LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-JRNL-236980

Characterization of Nuclear Fuel using Multivariate Statistical Analysis

M. Robel, M. Robel, M. J. Kristo, M. J. Kristo

December 4, 2007

Journal of Environmental Radioactivity

Disclaimer

Characterization of nuclear fuel using multivariate statistical analysis

Martin Robel*, Michael J. Kristo

Chemistry, Materials, and Life Science Division

Lawrence Livermore National Laboratory

Abstract

Various combinations of reactor type and fuel composition have been characterized using principle components analysis (PCA) of the concentrations of 9 U and Pu isotopes in the fuel as a function of burnup. The use of PCA allows the reduction of the 9-dimensional data (isotopic concentrations) into a 3-dimensional approximation, giving a visual representation of the changes in nuclear fuel composition with burnup. Real-world variation in the concentrations of ^{234}U and ^{236}U in the fresh (unirradiated) fuel was accounted for. The effects of reprocessing were also simulated. The results suggest that, even after reprocessing, Pu isotopes can be used to determine both the type of reactor and the initial fuel composition with good discrimination. Finally, partial least squares discriminant analysis (PSLDA) was investigated as a substitute for PCA. Our results suggest that PLSDA is a better tool for this application where separation between known classes is most important.

Keywords: PCA; PLSDA; Classification; Nuclear Reactor; Nuclear Fuel; Partial Least Squares

1. Introduction

* Corresponding author. Tel.: +1 925 422 0314
E-mail address: robel1@llnl.gov (M. Robel)

Multivariate data from samples of known class can be used to generate plots against which data from unknown samples can be visually referenced. If the multivariate data clusters spatially according to class (reactor type and fuel composition in this case), then the unknown sample may be classified according to its distance from the data clusters of each known class (Duda, Hart, & Stork, 2001). For systems with 3 or fewer dimensions, raw or normalized data can be graphed directly to reveal trends that would not be apparent from examination of the raw data. For systems of greater than 3 dimensions, such as the evolution of nuclear fuel composition, plotting all of the data together in a comprehensible form is impossible. However, it is often possible to capture most of the information contained in higher dimensional systems (such as the 9-dimensional system considered here) and recast it in a meaningful 2-D or 3-D plot, as long as there is significant correlation between parameters. Principle Components Analysis (PCA) is a popular data reduction method which exploits this correlation to compress higher dimensional systems into fewer dimensions while retaining most of the information (Duda, Hart, & Stork, 2001).

The variation of isotopic concentrations versus burnup can be characteristic of a particular reactor type and fuel composition. Previous work (Nicolaou, 2006) used the data-reduction power of PCA to capture a large percentage (typically over 95%) of the information in the 9 U and Pu isotopic concentrations (^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu), i.e., a 9-dimensional system, using only 3 principle components (dimensions), allowing relatively easy visualization and sample classification. This investigation extends these analyses to account for realistic variation in fresh fuel composition. When building a PCA map as a reference against which unknowns are queried, variability in fuel composition translates to uncertainty, smearing out the classes

over the model space. This uncertainty needs to be accounted for in a realistic, comprehensive 'PCA map' which consists of reactor-fuel characteristic scatter plots.

Fresh UO_2 contains four isotopes of U in significant quantities –^{234}U, ^{235}U, ^{236}U, and ^{238}U. Even in fresh fuels of the same enrichment, ^{234}U and ^{236}U concentrations vary considerably. The natural abundance of ^{234}U varies slightly in uranium ores due to a combination of nuclear decay (^{234}U is produced in the decay chain of ^{238}U), chemical, and hydrologic factors (Bourdon, Henderson, Lundstrom, & Turner, 2003). Naturally occurring ^{236}U is almost non-existent (Zhao, 1994). However, the ^{236}U isotope is produced by transmutation of ^{235}U in an operating reactor. And while reprocessing was halted in the U.S. in the late 1970's, it has continued in Europe and Japan. Due to the global nature of the nuclear fuel industry, significant amounts of reprocessed U end up in almost all reactor fuel, leading to a variability of ^{236}U concentration in fresh fuel.

We first describe the changes in the PCA analysis of a single reactor type-fuel combination after including the variability of ^{234}U and ^{236}U in fresh fuel; the variability in ^{234}U and ^{236}U is graphically represented in 3-dimensional PCA plots. We then investigate the way in which this variability impacts the spatial separation between the PCA data from various reactor type-fuel combinations. In particular, we examine the ability to discriminate between trends for reactors of similar type and enrichment. By analyzing the U and Pu isotopes independently, we address the ability to discriminate between reactor types after reprocessing (separation of the U and Pu isotopes). The analysis of only U or only Pu isotopic concentrations simulates the challenge of determining the history and source of a sample of isolated, reprocessed U or Pu. Finally, we compare the discrimination performance of PLSDA to that of PCA for identical cases.

2. Materials and Methods

To perform these analyses, a database of fuel composition vs. burnup for a wide range of reactor types at various intervals in the burnup cycle was required. It is impractical to obtain such data from real nuclear fuel sample analyses. Instead, the ORIGEN-ARP code package (Bowman, 2000) was used to predict U and Pu isotopic compositions at various burnup values. ORIGEN-ARP uses the matrix exponential method to perform depletion and generation calculations. The ARP component specifically interpolates between pre-generated, burnup dependent, cross section libraries. Because the cross section libraries are pre-generated, ORIGEN-ARP is very fast, making it possible to run a large number of cases in a very short time on a desktop personal computer. We exploited this speed by running closely spaced burnup intervals, 20 for each case.

Key information about the types of reactors simulated is shown in Table 1. These reactors types were chosen to represent a broad spectrum of existing designs in use. The GE Boiling Water Reactor (BWR) and the Westinghouse Pressurized Water Reactor (PWR) are the primary power reactor types operating in the U.S. The Canadian Deuterium (CANDU) reactor, used in Canada and abroad, is notable for its ability to run on natural (not enriched in ^{235}U) uranium. The MAGNOX reactor, named after the magnesium based alloy fuel cladding, is a British design notable for its use of CO_2 as a coolant and graphite as a moderator. It is also fueled by natural U and was selected for comparison to the CANDU. The AGR (Advanced Gas Reactor) is similar to the MAGNOX design, but runs at higher temperatures (for improved thermal efficiency) and with higher enrichment fuel. The MOX-fueled PWR uses a mixture of natural U and reprocessed Pu. The VVER

Russian reactors were chosen to represent a major non-U.S. PWR design. The availability of models for these reactor types in ORIGEN-ARP version 5.00 was a key requirement. For simplicity, all reactors were simulated at 100% power for the entire burnup. The effects of decay after the end of irradiation were not incorporated into the data presented here. We did confirm the previous claim (Nicolaou, 2006) that a 10 year cooling time of an unknown sample does not change the origin determination.

