materials Management 52<sup>nd</sup> Annual Meeting*, INMM, Deerfield, IL.

Bender, SE, K Unlu, and CR Orton. 2011. Application of Compton Suppression Spectroscopy to Non-destructive Analysis of Spent Fuel for Nuclear Safeguards Purposes" In *Proceedings of the Institute of Nuclear Materials Management 52<sup>nd</sup> Annual Meeting*, INMM, Deerfield, IL.

## Presentations

Orton, CR (Presenter), CG Fraga, RN Christensen, and JM Schwantes. 2010. *The Multi-Isotope Process Monitor: FY10 Progress*. Presented at the Fuel Cycle Technologies Annual Meeting, October 27, 2010, Gaithersburg, MD.

Orton, CR (Poster Presenter), SA Bryan, JM Schwantes, TG Levitskaia, CG Fraga, and SM Peper. 2010. *Advanced Process Monitoring Techniques for Safeguarding Reprocessing Facilities*. Presented at Symposium on International Safeguards: Preparing for Future Verification Challenges, November 1-5, 2010, Vienna, Austria.

Orton, CR (Presenter), CG Fraga, SE Bender, K Unlu, KJ Dayman, S Landsberger, R Christensen, and JM Schwantes. (2011) *The Multi-Isotope Process Monitor: FY11 Progress*. Presented at FCR&D Working Group Meeting, May 4, 2011, Albuquerque, NM.

Bryan, SA (Presenter), TG Levitskaia, CR Orton, and MJ O'Hara. 2011. *Advanced on-line process monitoring*. Presented at US-China Action Plan Separations Working Group meeting, June 6, 2011, Beijing, China.

Orton, CR (Presenter), CE Rutherford, CG Fraga, and JM Schwantes. 2011. *The Multi-Isotope Process Monitor: Multivariate Analysis of Gamma Spectra*. Institute of Nuclear Materials Management 52<sup>nd</sup> Annual Meeting, July 17-21, 2011, Palm Desert, California.

Bender, SE\* (Poster Presenter), K Unlu, and CR Orton. 2011. *Application of Compton Suppression Spectroscopy to Non-destructive Analysis of Spent Fuel for Nuclear Safeguards Purposes*. Institute of Nuclear Materials Management 52<sup>nd</sup> Annual Meeting, July 17-21, 2011, Palm Desert, California.

Landsberger, S, KJ Dayman\* (Presenter), CR Orton, and JM Schwantes. 2011. *An Automated Measurement of Burnup Using Partial Least Squares*. Presented at 2011 American Nuclear Society Annual Meeting, June 28, 2011, Hollywood, FL.

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\*Presented by graduate student

## Acronyms and Abbreviations

BWR	Boiling-water reactors
CE	Combustion Engineering (corporation)
DOE	U.S. Department of Energy
FCR&D	Fuel Cycle Research and Development
FY	Fiscal year
HPGe	High purity germanium
MC&A	Material control and accounting
MIP	Multi-Isotope Process
MPACT	Material Protection, Accounting and Control Technologies
NA-24	Office of Nonproliferation and International Security (an office of the National Nuclear Security Administration—NNSA)
NE	DOE's Office of Nuclear Energy
NGSI	Next Generation Safeguards Initiative
NRT	Near real-time
PCA	principal component analysis
PLS	Partial Least Squares
PNNL	Pacific Northwest National Laboratory
PWR	Pressurized Water Reactor
W	Westinghouse (corporation)

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## 1.0 Introduction

In April 2010, the U.S. Department of Energy (DOE) issued a report to congress entitled, *Nuclear Energy Research and Development Roadmap* (U.S. Department of Energy 2010). One of the four objectives listed for the DOE's nuclear energy research and development activities is Objective 4: "Understand and minimize the risks of nuclear proliferation and terrorism." The primary focus of this project is to aid in the achievement of this objective.

Conventional nuclear material control and accounting (MC&A) at bulk handling facilities rely, in large part, on destructive analyses to quantify nuclear material and verify the location of all special nuclear material. Though their accuracy is superb, destructive analyses are extremely resource-intensive, have limited sampling rates, and are associated with a significant time lag from sampling to final reporting. In addition, the error associated with these analyses scales with the size of the facility (Office of Technology Assessment 1995, Appendix A). As such, highly precise destructive measurements of special nuclear material alone at large facilities may not be adequate to ensure diversions have not occurred. While it is not likely that more precise destructive measurement techniques will be developed in the near future, intelligent integration of a variety of on-line process monitoring tools capable of near real-time, non-destructive measurements may be successful in adequately safeguarding even the largest envisioned facility. A combination of these techniques utilizing both material accountancy and augmented material control via continuous process flow sheet verification could provide a more robust framework for MC&A.

Pacific Northwest National Laboratory (PNNL) is currently developing and demonstrating a technology capable of monitoring conditions at a nuclear reprocessing plant on-line, non-destructively and in near real-time called the MIP Monitor (Smith et al. 2007; Schwantes et al. 2008; Orton et al. 2008; Schwantes et al. 2009; Orton et al. 2009b; Orton et al. 2009a). The MIP Monitor is designed to track changes in the distribution of gamma-emitting elements as evidence that process conditions are changing (Benedict et al. 1981). Online process surveillance by the MIP Monitor is accomplished by coupling the gamma spectra recorded from process streams with multivariate analysis. Multivariate analysis can evaluate the spectral pattern of the gamma emitting nuclides in near-real-time for statistically relevant signs of significant changes to the process. By watching the process for unexpected changes, the MIP Monitor can warn of possible process migration to an unintended or undeclared operation. Because the pattern comparison is automatic and autonomous, proprietary operational or fuel information can be protected while assuring process integrity. However, if desired, process conditions can also be quantified using alternate multivariate calibration techniques, making the monitor a potentially valuable part of a comprehensive process control system. In addition, since the monitor is trained on the gamma rays inherent to nuclear fuel, the MIP monitor technique is not limited to aqueous reprocessing but can be applied to other recycling systems. A more detailed overview of the MIP Monitor can be found in the following references (Smith et al. 2007; Schwantes et al. 2008; Orton et al. 2008; Schwantes et al. 2009; Orton et al. 2009b; Orton et al. 2009a).

### 1.1 Background

This research commenced in 2006 with initial scoping studies into the feasibility of the MIP Monitor concept through limited computer simulations. In fiscal year 2008 (FY08), the project was funded and proof-of-concept simulation studies were performed. The results successfully demonstrated the merit of

the MIP Monitor approach. In late FY08 and into FY09, with help from the Office of Nonproliferation and International Security (NA-24), proof-of-concept experiments were initiated to confirm model results from the previous years. Since that time, experiments and simulations have been conducted to further characterize and enhance the performance of the MIP Monitoring approach. Experiments to date have focused on providing replicate data (which are required for multivariate analysis), as well as near-real-time data from well characterized spent fuels. While great strides have been made in understanding how the MIP Monitor reacts to process changes and fuel characteristics, much remains to be done to further characterize the potential of the approach in actual deployments within continuous flow systems.

The overall goals of this project are to continue an assessment of the strengths and limitations of the MIP Monitoring approach for monitoring streams within a nuclear reprocessing facility and to seek opportunities to apply this technology at the pilot and industrial scale. As limitations and strengths are discovered, they will be addressed or capitalized upon in order to develop the MIP Monitor into an effective tool for safeguarding nuclear material and operator process control. The MIP Monitor will then aid in the accomplishment of Objective 4 of the *Nuclear Energy Research and Development Roadmap* to, "... minimize the risks of nuclear proliferation and terrorism" (U.S. Department of Energy 2010).

