

FINAL REPORT

Nuclear Engineering Education Research Grant

“Technique Development to Support Clean-up and/or Disposal of Actinide Contaminated Soils and Sediments: Coupling Fission Track Analysis with Synchrotron X-ray Microprobe Analysis”

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1.0 Introduction

In this award from the U.S. Department of Energy, we developed a method to couple fission track analysis (FTA) with other *in-situ* techniques for studying actinide contamination of soils and sediments. The overall goal of this project was to develop quantitative FTA to provide images of the microscale spatial distributions of high fissile actinides (e.g., ^{235}U , ^{239}Pu) sorbed to environmental particles such as sediments and colloids. We developed methods to provide absolute actinide surface concentrations on the particles, regardless of particle size. We are also working to provide particle size information by our approach. We also coupled our newly devised FTA methods with the quantitative determination of stable element distributions in the same particles using synchrotron x-ray microprobe analysis (SXMA).

2.0 Background

Large quantities of soils and sediments at many of the DOE sites are contaminated with low activity levels of anthropogenic U and Pu [e.g., 1]; in the largest volumes of these soils and sediments, U and Pu are often present at relatively low levels, e.g., approximately 1 to 2 orders of magnitude above fallout [2]. These bulk concentrations are too low to determine chemical speciation or partitioning information by typical spectroscopic methods; at the same time, however, the activity levels are high enough for regulatory agencies and the DOE to consider clean-up [1]. In these situations, DOE is usually forced to use the expensive, relatively ineffective "muck, suck, and truck" method for clean-up [2]. This typically involves excavation of contaminated material and placement in an engineered facility, which actually only transfers the problem from one location to another [3]. To develop remediation strategies, understanding how the actinides are partitioned to the soil and the chemistry controlling that partitioning are essential [3, 4].

2.1 Actinide Partitioning to Soils and Sediments and Strategies for Remediation

Knowledge of the chemical and physical forms of U and Pu in sediments can be quite useful in developing remediation alternatives [5]. For example, if the actinides are bound to the soil or sediment in very refractory forms, then reducing actinide activity levels by leaching or extraction will likely be quite difficult and expensive; however, physical removal of the refractory materials may be possible if they are magnetic or of a specific particle size. Conversely, if the actinides are partitioned to natural or anthropogenic organic matter in the soil or sediment, chemical treatments designed to target the organic matter and the contaminant associated with it, such as supercritical fluid extraction, may be viable approaches [e.g., 6, 7]. Because actinide partitioning to soils and sediments varies from site to site, analytical methods to define actinide partitioning that are applicable for low levels of contamination are needed by environmental regulators and engineers to develop mitigation strategies.

We at WSU [5, 8, 9, 10] and others [e.g., 11, 12, 13] have demonstrated that sequential chemical extractions (SEs) are useful bulk scale tools for defining the partitioning of actinides to soils and sediments. SEs involve the successive leaching of a soil or sediment using increasingly aggressive chemical treatments. Partitioning to a geochemical phase can be inferred if the extraction of stable metal ions is monitored along with the extraction of the contaminant. This is shown in Figure 2.1. Here, the WSU team used a SE method by Smith [14] and Schultz et al. [15, 16, 17] that defined six different geochemical fractions: exchangeable, carbonate, reducible, oxidizeable, acid sulfide leachable, and residual. Fig. 2.1.A shows the partitioning of six different stable elements according to our extraction scheme. Figs. 2.1.B and 2.1.C show the partitioning of Pu and U, respectively. These results indicate that the U is very refractory, and isotopic information suggests that it is primordial (data not shown). The majority of the Pu appears to be partitioned into an oxidizeable phase, with another measureable fraction partitioned with reducible phases. We believe that the oxidizeable phase is natural organic matter, whereas the reducible phase is composed of amorphous Fe and Al oxides. From this data, we could propose a remediation treatment involving those target phases (natural organic matter and amorphous Fe and Al oxides), and remove greater than 90% of the Pu from this sediment. We have applied supercritical fluid extraction to this sediment, and then used SEs to study changes in partitioning of Pu, U, and the stable elements as a result of this treatment [6]. Recently, the DOE has become interested in the