Actual quality assurance sample data provided by various nuclear fuel vendors as well as minimum and maximum concentrations from our own analysis of ~17 lots of fresh fuel were used to determine reasonable ranges for the ^{234}U and ^{236}U concentrations in real fuel. We also considered the ASTM specifications for the minimum and maximum concentrations of these isotopes in uranium dioxide fuel (ASTM, 2003), but we found that these limits were much broader than the actual concentrations measured in nuclear fuel by either the manufacturers or ourselves. Consequently, it was unclear to what extent these regulatory limits would reflect actual fuel composition. The min-max values used for this study (see table 2) are not intended to represent statistically rigorous limits, then, but rather an attempt to provide a good, conservative basis for assessing the feasibility of this statistical analysis method for discrimination, given real-world variability in fresh fuel composition.

PCA and PLSDA analyses were performed using PLS_Toolbox, a MATLAB add-on from Eigenvector Research (Wise et al., 2005). Plots were generated using MATLAB version 7.2 (MATLAB, 2006).

3. Results and Discussion

We achieved qualitative reproduction of previous work (Nicolaou, 2006). However, because of updates and improvements to the models in ORIGEN-ARP, Nicolaou's results, which were obtained using ORIGEN2, could not be exactly replicated. For example, the liquid metal fast breeder reactor (LMFBR) model, which was included in ORIGEN2, is not included in ORIGEN-ARP. Also, for CANDU models, ORIGEN2 over-predicts the total Pu/U ratio by 13% as compared to 1% for ORIGEN-S, the ORIGEN component of ORIGEN-ARP (Gauld & Litwin, 1995). Finally, there are no appropriate MOX cross section libraries for ORIGEN2. The latest code package is more accurate, supports more reactor/fuel types (but not LMFBR), and benefits from more rigorous benchmarking (I. Gauld, personal communication, 2007).

[figure 1]

Some trends are immediately apparent from the PCA results shown in Figure 1. Similar reactor types with the same starting fuel composition are tightly grouped, particularly toward the beginning of irradiation; they all start at the same point. Principle Component 3 (PC3) is most important in discriminating between cases which start with identical fuel. Principle Component 2 (PC2) is clearly reflective of enrichment as shown in Figure 2a. In 2-dimensional plots, such as those in Figure 2, the importance of each nuclide concentration to each principle component (its "loading") is plotted graphically as a ★, the importance being proportional to distance from the origin. For example, in Figure 2b, ^{238}U is seen to have little influence on PC3, while ^{239}Pu has the greatest effect.

[figure 2]

We next looked at how variability in ^{234}U and ^{236}U concentrations manifest in PC space. First, for a single reactor, certain trends become apparent. Varying the concentration of a single isotope (in this case, ^{234}U) in the fresh fuel produces a new curve which runs

approximately parallel (in 3 dimensions) to the original throughout core life. Furthermore, fine variation from the lower to the upper limit for this isotopic concentration produces a pattern of parallel curves that can be accurately represented by a single surface connecting the two extremes of isotopic variability. Variation of a second isotope (^{236}U) produces similar results, only along a different plane. Varying both ^{234}U and ^{236}U produces a pattern of curving parallel lines whose outer limits are accurately represented by a closed volume resembling an extrusion with four flat sides and a parallelogram cross section, as shown in Figure 3 below.

[figure 3]

[figure 4]

[figure 5]

Simulated Reprocessing

Spent fuel from power reactors that use enriched fuel contains ^{235}U in concentrations significantly higher than naturally occurring U. Spent fuel also contains significant levels of fissile Pu from the transmutation of ^{238}U in the operating reactor. Several countries use spent fuel reprocessing to recover these fissile isotopes. Chemical reprocessing of nuclear fuel consists of dissolving spent reactor fuel in acid and chemically separating the U and Pu from the highly radioactive fission products. The separated U and Pu can then be recycled for use in power reactors.

Figure 6 shows the PCA analysis using only the U isotopic concentrations; Figure 7 shows the PCA analysis using only the Pu isotopic concentrations. As shown in these two figures, reducing the number of input parameters to the PCA analysis does not necessarily degrade the ability to differentiate between reactor types. In the case shown in figure 7,

elimination of a number of input parameters (all of the U isotopes) has actually improved the differentiation.

[figure 6]

[figure 7]

PCA selects orthogonal axes to best describe the entire range of data input to the analysis. The first Principle Component axis is calculated to encompass the greatest variation in the data; subsequent axes are constrained to be orthogonal to the preceding axis. Removal of the U isotopic concentrations from the PCA analysis results in determination of PC's that capture the greatest variance in the Pu data. Since the generation of the Pu isotopes is most strongly affected by reactor type, i.e., neutron spectrum, using only Pu isotopic concentrations for PCA reveals more of the differences between reactor type-fuel combinations than PCA of all 9 isotopes. Essentially, much of the U data acts as a sort of background, obscuring the distinguishing characteristics of the different reactors. By removing the U data, one simply improves the "signal-to-noise" ratio.

This result is not surprising, because the goal of PCA is to determine the set of orthogonal axes that best describe the entire higher dimensional system with fewer dimensions. However, if one's goal is not to describe, but to differentiate, between data groups (classes), PCA will not necessarily choose the optimal axes. In this case, removal of the U isotopes causes PCA to choose axes with a different orientation –one that is better suited for differentiating between reactor types.