## 1.2 Potential Impact

Though the MIP Monitor is still in its infancy, the approach shows potential for providing cost saving improvements to domestic and international MC&A as well as process monitoring. The MIP Monitor has the potential to increase process monitoring efficiency and effectiveness by providing continuous verification of process integrity, which should allow the number and frequency of costly destructive analysis measurements to be reduced at bulk handling facilities. In addition to MC&A improvements, a mature MIP Monitor may also provide operators with a cost-effective process monitoring control tool. Current monitoring methods require highly radioactive grab samples to be collected from the process stream in order to confirm process conditions. The MIP Monitor could potentially monitor these process variables non-destructively and in near-real-time. Such an approach could significantly reduce operator costs as well as the doses received by analysts.

The MIP Monitor approach may also be an effective approach to spent fuel burnup measurements, which are traditionally performed using conventional gamma spectroscopy. By focusing on multivariate patterns rather than the ratios of a few isotopes, changes in spectral patterns might be used to improve on the accuracy of conventional burnup analysis. Increasing the accuracy of measured burnup levels of spent fuel will increase the fidelity of the initial plutonium concentration value in spent fuel, providing a more accurate starting point for MC&A.

## 1.3 Tasks for FY11

Tasks supporting the accomplishment of the overall goal of the MIP Monitor during FY11 include

- i. continuing experimental efforts to more fully test and evaluate the MIP Monitoring approach, taking advantage of the stock of a variety of well characterized spent nuclear fuel samples currently available at the hot-cell facility at PNNL using multiple detector types (such as high-purity germanium (HPGe), cadmium zinc telluride (CZT), lanthanum bromide (LaBr<sub>3</sub>), and sodium iodide (NaI));

- ii. enhance multivariate techniques for recognizing and quantifying gamma ray spectral patterns and transitioning these efforts to near real-time applications. This task will include continuing a detailed sensitivity analysis to identify specific gamma lines and signature nuclides influencing spectral changes as a function of process conditions;
- iii. working with researchers at Pennsylvania State University and University of Texas at Austin to investigate the feasibility of coincidence and anti-coincidence (Compton suppression) measurements as part of the MIP Monitoring approach to both enhance the signal to noise ratio and investigate the yet-untapped gamma-gamma coincidence signals residing in spent fuel;
- iv. training the next generation of nuclear scientists within the U.S., including coordinating the graduate student efforts at the collaborating universities;
- v. coordinating Material Protection, Accounting and Control Technologies (MPACT) MIP Monitor scope with related activities in other programs (e.g., Office of Nuclear Energy (NE) separations campaign, NA-24 process monitoring campaign, and PNNL internal investments for developing new process monitoring technologies). Also, coordinating the work with any potential international partners that might be able to provide operational data and/or facilities for additional MIP Monitor testing and research;
- vi. designing and building a simplified bench-scale flow loop for use evaluating the MIP Monitor performance in a real-time environment.

## 1.4 Milestones and Status

The milestones associated with FY11 are as follows:

- i. Coordinate University of Texas Graduate Student Efforts and Subcontracts
- ii. Coordinate Penn State University Graduate Student Efforts and Subcontracts
- iii. Send Technical Update Memo to National Technical Director
- iv. Construct and Test Bench-Top Flow Loop System
- v. Interim Report

With the submission of this report (milestone 5), all of the milestones for FY11 have been completed.

## 2.0 Progress on Tasks

The following subsections contain a summary of work performed on each of the project tasks. Some research highlights are also included.

### 2.1 Task 1

Experimental efforts were limited during FY11. Due to the extensive experimental activity during previous years, a large inventory of spent-fuel solutions is available at PNNL. Maintenance was performed on the samples to alleviate the effects of radiolysis on the sample containers. The maintenance consisted of moving the liquid samples to new containers if the previous container showed signs of radiation damage and discarding the old container. This activity preserves the inventory for future use. In addition to maintenance, dilute samples were prepared for use in the bench-scale flow-loop system. These samples consisted of three fuel types, dissolved, but not separated.

Gamma spectra were collected from the samples in the inventory using primarily a LaBr<sub>3</sub> and CZT detector. The result is a more comprehensive spectral library of our current inventory for these particular types of detectors. While some spectra were collected using a NaI detector, additional collection will be necessary to record the spectrum for each of the samples. This spectrum collection effort is a continuation of work that has been ongoing in parallel with the spent fuel samples dissolutions and separations. This effort was aided by the addition of a new detector base that was received in late FY10, which allowed simultaneous spectrum collection by two detectors. Specific information on the detectors and counting setup can be found in the MIP Monitor Project's FY10 report (Orton et al. 2010).

### 2.2 Task 2

Task 2 was a major emphasis of FY11 work. Multivariate analysis was performed on the spectral sets collected during FY11 using the LaBr<sub>3</sub> and CZT detectors. The results were compared to previous analyses done on the spectra collected on the HPGe detector. Samples included four different boiling-water reactor (BWR) fuel types, three of which had the same cooling time of ~30 years, with burnups of approximately 16, 24, 30 MWd/kgU respectively. The fourth fuel type had a cooling time of ~20 years and a burnup of ~70 MWd/kgU. The samples of dissolved fuel, before separation, yielded noteworthy results. When principal component analysis (PCA) (Malinowski 2008) was performed on the CZT spectrum of the 16, 24, and 30 MWd/kgU samples, there was obvious and expected organization by burnup. When PCA was performed on the LaBr<sub>3</sub> spectra, however, the 16-MWd/kgU samples were distinctly separate from the other samples, including the 70-MWd/kgU samples. When the spectra were examined, the LaBr<sub>3</sub> spectra contained visible peak shifts at 661.7 keV, which gamma-ray is from <sup>137</sup>Cs, and is the major contributor expected in the dissolver spectrum. The shift was not expected and is most likely an artifact of the detector itself and perhaps the high count rate induced by the dissolver solutions. A similar shift was not observed in the gamma-ray spectra collected from the organic extract solutions, which have much lower gamma-ray intensity, and lack the dominating 661.7 keV gamma line. Preliminary attempts to align the spectra were unsuccessful and therefore quantitative analysis of the burnup was not performed. Quantitative multivariate analysis of the burnup of the fuel samples was performed on the CZT spectra using Partial Least Squares (PLS) (Beebe et al. 1998) and compared to previous analysis on the HPGe spectra. Twenty-two spectra were used to calibrate the PLS model, while four spectra were left out of the calibration and used as test spectra. The result is shown in Table 1.

**Table 1.** PLS predictions of burnup using gamma-ray spectra of spent nuclear fuel dissolver solutions

Detector	LV	RMSEP	16 (MWd/kgU)	24 (MWd/kgU)	24 (MWd/kgU)	30 (MWd/kgU)
HPGe	4	0.270	16.35	24.21	23.88	29.66
CZT	4	0.708	16.50	24.42	24.44	28.82

While the results are comparable, it is clear that the HPGe spectra perform slightly better than the CZT spectra. In either case, the prediction was within 2 MWd/kgU or 4% of the measured value, demonstrating that the predictions can be very accurate. While these results are promising, additional measurements will be necessary to further provide additional confidence in the method.