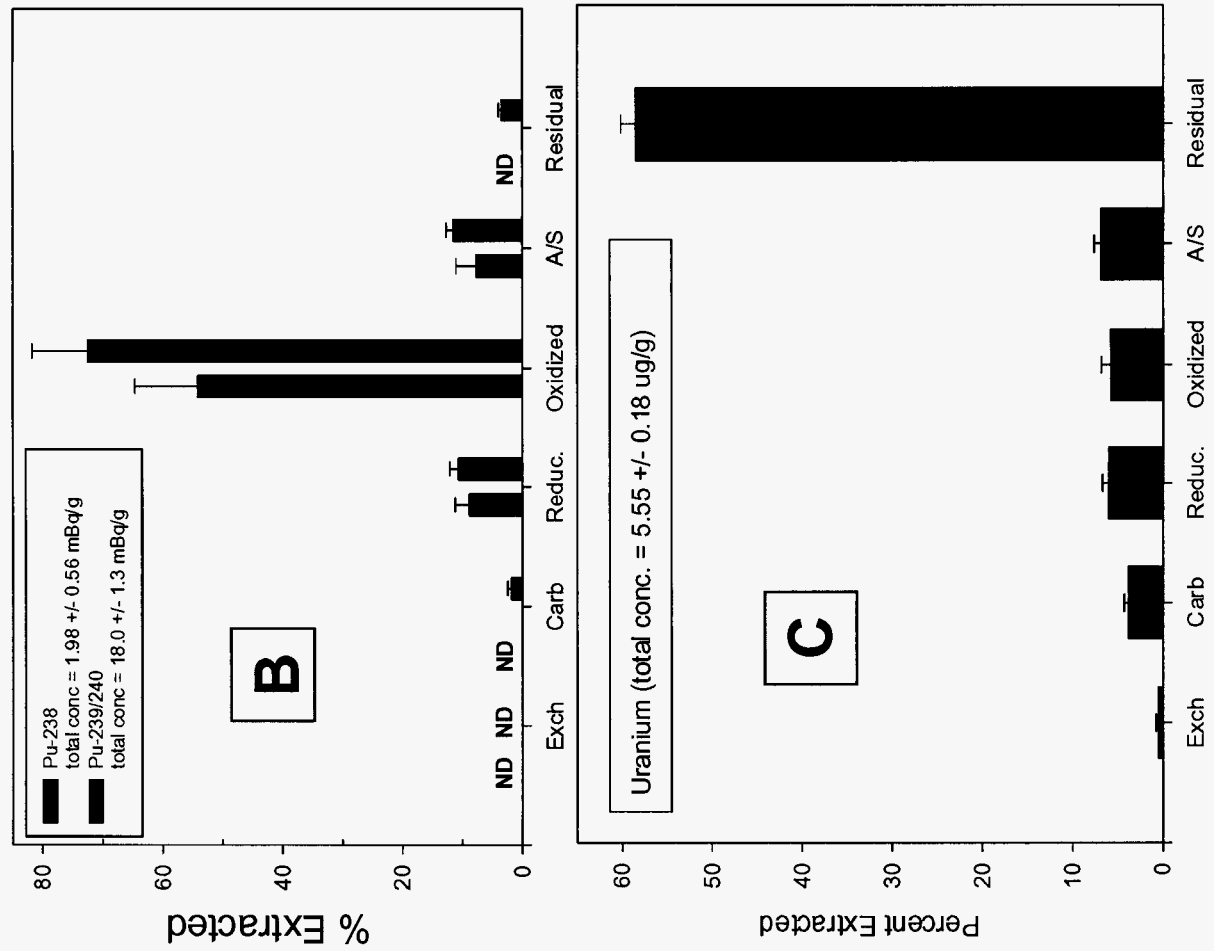
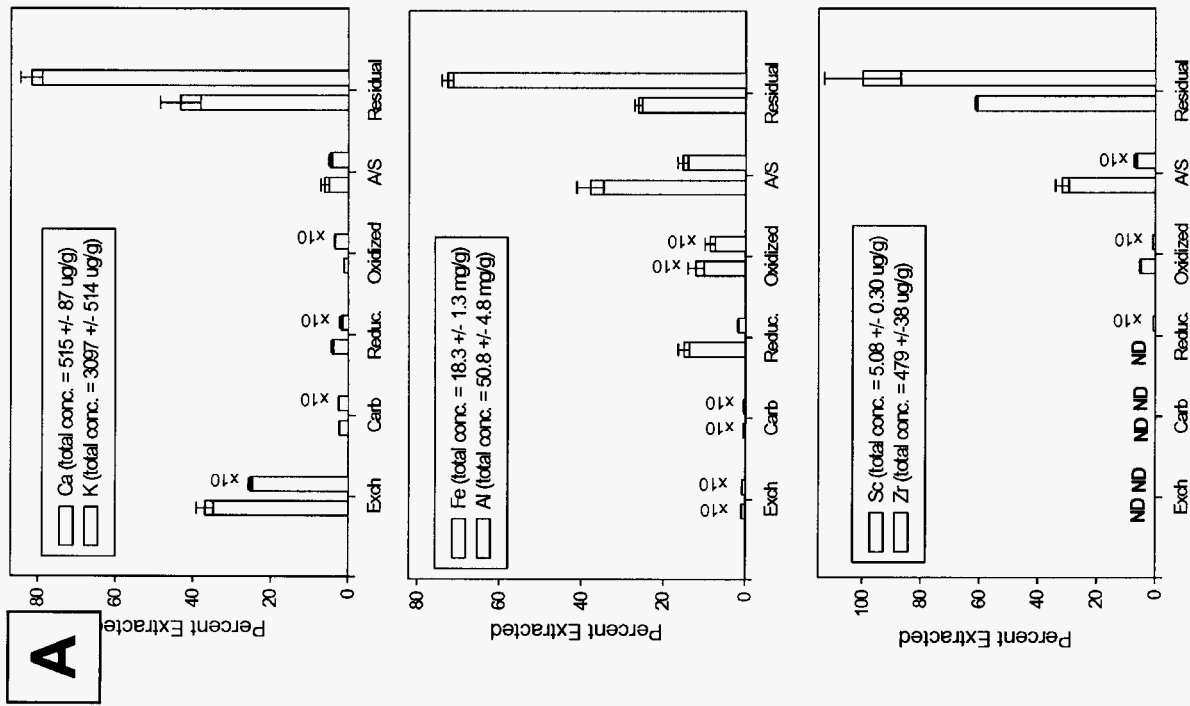