Partial Least Squares Discriminant Analysis

Finally, we investigated the use of Partial Least Squares Discriminant Analysis (PLSDA), an alternative dimension reduction tool. PLSDA selects axes that maximize discrimination between classes, as opposed to PCA, which selects axes to best represent the entire data cluster (Barker & Rayens, 2003). Analyses of 5 reactor types starting with identical fuel are shown in Figure 8. Note that each reactor has 4 data points at each burnup stage, but only two are clearly visible in this projection. The latent variables (LV) in PLSDA are analogous to PC's in PCA.

[figure 8]

These two analyses use Pu isotopic concentrations only[1]. This example illustrates the superiority of PLSDA over PCA for resolving classes.

4. Conclusion

The higher dimensional systems describing nuclear fuel isotopics vs. burnup were reduced to 3 dimensions using Principle Components Analysis. Because the generation and depletion of many isotopes is highly correlated, a large percentage of the total variance is captured by the first 3 Principle Components. Accounting for realistic variability in ^{234}U and ^{236}U present in fresh fuel causes some overlap between cases, particularly early in core life and for similar reactor types with similar fuel. This overlap between reactor type-fuel combinations represents potential uncertainty in the identification of an unknown sample. However, as shown by the simulated post-reprocessing analyses, strategic selection of nuclides input to the database can improve between-case separation distance substantially. This specific result reflects a fundamental shortcoming of Principle Components Analysis

[1] The reader should not conclude, based on these plots, that the VVER-440 is easily distinguished from the other PWR's; the VVER-440 model used to generate this data is reported to give high values for Pu-239 (Murphy, 2004).

as applied to discrimination. Partial Least Squares Discriminant Analysis appears to be a more effective tool for the ultimate objective of generating a comprehensive map of reactor/fuel characteristics in 2 or 3 dimensions by compressing information from an arbitrary number of parameters.

Acknowledgements

The authors wish to express their gratitude to I. Hutcheon for supporting this research and to S. Bowman, I. Gauld, G. Nicolaou, J. Shaver, and D.Vogt for valuable technical insight and feedback. This work was performed under the auspice of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

References

Annual book of ASTM standards, 2003. Section 12, vol. 12.01

Barker, M. & Rayens, W., 2003. Partial least squares for discrimination, J. Chemometrics, 17, 166-173.

Bourdon, B., Henderson, G. M., Lundstrom, C. C., & Turner, S. P., editors, 2003. Uranium-Series Geochemistry, Reviews in Mineralogy and Geochemistry, V. 52.

Bowman, S.M., and Leal, L. C., 2000. ORIGEN-ARP: automatic rapid process for spent fuel depletion, decay, and source term analysis, ORNL/NUREG/CSD-2/V1/R6.

Duda, R. O., Hart, P. E., & Stork, D. G., 2001. Pattern Classification, 2nd Ed. John Wiley & Sons, Canada.

Gauld, I. C. & Litwin, K. A., 1995. Verification and validation of the ORIGEN-S code and nuclear data libraries, Atomic Energy of Canada, Limited, Chalk River, ON, Canada, Tech. Rep. AECL RC-1429.

MATLAB Documentation Set, 2006. http://www.mathworks.com/access/helpdesk/help/techdoc/matlab.html.

Murphy, B.D., 2004. ORIGEN-ARP cross-section libraries for Magnox, advanced gas-cooled, and VVER reactor designs, ORNL/TM-2003/263.

Nicolaou, G., 2006. Determination of the origin of unknown irradiated nuclear fuel, J. Environ. Rad., 86, 313-18

Wise, B. M. et al., 2005. PLS_Toolbox Version 3.5 for use with MATLAB™, Eigenvector Research, Inc.

Zhao, X. L. et al., 1994. The first detection of naturally-occurring 236U with accelerator mass spectrometry, Nucl. Instr. & Meth. B. 92, 249.

Table 1. Reactor types simulated in ORIGEN-ARP

Reactor Type	Enrichment [weight %]	Burnup [GWd/MTU]
GE BWR, 8x8	1.5 – 5[a]	15 to 50 [b]
Westinghouse PWR, 17x17	1.5 – 5[a]	15 to 50[b]
CANDU-28, -37, natural U	0.711	10
CANDU-28, -37, slightly enriched	1.2	10
MAGNOX, natural U	0.711	10
AGR	1.5, 2.5, 3	15 to 30[b]
MOX PWR, 17x17	4.7[c]	50
VVER 440 (Russian PWR)	1.5 – 5[a]	15 to 50[b]
VVER 1000	1.5 – 5[a]	15 to 50[b]

[a] Enrichment was incremented from 1.5% to 5% in 0.5% steps.

[b] Burnup was varied with enrichment using the thumb-rule: 10 GWd / % enrichment.

[c] For MOX, % fissile (^{235}U, ^{239}Pu, and ^{241}Pu) is considered equivalent to % ^{235}U.

Table 2. Example of min-max values for ^{234}U and ^{236}U from vendor data and our own analysis. These values were used for the 3% enriched LWR fuel in burnup simulations.

Isotope	Lower concentration limit (ppm)	Upper concentration limit (ppm)
^{234}U	172	300
^{236}U	4	622