The spectra from the organic extract of the 24 MWd/kgU were analyzed using PCA and PLS for both the LaBr<sub>3</sub> and CZT detectors and compared to previous results obtained for the HPGe detector. For this study three samples of the dissolver solution were separated at five different acid concentrations. Two of the three spectra taken from the organic extract at each acid concentration were used to calibrate a PLS model and the third was used to test it. A comparison of the results is illustrated in Table 2.

**Table 2.** PLS predictions of the acid concentration of dissolved spent fuel before separation using gamma-ray spectra of the organic extract solutions

Detector	LV	RMSEP	0.3 (M)	1.3 (M)	2.5 (M)	3.8 (M)	5.1 (M)
HPGe	2	0.224	0.62	1.20	2.65	3.53	4.89
LaBr <sub>3</sub>	4	0.245	0.73	1.14	2.48	3.06	4.94
CZT	2	0.487	0.06	1.62	2.13	4.20	4.25

In this case, it can be seen that the root mean squared error of prediction for the LaBr<sub>3</sub> is comparable to that of the HPGe, and both are much better than that of the CZT; however, given the absolute difference between the predictions and the measured values, it is not entirely clear which detector yields the most favorable result. Each acid concentration seems to have its own winner. Additional data will be necessary to decide the ideal detector for the MIP Monitor and to get a better concept of what kind of deviations can be expected in a real process monitoring scenario.

In both the burnup and acid-concentration predictions, the fundamental source of spectral variations between differing samples are non-linear. The methods used up to this point have been linear methods, which may or may not be ideal for the characteristics of interest. In order to explore non-linear multivariate options, two PNNL staff members attended a training specifically on non-linear multivariate methods. Additionally, a graduate student from University of Texas has been conducting further research into nonlinear multivariate analysis techniques such as multiclass Support Vector Machine and “the kernel trick” used in making linear techniques work to capture nonlinear information. These new skills will be applied to the multivariate problem and the results of this effort are anticipated to be reported during FY12.

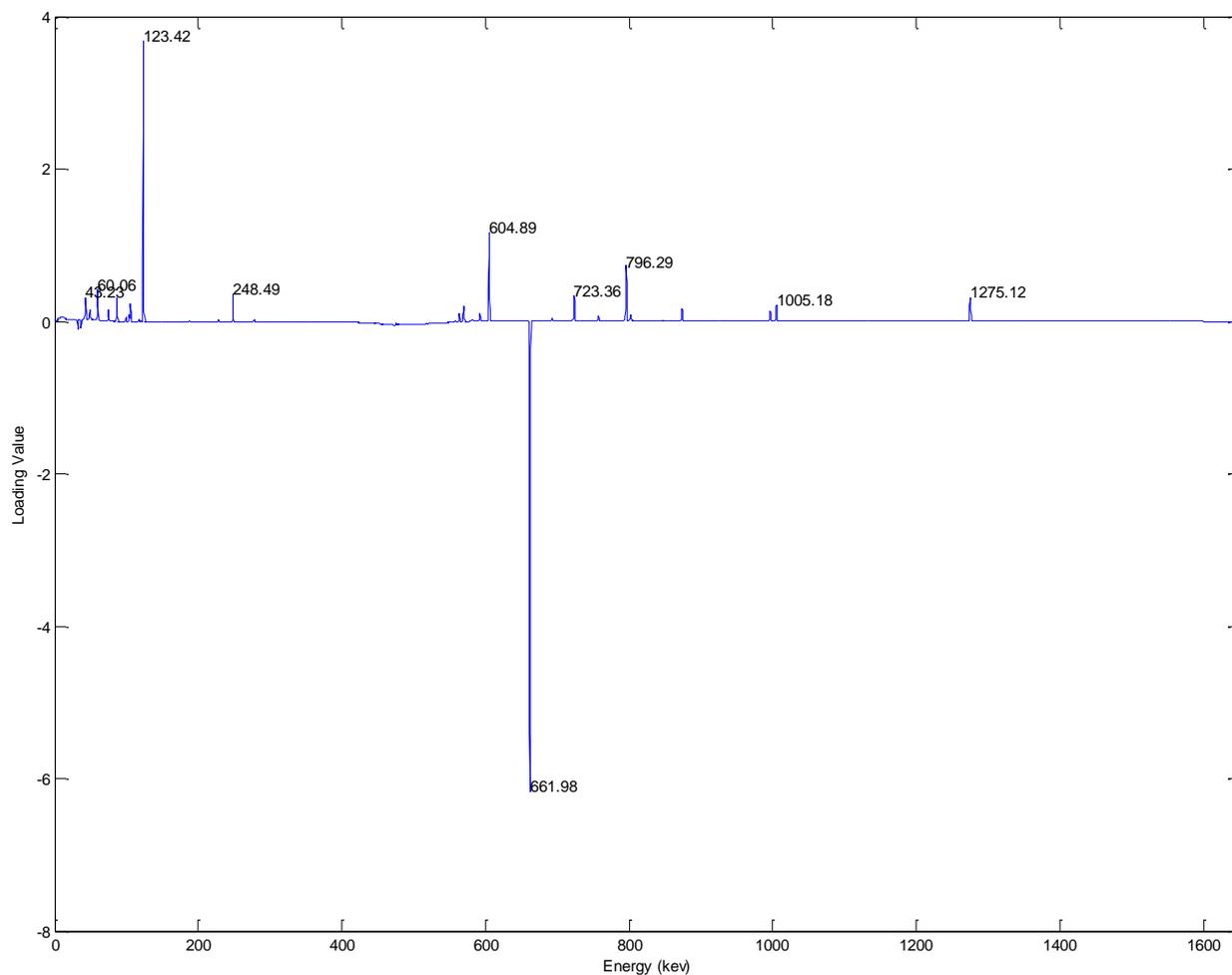
Additional multivariate analysis studies were conducted via spent nuclear fuel modeling and simulated spectra by the University of Texas. The simulation exercise was intended to investigate the ability of PLS to predict the burnup of a variety of spent fuel samples in several situations. Due to the limited availability of spent fuel samples, the majority of the analyses were performed using simulated fuel samples and synthetic spectra produced by ORIGEN-ARP and Synth. Three fuel types were considered: Combustion Engineering (CE) 14 x 14 (PWR), Westinghouse (W) 17 x 17 (PWR), and General Electric 9 x 9 (BWR). Samples of the CE 14 x 14 fuel were generated at burnup values ranging from 10 to 70 MWd/kgU in increments of 5 MWd/kgU. To provide additional samples, nuclide inventories were also generated for this fuel type at burnup values of 32.5, 37.5, 42.5, and 47.5 MWd/kgU. These nuclide inventories were used as source terms for Synth, and synthetic gamma spectra were generated. These spectra were used as training set to calibrate all subsequent models. For a testing set to test the quality of the models’ predictions, synthetic spectra of all three fuel types at burnup values of 33, 37, 42, 62, and 75 MWd/kgU were generated.