Figure 2.1: Taken from Loyland et al. [7]. Data in **A** shows the sequential leaching of stable elements, whereas **B** shows Pu isotopes and **C** shows total U. We see no evidence for isotopic fractionation of Pu. Our data suggests that Pu is associated primarily with oxidizable materials and amorphous Fe and Al, whereas U is associated with more refractory matrices. For this sample, U is primordial.

partitioning of plutonium and other actinides to colloidal materials; we have demonstrated that such information can be obtained with our SE methods [5].

While SEs are useful for studying bulk-level partitioning, it is the chemistry of the solid:water interface that controls U and Pu sorption to soil and sediment grains. For remediation applications, the chemistry of this solid:water interface must be manipulated to extract contaminants from the soil surface. This is the basis for treatment methods such as soil washing [e.g., 18], supercritical fluid extraction [e.g., 19], etc. Interestingly, our work has demonstrated the U and Pu contamination in most soils and sediments is not homogeneously distributed among all sediment particles [5]. Rather, discrete particles appear to dominate the sorption of these contaminants. Consequently, remediation techniques should focus on chemical or physical properties of these specific particles to be successful. Since the nature of the U or Pu contamination varies from one site to another, the chemical nature of the discrete particles to which the actinides sorb varies from system to system. In other words, the information obtained on actinide partitioning and the chemical nature of the particles to which they partition at one site is usually not transferable to other sites. Thus, screening analytical methods are needed to elucidate the actinide partitioning and the chemistry of the solid:water interfaces of the environmental particles involved.

2.2 U and/or Pu Contaminated Particles and the Chemistry of the Solid:Water Interface

With such low bulk concentrations of U and Pu in the soils and sediments, finding the discrete particles to which these contaminants are sorbed is analogous to finding a "needle in a haystack". However, through our current NEER funding we have demonstrated that fission track analysis (FTA) is very useful in this regard [5, 20]. In FTA, a neutron source is used to induce fission in isotopes with high neutron capture cross sections (e.g., ^{235}U and ^{239}Pu). The fission events are recorded in the detector as damage tracks that can be enhanced by chemical etching.