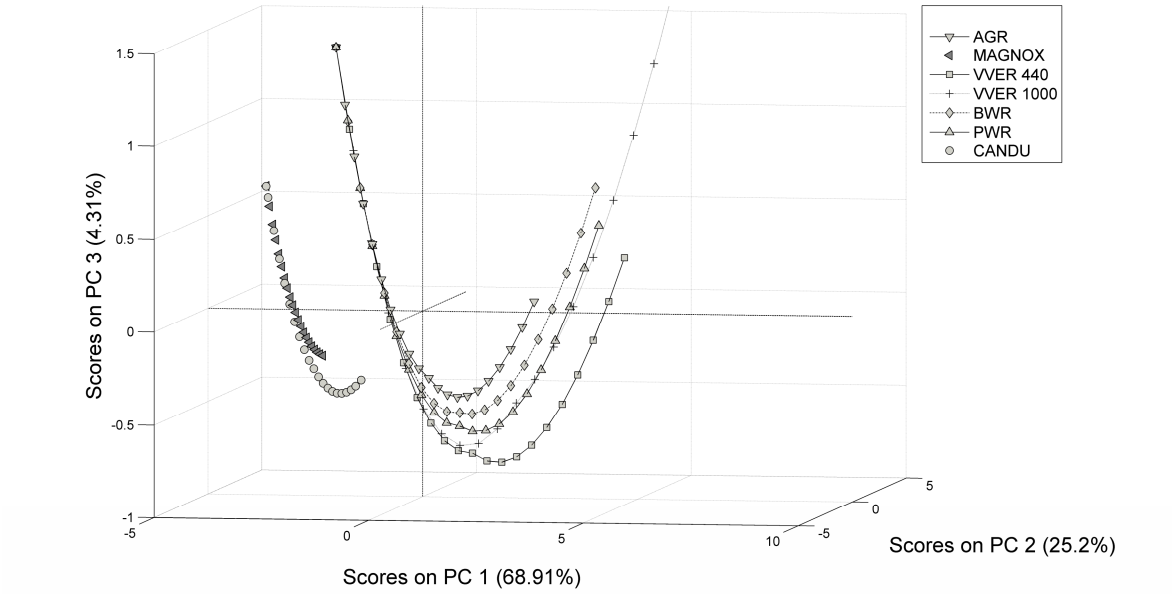
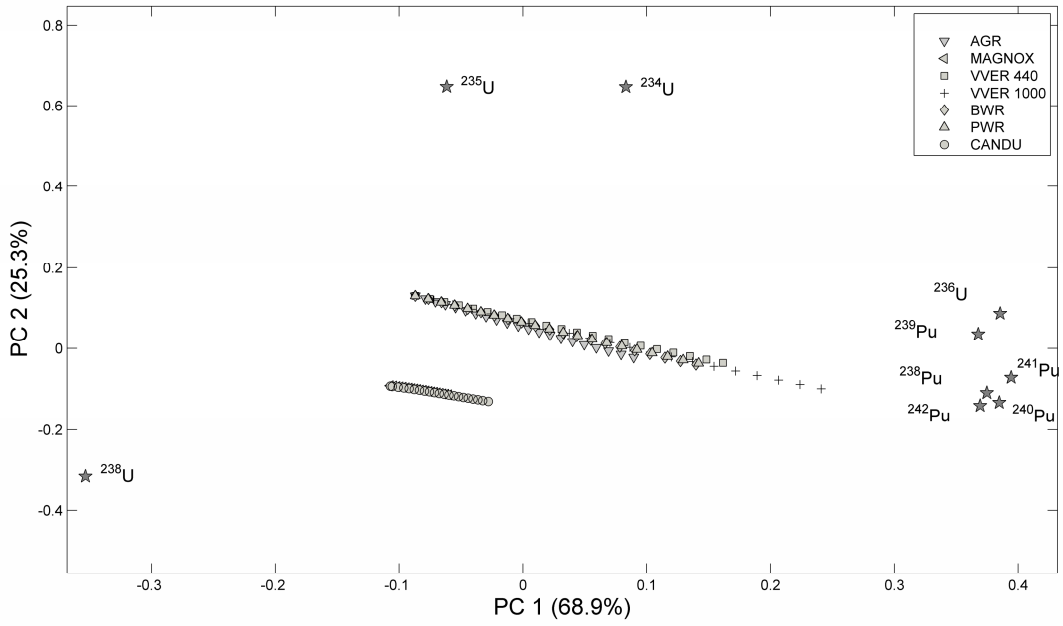
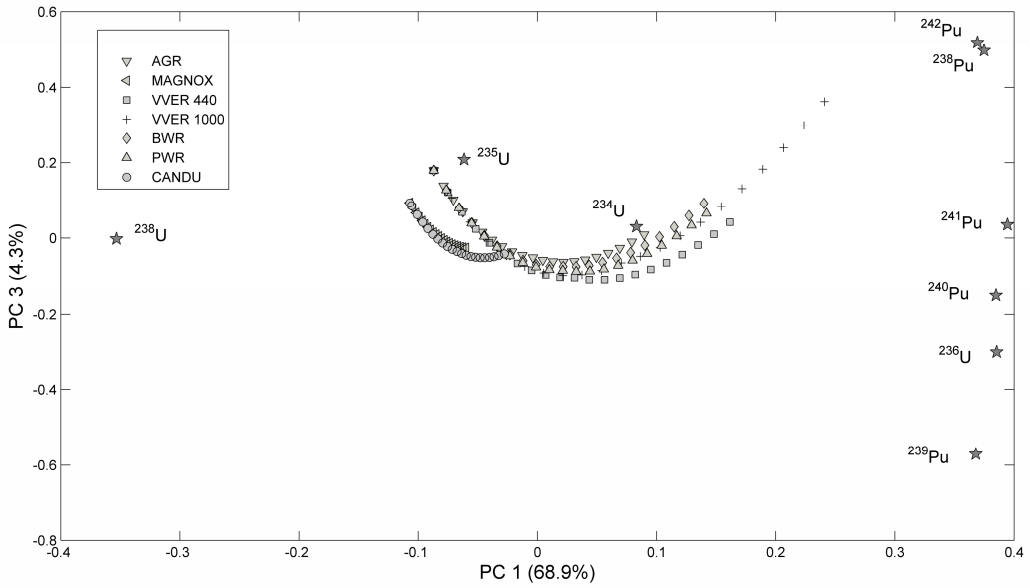


Figure 1. Plots of various reactor-fuel combinations showing how each combination changes with burnup (a single curve) and how the data for different reactor-fuel combinations relate to each other. In this case, 98.5% of the information described by the variation in 9 isotopes with burnup is compressed to 3 dimensions. The MAGNOX and CANDU reactors start with identical natural uranium fuel. All other reactors shown were loaded with 3% enriched UO_2 of identical composition.