There were several goals of this study:

- (i) To identify gamma-ray signatures sensitive to changes in burnup
- (ii) To test if PLS may be used to estimate the burnup of a known fuel sample given a wider set of fuel parameters
- (iii) To explore the effect of focusing on different areas of interest within the spectra identified in (i) and using these as inputs for the model
- (iv) To explore the effect of the training set, specifically the number and distribution of the burnup values, on the quality of the predictions
- (v) To explore the effect of nuclides of interests’ nonlinear buildup with increasing burnup
- (vi) To see if a model calibrated for one type of fuel assembly could make accurate burnup estimations using spectra arising from a different type of fuel (both reactor type and specific assembly type)

To identify gamma-ray signatures sensitive to burnup, PLS models were constructed using the CE 14 x 14 training set, and the resulting loadings of the latent variables were consulted. The latent variables generated in PLS (and PCA) are linear combinations of the original measured variables (the channels in the gamma spectra in this work), and the coefficients of these linear combinations give information as to how each measured variable contributes to a particular latent variable. For example, if the first latent variable has large coefficients in the channels corresponding to the 661.7 keV peak of <sup>137</sup>Cs, then this

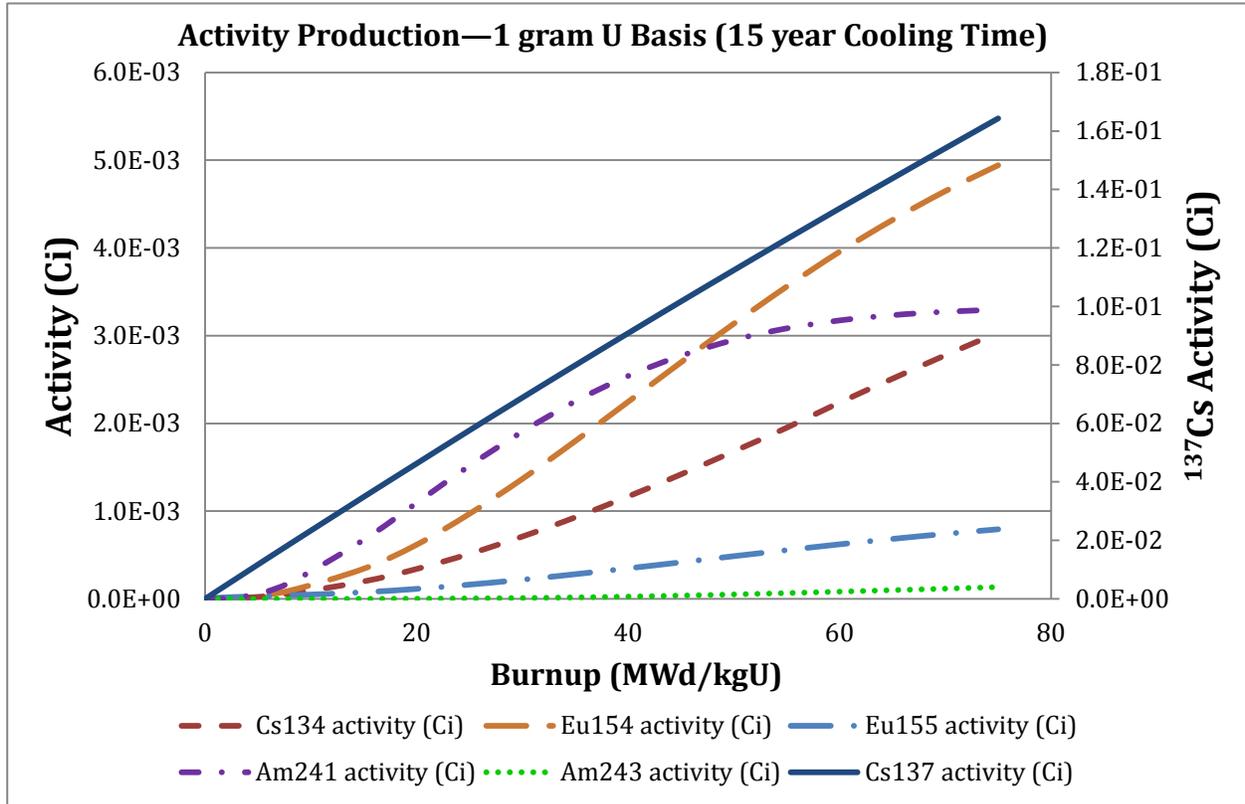
gamma-ray signature is important to this latent variable. In this case, all the latent variables corresponded to burnup (as the enrichment, reactor and fuel assembly time, cooling time, etc. were all standardized throughout the training set), so any signature identified as being important in the model signifies a signature sensitive to burnup. Practically, these loadings are examined in the form of plots of the loadings for one or more latent variables versus the measured variables. Figure 1 is one such plot, with selected areas of interest labeled with the corresponding gamma-ray energy. These gamma rays arise from  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{154}\text{Eu}$ ,  $^{155}\text{Eu}$ ,  $^{241}\text{Am}$ , and  $^{243}\text{Am}$ .



**Figure 1.** An example of a loadings plot, identifying particular regions of the spectrum as being important in an estimation of burnup, signified by the peaks, which are large coefficients of the linear combinations forming a particular latent variable used in the PLS model

In order to investigate (iii), (iv), and (v), several versions of the training set were prepared. Based on the areas of interest identified in (i), it was decided to parse the training set (and validation set) spectra to only include areas of interest and compare the predictions made by models based on these parsed spectra to models based on the full spectra. In deciding how to parse the spectra, a simple investigation of how

the suggested nuclides potentially important to burnup in (i) build up with increasing burnup was carried out. The result of this study is shown in Figure 2.