We have been working to develop FTA as a method of locating contaminated soil and sediment particles, as shown in Figure 2.2, A and B. The "star-burst" patterns of the fission tracks demonstrate that ^{235}U and/or ^{239}Pu are associated with discrete particles [5]. The size of the star-bursts in the images correlate to the size of the particles to which the ^{235}U or ^{239}Pu are sorbed. We have developed a method to locate those particles for further study. We employ copper locator grids typically used in scanning electron microscopy (SEM). Copper does not have a high neutron capture cross section, and the method for obtaining the image of the copper grid in the fission track detector has been submitted for patent consideration [a limited description can be found in 20]. The utility of this approach is easily seen in Fig. 2.2, C-F. Figs. 2.2.C and D show the images of both the SEM locator grid and a "hot particle", recorded in a fission track detector. Figs. 2.2.E and F are SEM images of the sample itself, with the locator grid and soil particles distributed within the image. The exact location of the "hot particle" is circled in Fig. 2.2.E and enlarged in Fig. 2.2.F. Although the bulk concentrations of U and Pu in this sediment are very low, the concentration in that specific particle is high.

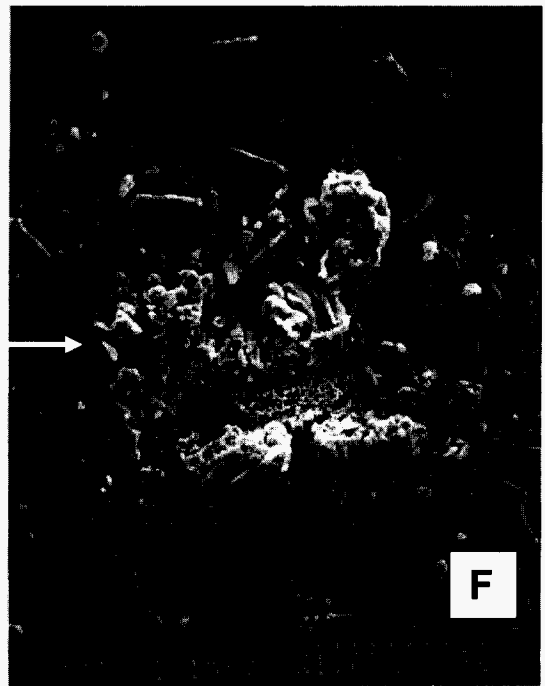
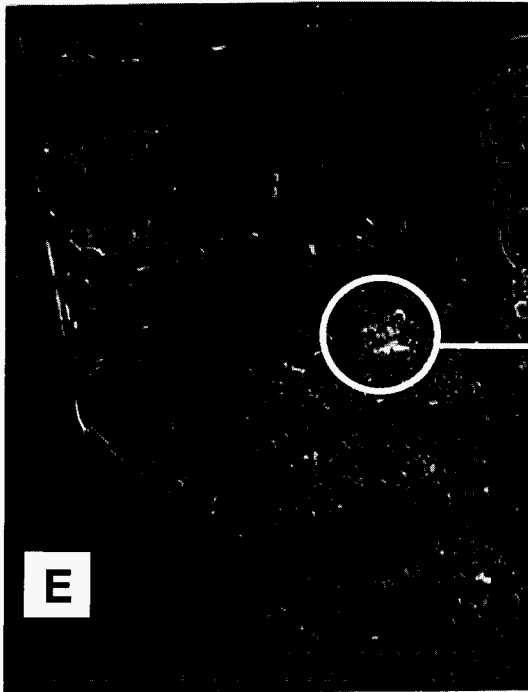
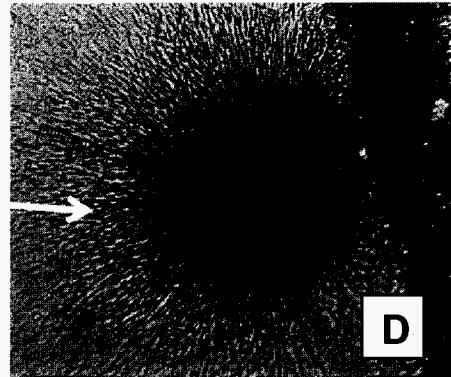
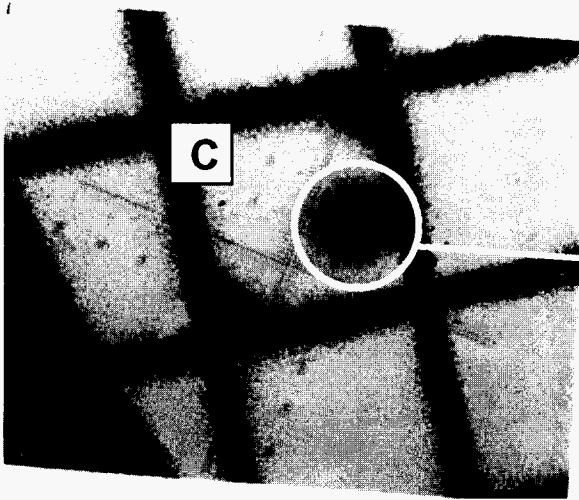
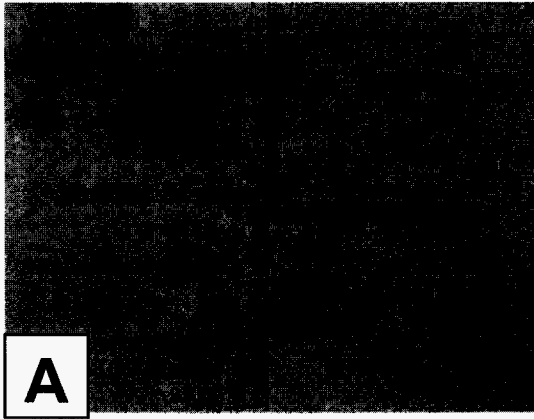
Figure 2.2 (next page): Fission track analysis of soils and sediments contaminated with ^{235}U or ^{239}Pu . (A and B) A fission track image obtained from FTA of a sediment from the Savannah River Site in SC. This sediment was collected from a reservoir used as a secondary cooling system for a defense production reactor. The sediment was contaminated with U and Pu due to leaks in the fuel system. Sediment particles were immobilized into a cellulose pellet [] and placed in contact with a fission track detector. The "star-burst" patterns demonstrate that ^{239}Pu is partitioned to discrete particles.