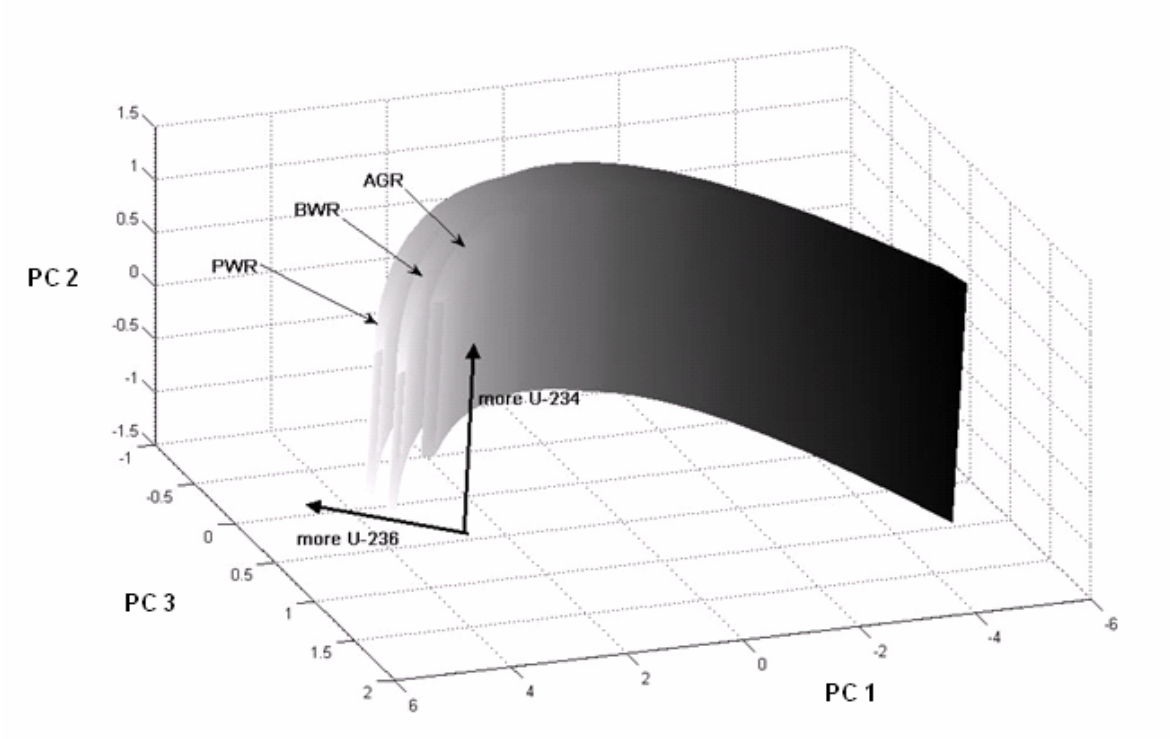


285 **(a)**



(b)

Figure 2. 2-D plots of the same reactor-fuel burnup curves shown in Figure 1. The overlay of scores (plotted data in PC space) and loadings (weighting of different isotopes 290 within each principle component, indicated by a ★) shows how the PC plot is related to the underlying isotopic concentrations.



295 **Figure 3.** PCA of 3 reactors with 3% enriched UO_2. Variability in the concentration of ^{234}U and ^{236}U in fresh fuel, based on manufacturers' QA data, defines a 3D region. The four corners of the cross-section correspond to the extremes of ^{234}U and ^{236}U concentration in the fresh fuel. The shading corresponds to burnup; shading grows lighter with burnup.

300

305

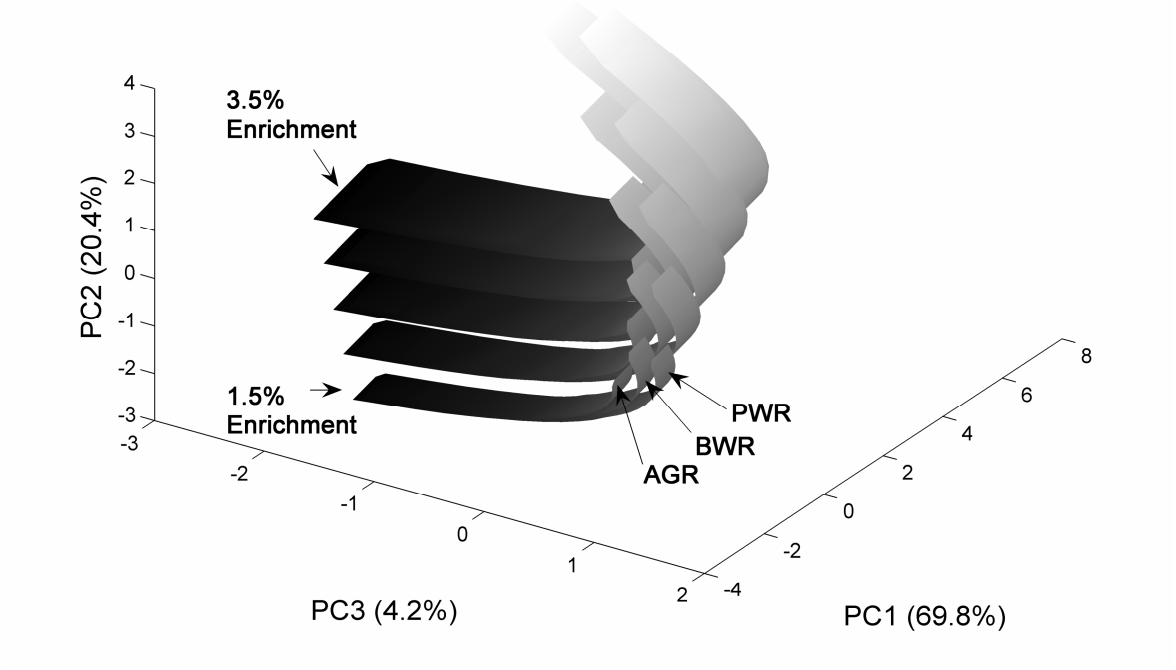


Figure 4. Analysis expanded to explore the effects of varying enrichment. Increments of 0.5% in enrichment are still well resolved in 3 dimensions, despite uncertainty in both ^{234}U and ^{236}U.