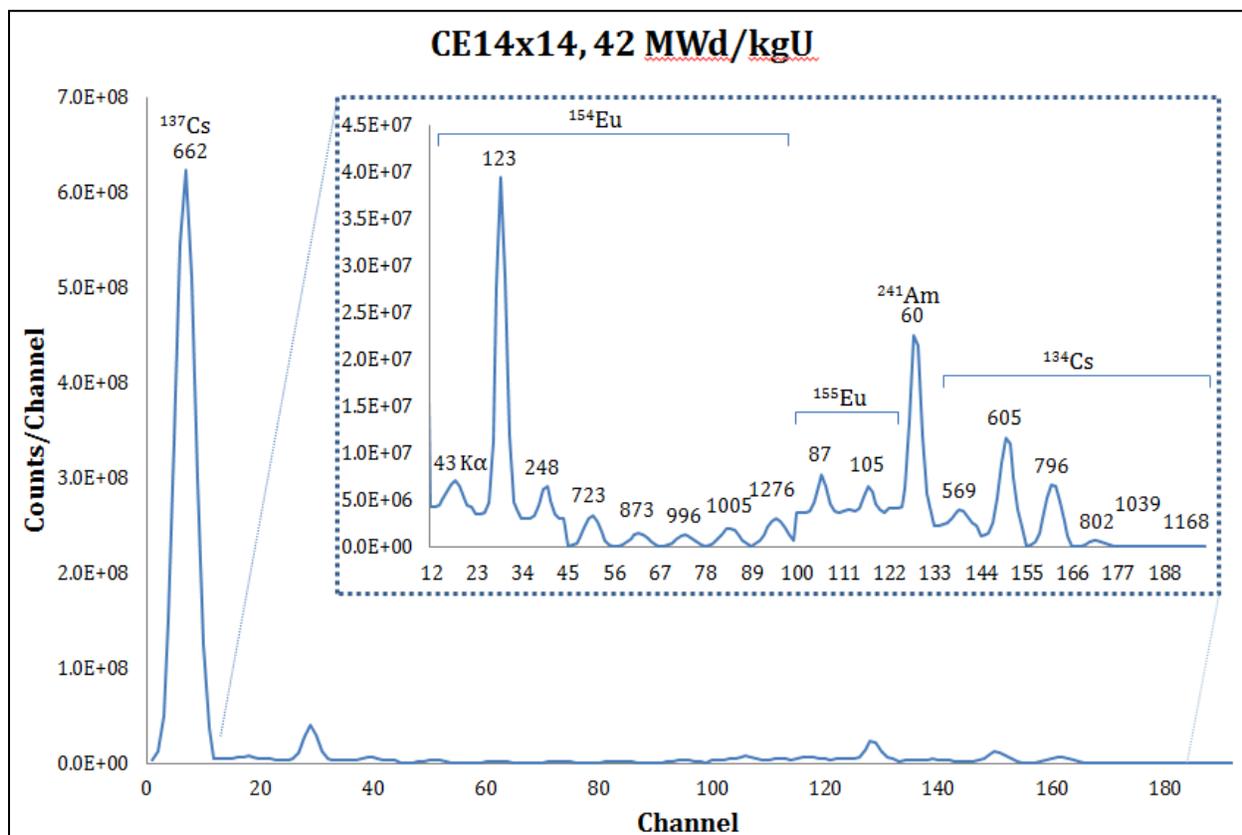


**Figure 2.** The activity of the nuclides suggested in (1) as a function of the burnup of a fuel. Generated with ORIGEN-ARP

Clearly, all the nuclides, save <sup>137</sup>Cs, build up nonlinearly to differing degrees. For instance, overall, <sup>134</sup>Cs grows in nonlinearly, but its dependence on burnup is roughly linear above 35 MWd/kgU. Since PLS is inherently linear and assumes the predictor variable (burnup in this work) has a linear dependence on the latent variables (which are linear combinations of the measured variables input into the model), different groupings of the nuclides (which we refer to as parsing schemes) were formed and the spectra were parsed to only include gamma rays arising from the selected nuclides. These schemes are shown in Table 3. An example of a parsed spectrum is given in Figure 3.

**Table 3.** The parsing schemes used to explore the effect of different degrees of linearity in burnup's dependence on the latent variables on the accuracy of the predictions made by the model

Parsing Scheme	Nuclides Used
A	$^{137}\text{Cs}$
B	$^{137}\text{Cs}$ , $^{154}\text{Eu}$ , $^{155}\text{Eu}$
C	$^{137}\text{Cs}$ , $^{154}\text{Eu}$ , $^{155}\text{Eu}$ , $^{241}\text{Am}$
D	$^{137}\text{Cs}$ , $^{154}\text{Eu}$ , $^{155}\text{Eu}$ , $^{241}\text{Am}$ , $^{134}\text{Cs}$ , $^{243}\text{Am}$

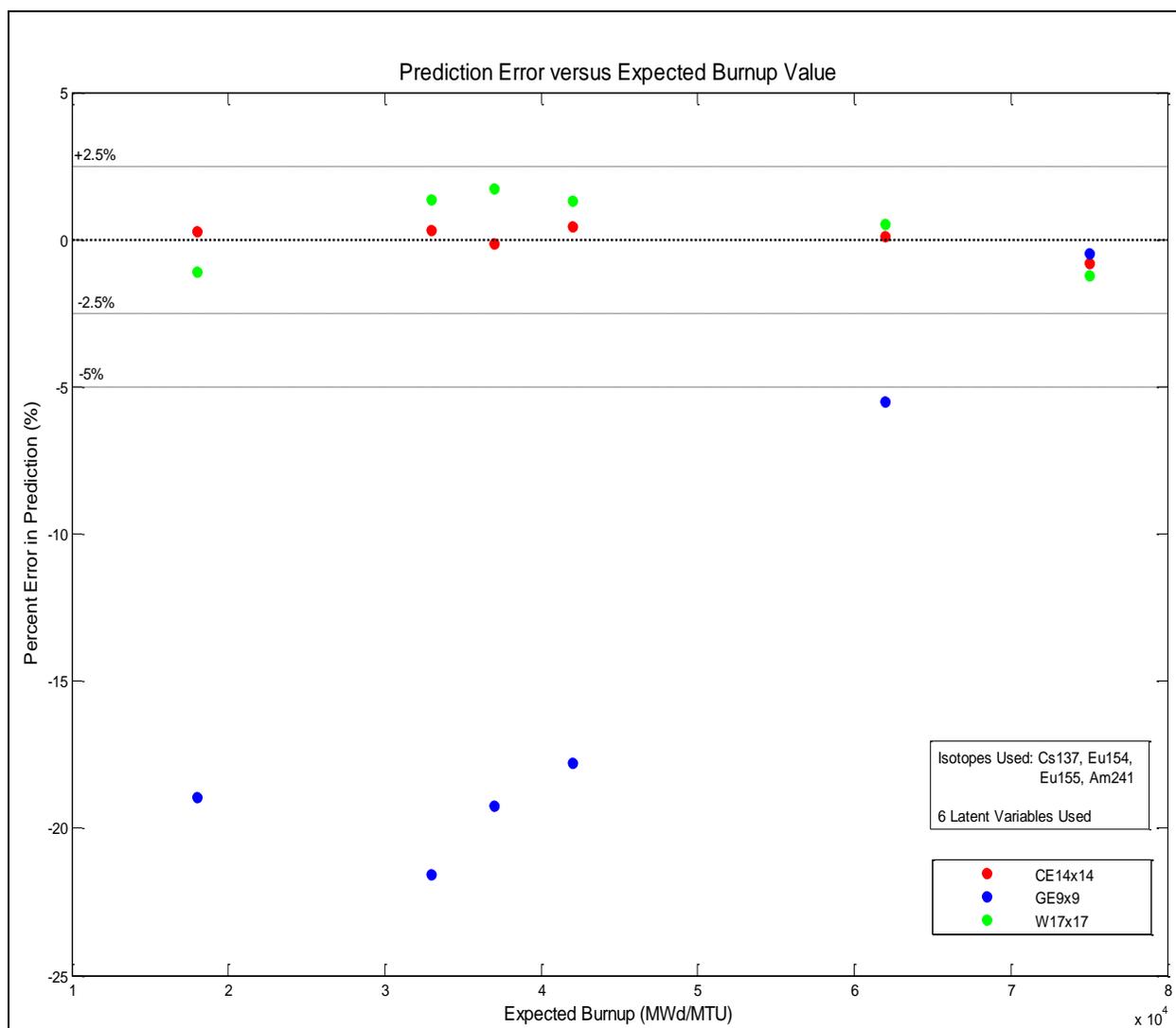


**Figure 3.** An example of a spectra that has been parsed to only include signals from  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{154}\text{Eu}$ ,  $^{155}\text{Eu}$ , and  $^{241}\text{Am}$

Lastly, these five training sets of spectra (four parsing schemes plus the set comprised of full, unparsed spectra) were duplicated with the additional samples with burnup values of 32.5, 37.5, 42.5, and

47.5 MWd/kgU included. PLS models were generated and tested using the testing set samples (which were parsed to match the training set used), and the accuracy of the burnup estimations examined.