(C and D). Fission track images of SEM grids superimposed with ^{235}U - or ^{239}Pu -laden soil particle. A single "hot particle" that generated many fission tracks is circled in yellow in C and enlarged in D.

(E and F) A scanning electron microscopy image of the "hot particle" identified and located from images C and D. Notice that the SEM image in E and the FTA image shown in C are almost exact overlays. The particle that generated the fission tracks is circled in yellow in E, and magnified in F. Notice that the "hot" particle material is different from the other, surrounding soil materials.

Note that energy dispersive x-ray analysis of the particle shown in the SEM image was attempted, but the quantity of U or Pu was not large enough to detect. Thus, no elemental information was obtained.

Figure 2.2



While FTA is useful for determining extremely low concentrations of ^{235}U and ^{239}Pu and can provide information on the two-dimensional spatial distribution of these isotopes in a sample, it does not provide chemical information about the particle, or information on the solid:water interface. For example, elemental composition of the particle is useful for understanding the chemistry of sorption to that surface. Microprobe techniques such as energy dispersive x-ray analysis (EDX) coupled with SEM sometimes provides elemental information, but we were unsuccessful obtaining meaningful EDX data on the particle shown in Figure 2.2.E. We have studied the particle using synchrotron-based x-ray microprobe fluorescence (synchrotron x-ray microanalysis, SXMA), and obtained limited elemental composition information as shown in Figure 2.3.

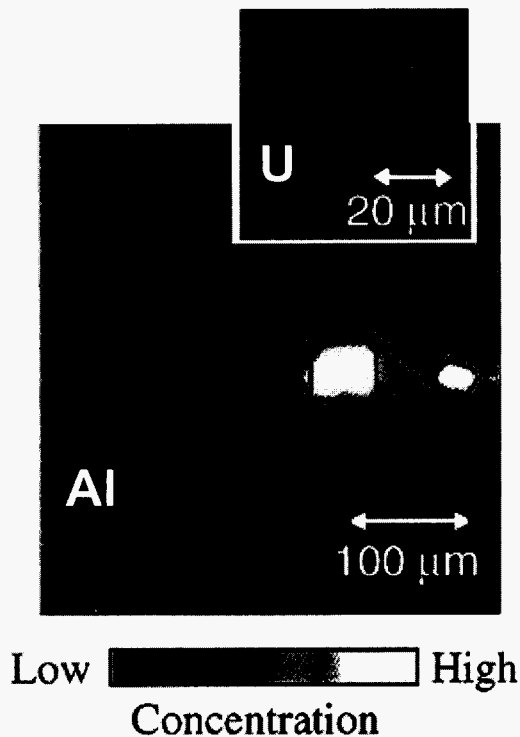


Figure 2.3: Synchrotron x-ray microprobe analysis (SXMA) image of the contaminated particle shown in Fig. 2.2 (C-F). The particle is composed primarily of Al, consistent with the large quantity of aluminosilicate clay minerals typically present in the sediments. In addition, the microprobe results indicate that U is co-associated with the clay mineral (top expanded region). The combination of the SEM and fission track work enable location of the particle, but the most useful elemental analysis information was obtained from the synchrotron x-ray fluorescence work. Note, however, that SXMA is not sensitive to natural organic matter that might be present on this particle.