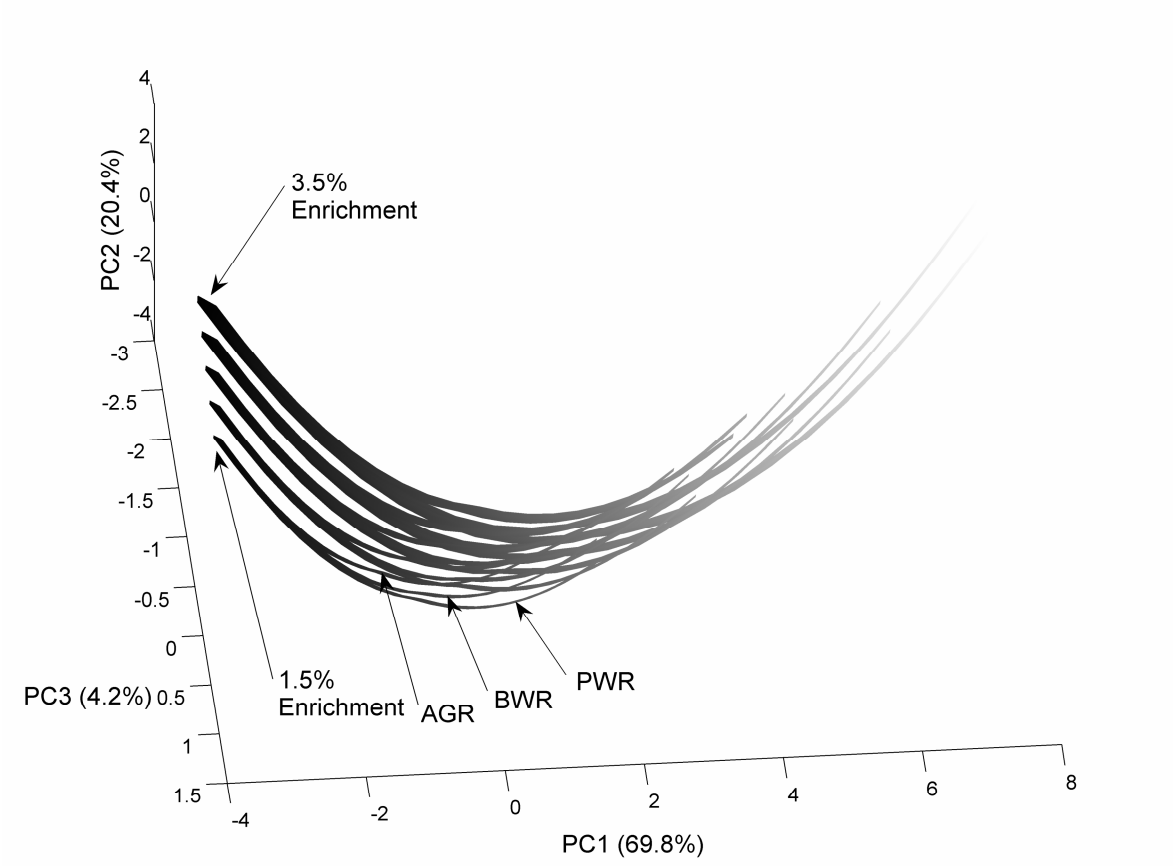
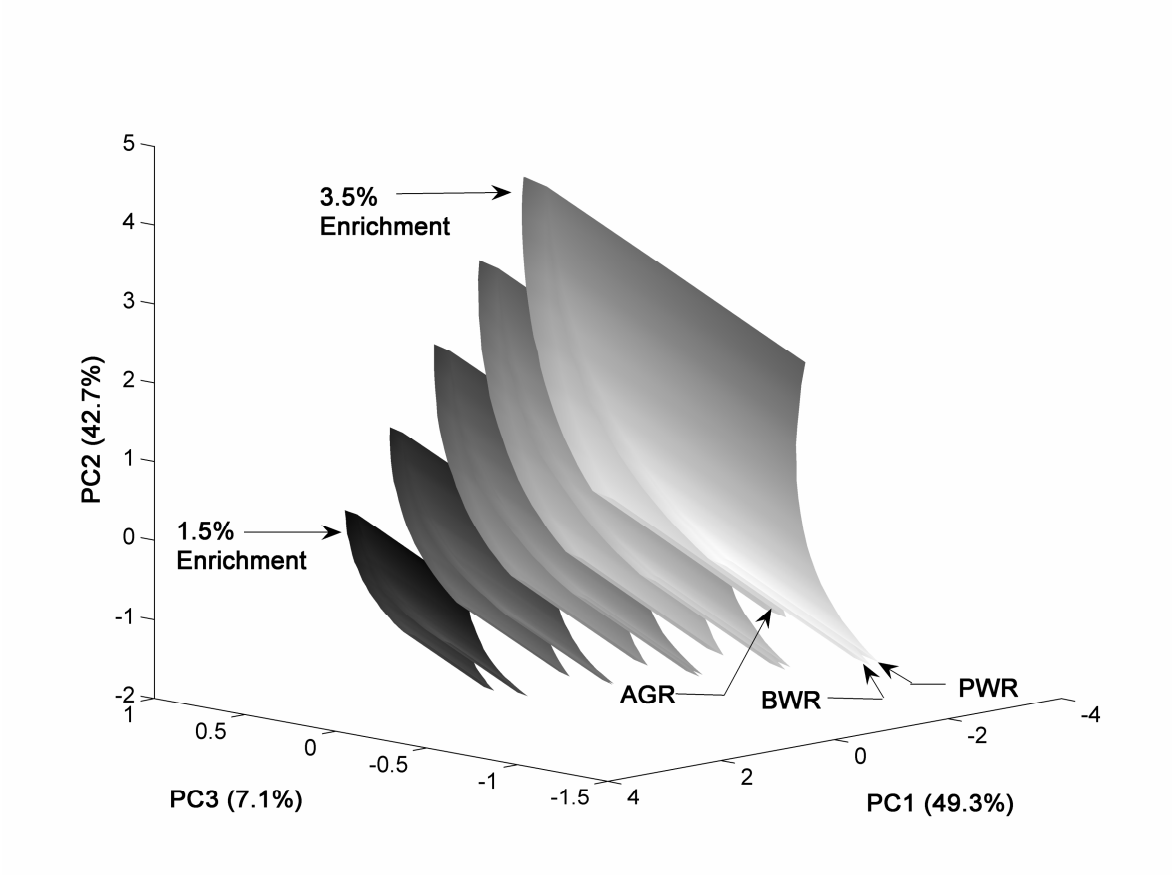