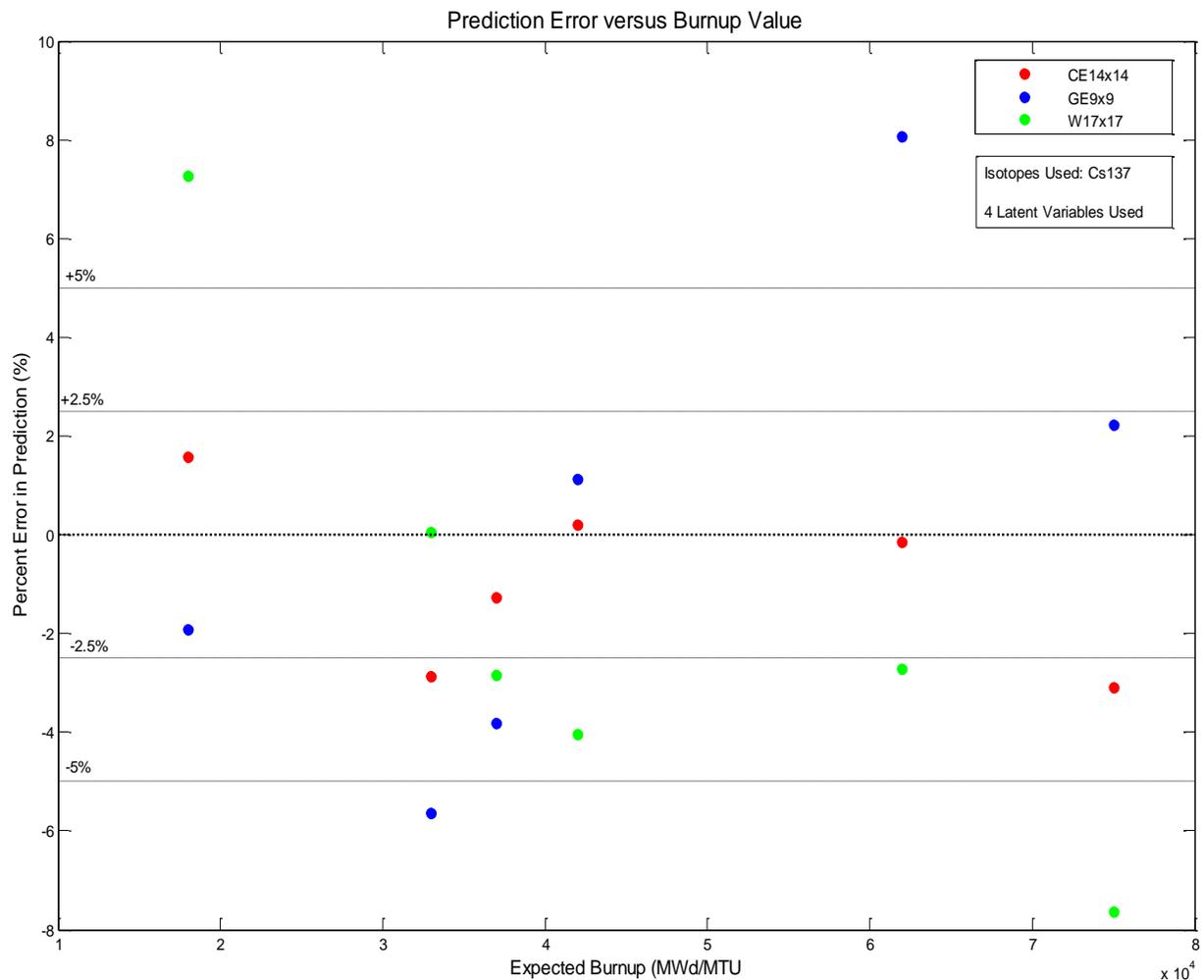
The best results are displayed in Table 4 and illustrated in Figure 4, which show the relative error in the burnup predictions made for the testing set samples. These results used gamma rays arising from the nuclides in parsing set C and the additional training set samples. As can be seen, the burnup of the CE 14 x 14 samples, on which the model was trained, was predicted very well. Additionally, the CE 14 x 14 model performed well on the samples of W 17 x 17 (also a PWR) fuel. Overall, the PWR testing set samples were predicted to within 0.7% average relative error. However, using this model, the burnup of the BWR samples was not predicted well. This is most likely due to differences in the production pathways, specifically the effective cross sections of the reactions in the pathways, of the various gamma-emitting nuclides. These differences suggest that multivariate analysis and pattern recognition on the gamma spectra could be used to identify the type of reactor/fuel assembly. As Figure 5 shows, using a different model, reasonable predictions may be made on samples for which the model has not been calibrated (although it is presently unclear the sensitivity of the predictions on how similar the training and testing set samples must be). Using only the signals from  $^{137}\text{Cs}$ , the burnup of the PWR samples and the BWR samples were predicted to be approximately within 2.8% and 3.8% of their measured values, respectively.



**Figure 4.** Prediction error versus the burnup of the samples in the testing set for the best-performing model

**Table 4.** Best results of burnup predictions made with PLS

Assembly Type	Burnup [MWd/kgU]	Prediction [MWd/kgU]	Relative Error [%]	Average  Error  [%]
<b>CE14x14 (PWR)</b>	18	18.049	0.271	0.349
	33	33.107	0.324	
	37	36.952	-0.129	
	42	42.190	0.453	
	62	62.079	0.127	
	75	74.409	-0.789	
<b>W17x17 (PWR)</b>	18	17.806	-1.080	1.197
	33	33.451	1.366	
	37	37.637	1.722	
	42	42.548	1.305	
	62	62.315	0.507	
	75	74.098	-1.202	
<b>GE9x9 (BWR)</b>	18	14.587	-18.963	13.926
	33	25.876	-21.587	
	37	29.880	-19.245	
	42	34.530	-17.786	
	62	58.576	-5.522	
	75	74.660	-0.453	



**Figure 5.** Prediction error versus the burnup of the samples in the testing set using alternative PLS model that allows for reasonable burnup estimation of all three fuel assemblies

The findings of the simulation exercise (listed in the same order as its goals) are as follows:

- (i) Gamma-emitting nuclides sensitive to burnup were identified using the loadings plots. These nuclides include  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{154}\text{Eu}$ ,  $^{155}\text{Eu}$ ,  $^{241}\text{Am}$ , and  $^{243}\text{Am}$ .
- (ii) Given a model calibrated with synthetic spectra of simulated CE 14 x 14 fuel, PLS was able to predict the burnup of CE 14 x 14 and W 17 x 17 samples to within 0.7% average relative error.
- (iii) Parsing the spectra to only include certain areas of interest and using these parsed spectra for the PLS modeling was able to produce the best results in terms of relative errors in prediction.
- (iv) Inclusion of additional training set samples increased the quality of the predictions made by PLS.
- (v) Using a model that only utilized signals arising from  $^{137}\text{Cs}$  (whose concentration has a linear dependence on burnup) allowed for a model calibrated on a PWR fuel type to make reasonable predictions on both the PWR and BWR samples considered in this work. A model that included

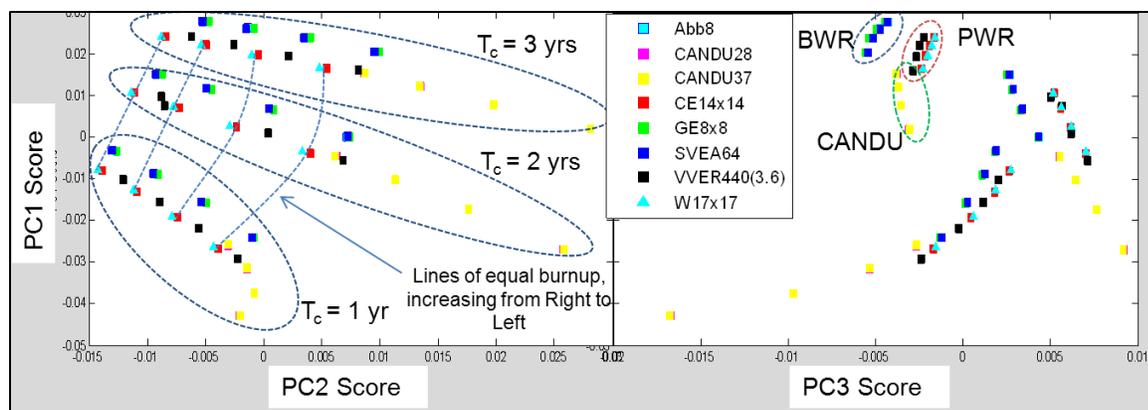
some nuclides of interest that have a more nonlinear behavior with regards to concentration and burnup allowed for more accurate predictions, but this model was unable to make adequate predictions on the BWR fuel for which model had not be calibrated.

The simulation exercise work confirms that if the cooling time, type of reactor/assembly, enrichment, etc. are known (and a corresponding model constructed), then a PLS model can determine the burnup of the sample with some degree of accuracy. An additional study was performed by the University of Texas to explore characterization of the fuel type at various burnups and cooling times through PCA of the gamma spectra. A list of the different reactor types and considered parameters is given in Table 5.

**Table 5.** Summary of the sample space used in the PCA analysis of spent fuel gamma spectra

Fuel Type	Reactor Type	Specific Power (MW/MTU)	Burnup (MWd/kgU)	Enrichment (%)	Cooling Times (months)
CE 14 x 14	PWR	32	20, 25, 30, 35	2.5	12, 24, 36
W 17 x 17	PWR	32	20, 25, 30, 35	2.5	12, 24, 36
GE 8 x 8	BWR	23	20, 25, 30, 35	2.5	12, 24, 36
Abb 8 x 8	BWR	23	20, 25, 30, 35	2.5	12, 24, 36
VVER440 (3.6)	PWR	32	20, 25, 30, 35	3.6	12, 24, 36
SVEA-64	BWR	23	20, 25, 30, 35	2.5	12, 24, 36
CANDU28	PHWR	22	5, 7.5, 10, 12.5	0.71	12, 24, 36
CANDU37	PHWR	22	5, 7.5, 10, 12.5	0.71	12, 24, 36

Significant results of the PCA can be seen in Figure 6.



**Figure 6.** Scores plot of PCA of simulated gamma spectra of the fuel listed in Table 5

In Figure 6, PC 1 demonstrates a major sensitivity to cooling time, identifying it as the largest cause of variation between the samples. However, also captured in PC 1 is some additional information with regard to fuel type and burnup. PC 2 is dominated by variations due to burnup. PC 3 contains information regarding all three characteristics, as do PC 1 and PC 2 to a minor degree. Overall, however, the plot illustrates that multivariate analysis picks up on the subtle pattern differences unique to each of these three characteristics. The analysis and results, including those not listed in this report, provide information to preliminarily suggest the most effective direction of the research and development of the analysis methods for spent nuclear fuel spectra, including the use of additional techniques. Mr. Dayman, a graduate student from the University of Texas, will be focusing on the analysis approach and techniques as the subject of his thesis and dissertation. PNNL will also continue to develop the approach and this task will be a major emphasis in the lab's FY12 scope.

### 2.3 Task 3

During FY11 virtually all of the research conducted on Compton suppression and gamma-gamma coincidence has been conducted at Pennsylvania State University and University of Texas. At University of Texas, spent fuel samples prepared at PNNL were sent to be analyzed using the gamma-gamma coincidence system the end of FY10. Though initial results showed some ability to Compton suppress the samples, very few gamma-gamma coincidences of interest were identified. After further investigation it was discovered that due to the long cooling time of the fuels, most of the nuclides with gamma-gamma coincident emissions were no longer present. A study was then conducted to identify what potential coincident gamma-rays would be available in fuel that had been cooled for less time. PWR fuel was modeled with 4%  $^{235}\text{U}$  enrichment, burnup time of 45 MWd/kgU, average power of 32 MW/MTU and a cooling time of 3 years and the output was used as a basis too to identify radioactive nuclides of interest that also have coincident gamma-rays. The results of this study were then published as part of a University of Texas Master's degree report. Graduate student Samuel Schreiber finished his master's degree with the publication of the report entitled *Identification of the Radionuclides in Spent Nuclear Fuel that May be Detected by Compton Suppression and Gamma-gamma Coincidence Methods*.

At Pennsylvania State University, the Compton suppression system was modeled and the model validation commenced. Initial modeling efforts were conducted in MCNP, but due to some limitations of

the code, a second model was created in GEANT. A source term for spent fuel was also created in order to model the detector response to the complex spectra. The ultimate goal of the model, once validated, will be to modify and use it to represent a theoretical setup and detector for the MIP Monitor in a facility and simulate the Compton suppressed spectra. The simulated spectra would then be fed into multivariate analysis to explore potential applications where using the Compton suppressed spectra is ideal. The model would also be useful to explore and test theoretical implementations of normal detectors in a reprocessing facility. The initial modeling work has resulted in the submission of Pennsylvania State University graduate student Sarah Bender's master's thesis entitled *Application of Monte Carlo Modeling of Compton Suppression Spectroscopy to Spent Fuel Material Accountancy*, which details the modeling of the Penn State Compton suppression system and how such techniques might benefit the MIP Monitor.

## 2.4 Task 4

During FY11 many activities were conducted to aid in the training of the next generation of nuclear scientists. At the University of Texas at Austin these activities include

- a visit by a PNNL staff member to the University of Texas to give a seminar to the Nuclear Energy program and to tour facilities and discuss potential collaborations (sponsored by multiple funding agents);
- sponsoring a portion of Mr. Dayman's graduate studies during the 2010-2011 school year and the participation of his advisor's contribution to the MIP Monitor project;
- in conjunction with Mr. Dayman and Dr. Sheldon Landberger, preparing an NE University Program proposal for supporting work for the MIP Monitor;
- directing the research efforts of Mr. Dayman;
- directing the research efforts of Mr. Schreiber;
- serving as a reader for Mr. Schreiber's master's report;
- hosting Mr. Dayman at PNNL during the summer.

At Pennsylvania State University, activities include

- sponsoring the research of Ms. Bender's graduate studies and the interaction and technical contributions of her advisor to the MIP Monitor project, which necessitated minimal funding support because she is a DHS fellowship recipient;
- assisting the in the direction of Ms. Bender's research;
- a visit by a PNNL staff member to the Pennsylvania State University to discuss the progress of Ms. Bender and tour the universities facilities to foster future collaborations (trip funded under a separate funding agency);
- hosting Ms. Bender at PNNL during the summer in fulfillment of her practicum;

- serving as a reader for Ms. Bender's master's thesis.

Mr. Dayman attended and presented the MIP monitor at the ANS meeting in June. He and Ms. Bender were able to attend INMM while at PNNL. Mr. Dayman's trip to INMM and participation was funded by the Next Generation Safeguards Initiative (NGSI) Human Capital Development project at PNNL. Ms. Bender presented a poster on her master's thesis at INMM and was sponsored by her fellowship.

Ms. Bender will continue her work developing the GEANT models of the PSU Compton suppression system as her PhD work, and her graduate studies will continue to be supported under her fellowship. Minimal MIP Monitor funding will be used to support her research activities.