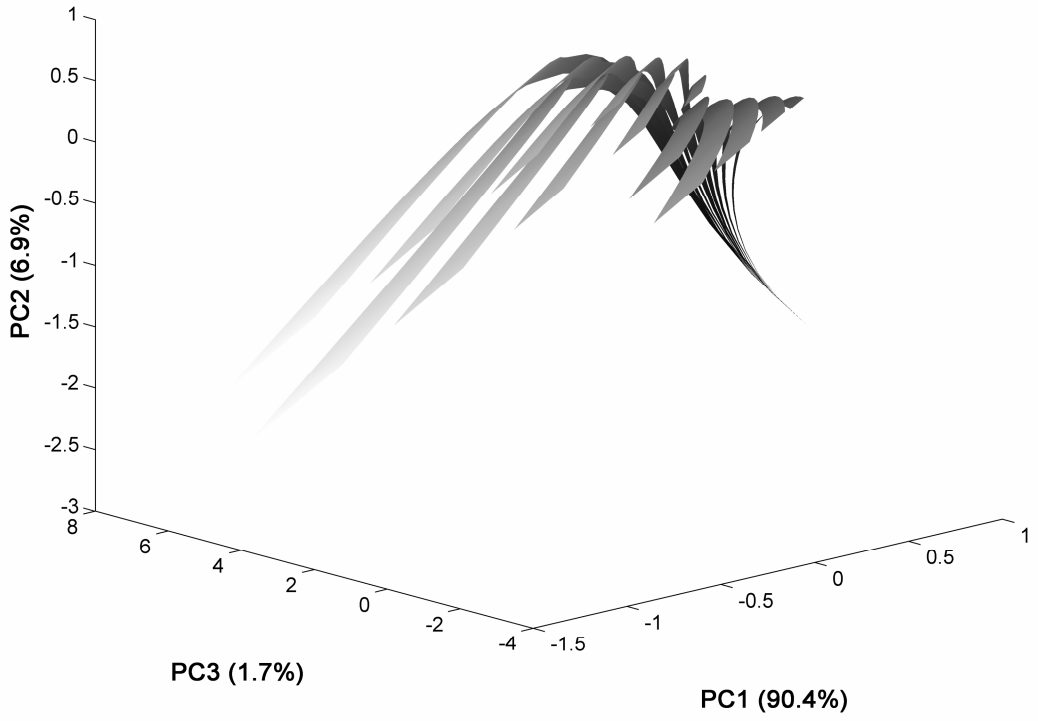
Figure 5. The same trends shown in Figure 4, but rotated to show separation of reactor types early in burnup. All 3 reactors start with identical fuel composition.



335

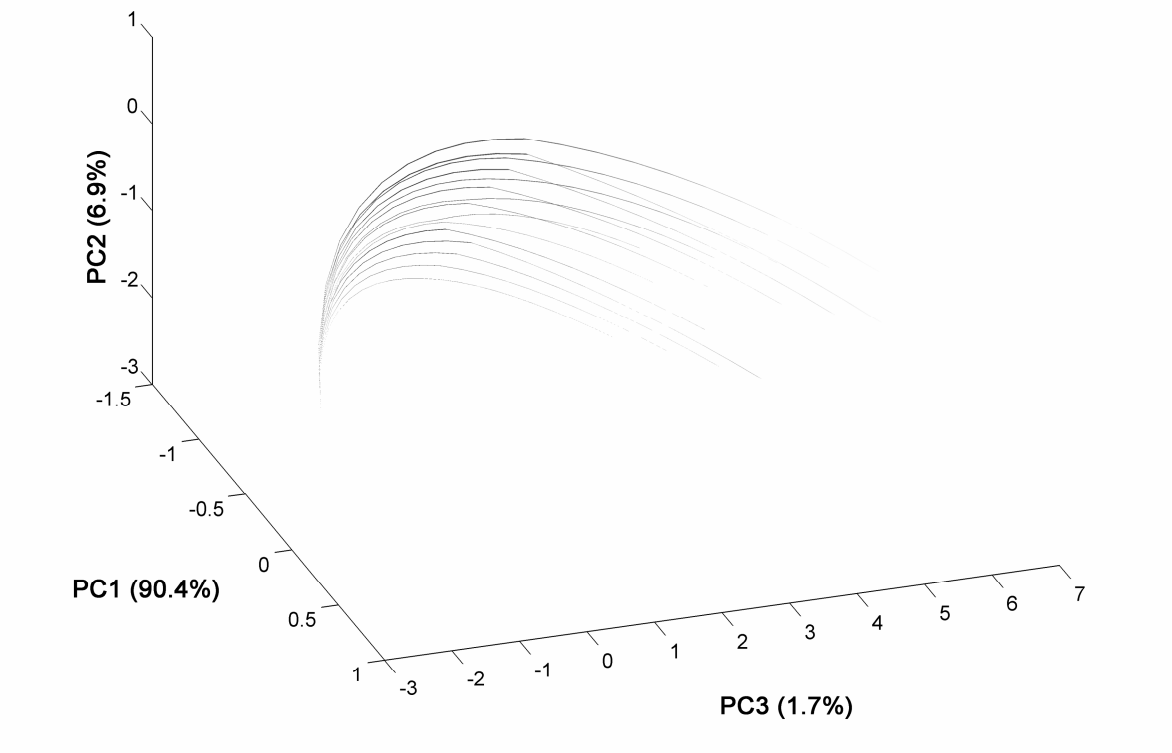
Figure 6. PCA of uranium isotopes only. AGR remains well resolved, but PWR and BWR trends overlap throughout core life.