Additionally, Mr. Dayman received a Department of Homeland Security fellowship award starting in the fall of 2011. He will continue to research the MIP monitor as part of his graduate work, but his required financial support by the MIP Monitor project will be minimal.

Ms. Bender and Mr. Dayman are also jointly working on a journal manuscript comparing the multivariate methods explored as part of the MIP Monitor project to the traditional gamma-ray methods for burnup analysis.

## **2.5 Task 5**

The activities of the MIP Monitor project were coordinated with efforts of the international safeguards process monitoring group. This included the preparation of a conference paper and presentation for the 2011 INMM Annual meeting, which was based a small experiment studying the uncertainty associated with the MIP Monitor but was funded under NGSI. Additional details can be found in the conference paper.

Under an internally funded effort, the MIP Monitor was presented at the Symposium for International Safeguards at the IAEA in November of 2010. Contacts for potential future collaboration with international partners were obtained while at the symposium.

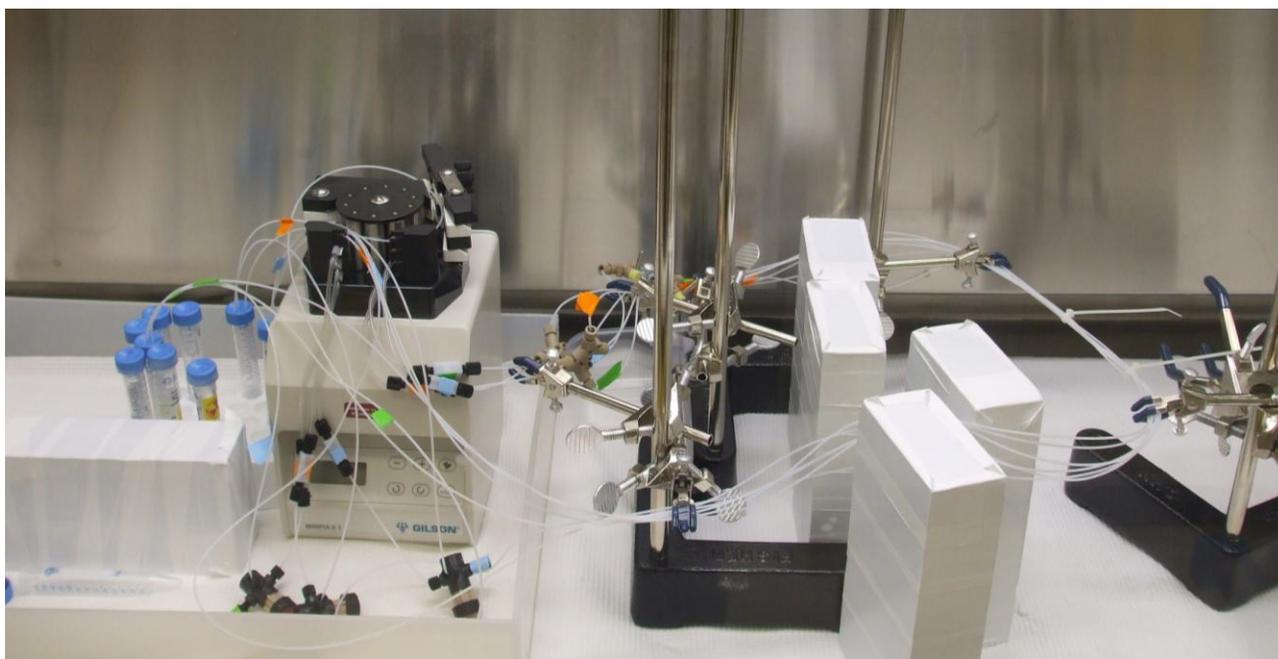
An abstract regarding an overview of the MIP Monitor technology was submitted to the GLOBAL 2011 conference in Japan. The conference was scheduled for September 2011, but due to the incident at Fukushima, it was delayed until December of 2011. The abstract was accepted, and invited for a presentation. The purpose of the trip is to seek out and foster collaboration between the JAEA and the MIP Monitor project with the ultimate goal to obtain process data to aid in the development of the technology.

Preparations were made to host a Chinese delegation during FY11, including the preparation of a one page summary of and a presentation on the MIP Monitor. This effort is being led by Steven Kung at DOE with major participation of the Separations Working Group within FCR&D. Though the visit has been postponed till next fiscal year, a PNNL staffer, Sam Bryan, joined the DOE delegation to China in June and presented the MIP Monitor as part of an overview of the different process monitoring technologies being developed at PNNL (Bryan and Levitskaia 2007). The goal of the interaction is to find potential opportunities to get process data that will be useful for the MIP Monitor development.

The MIP Monitor was discussed with visitors from the National Nuclear Laboratory (U.K.) at PNNL including potential collaborations and data exchanges.

## 2.6 Task 6

A major milestone for FY11 was the construction of a bench-scale flow loop to be used for near real-time experiments. The flow loop was initially completed in May 2011, tested and then slightly modified in June 2011 (see Figure 7). After initial testing with water, dilute dissolved spent nuclear fuel samples were introduced to the system and spectra were collected using a LaBr<sub>3</sub> detector. The design allows for the mixing of gamma signals without mixing the spent fuel solutions. Spectral data have been collected in both static and dynamic scenarios. The analysis of the spectra is ongoing, and initial results of the dynamic test are anticipated to be presented at the MPACT working group meeting to be held in September of 2011.



**Figure 7.** Photograph of the bench scale flow loop system inside a fume hood. The detector is placed in the far right clamp during operation to collect spectra while being shielding from the dissolved spent fuel sample reservoirs located on the far left.

### 3.0 Conclusion

The Multi-Isotope Process Monitor project had several accomplishments during FY 10. They include

- a simplified bench scale flow loop was constructed, tested, and used to gather spectra from spent fuel solutions prepared in previous years (Milestone Activity)
- spent fuel solutions were maintained to provide continued access to spent fuel solutions for testing of the MIP Monitor
- gamma spectra were collected and analyzed by a variety of multivariate techniques on samples of the dissolver, raffinate and extract solutions from the processed fuel using high purity germanium (HPGe), cadmium zinc telluride (CZT), lanthanum bromide (LaBr<sub>3</sub>), and sodium iodide (NaI) detectors
- additional data analysis techniques and approaches were explored, and the results will help direct further development
- subcontracts were setup to support graduate students and their research efforts at Pennsylvania State University and University of Texas at Austin (milestone activity)
- two graduate students finished and published master's theses with topics directly relating to MIP Monitor development
- contact was made on several fronts to engage international partners with the intent to collaborate in order to gain access to large amounts of reprocessing data for further MIP Monitor development
- several publications and presentations, including several that concerned the MIP Monitor but were funded either internal to the lab or whose funding was shared between DOE programs

## 4.0 Future Work

PNNL will work in conjunction with University of Texas to develop the multivariate analysis approach for the MIP Monitor. Experimental work, including using the bench-scale flow loop, will continue as required by method development. Pennsylvania State University, with oversight from PNNL, will continue to develop their GEANT model with the intent of making it capable of helping design a deployable system. The PNNL team will continue to support the training of students and young staff. Efforts will continue to be made to secure partners both domestic (if possible) and international to secure spectral process data that can aid in the development of the MIP monitor techniques. It is anticipated that this will include investigation potential application and deployment in support of pyroprocessing reprocessing systems. Significant results from all aspects from the MIP Monitor research will continue to be published in peer-reviewed journals and presented at conferences.

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