340



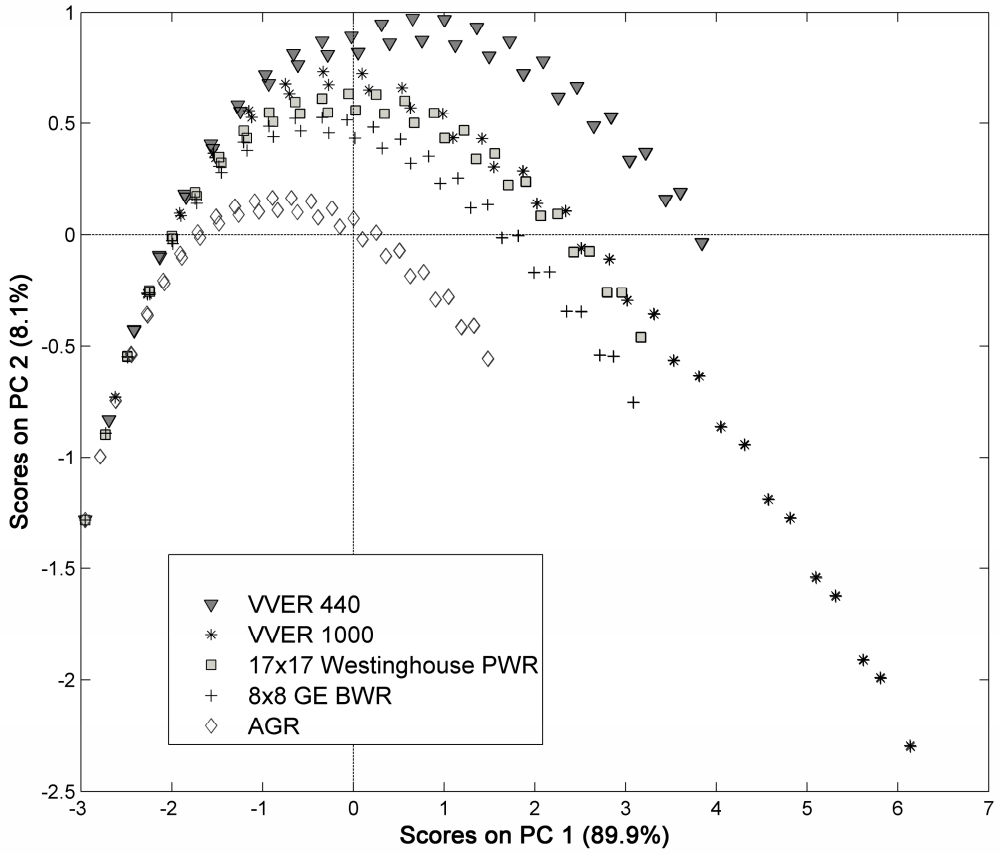
345

(a)

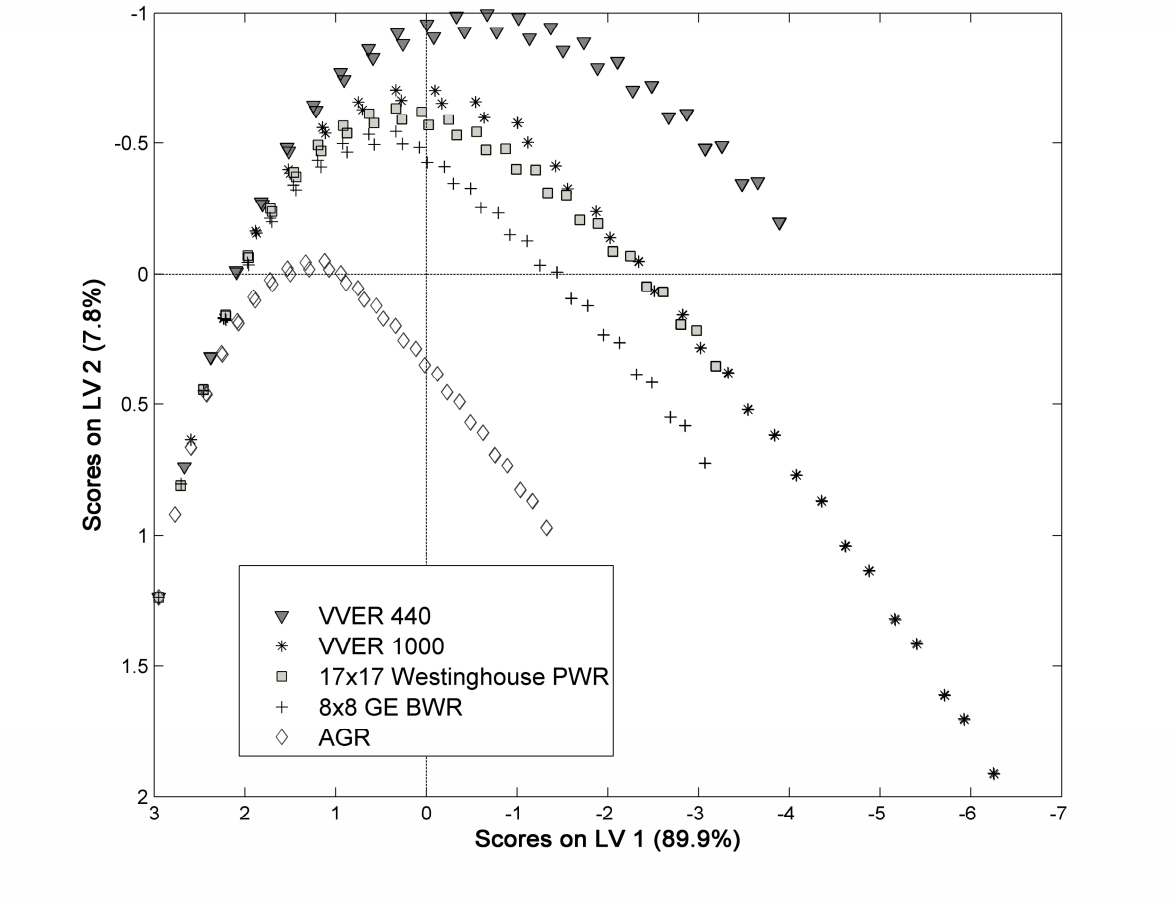


(b)

Figure 7. PCA of Pu isotopes only. All reactor type/fuel combinations are well resolved starting very early in core life. Figure 7b is the same plot rotated.


Scores on PC 2 (8.1%)
Scores on PC 1 (89.9%)
VVER 440
VVER 1000
17x17 Westinghouse PWR
8x8 GE BWR
AGR

(a)



355

(b)

Figure 8. PCA (a) vs. PLSDA (b) of same 5 reactor types using only Pu isotopic concentrations as inputs. Note that these plots account for variability in ^{234}U and ^{236}U.