3.0 Specific Progress and Accomplishments with Current NEER Funding

From the period of 5/1/00 to 4/31/03, NEER funding at WSU has been used to support the fission track work that we have completed to date. This research has resulted in the generation of three peer-reviewed publications:

1. S. B. Clark, M. H. Lee, and H. Kurosaki (submitted), "Spatial Locating Systems for Fission Track Analysis of Environmental Particles", *Radiochimica Acta*.
2. H. Kurosaki, S. P. Lamont, R. Filby, S. B. Clark, and D. R. Peterman (in press), "Developing Combined Fission Track Analysis and Alpha Track Analysis to Study the Spatial Distributions of U and Pu Sorbed to Environmental Particles", *Journal of Nuclear Science and Technology*.
3. S. M. Loyland-Asbury, S. P. Lamont, and S. B. Clark (2001), "Plutonium Partitioning to Colloidal and Particulate Matter in an Acidic, Sandy Sediment: Implications for Remediation Alternatives and Plutonium Migration", *Environmental Science & Technology*, **35**(11), 2295-2300.

The following manuscript is currently in preparation and will be submitted for peer-review in Nov., 2002:

4. S. B. Clark (in preparation), "The Chemistry of the Partitioning of U and Pu to Soils and Sediments", in *Radioanalytical Methods for Waste Management and Environmental Restoration Activities*, K. Nash and C. Laue, eds., American Chemical Symposium Series; to be published in 2003.

In addition to the manuscripts listed above, results have been presented at various technical conferences, including American Nuclear Society meetings, and in various symposia organized within the Division of Nuclear Chemistry and Technology of the American Chemical Society. NEER funding at WSU has also been used to support the graduate and post-graduate education of students who are now employed as radiochemists. These former students are:

Dr. Stephen P. Lamont, Ph.D. Radiochemistry, WSU, 2000; currently employed as a radiochemist by Westinghouse Savannah River Company.

Mr. Hiromu Kurosaki, M.S. Radiochemistry, WSU, 2002; currently employed as a radiochemist by National Institutes of Standards and Technology.

The NEER funded activities at WSU also supported a graduate student and visiting scientist at WSU. Unfortunately because no additional NEER funding was received, they are no longer supported by DOE-NE:

Ms. Rosara Payne, Ph.D. graduate student in radiochemistry at WSU; expected graduation date is 2005.

Dr. Myung Ho Lee, Visiting Scientist (radiochemist) from Korean Atomic Energy Research Institute, in residence at WSU during the period of Feb. 2002 – Feb. 2004.

4.0 Literature Cited

- ¹ MacDonald, J. A. *Environ. Sci. Technol.* **1999** 33(15) 314A-319A.
- ² *Accelerating Clean-up: Paths to Closure*, 1998. U.S. Department of Energy, DOE/EM-0362; <http://www.em.doe.gov/closure/final/index.html>.
- ³ *Groundwater & Soil Cleanup*, 1999. National Research Council. National Academy Press: Washington D. C.
- ⁴ *Long-term Institutional Management of U.S. Department of Energy Legacy Waste Sites*: 2000. National Research Council, Board on Radioactive Waste Management, National Academy Press: Washington D. C.
- ⁵ S. M. Loyland-Asbury, S. P. Lamont, and S. B. Clark (2001), "Plutonium Partitioning to Colloidal and Particulate Matter in an Acidic, Sandy Sediment: Implications for Remediation Alternatives and Plutonium Migration", *Environmental Science & Technology*, 35(11), 2295-2300.
- ⁶ S. M. Loyland, M. Yeh, C. Phelps, and S. B. Clark (2001), "Effects of Supercritical Fluid Extractions on Metal Ion Partitioning as Indicated by Sequential Extractions", *Journal of Radioanalytical and Nuclear Chemistry*, 248(2), 493-500.
- ⁷ Mincher BJ, Fox RV, Holmes RGG, Robbins RA, Boardman C (2001) "Supercritical fluid extraction of plutonium and americium from soil using thenoyltrifluoroacetone and tributylphosphate complexation", *Radiochimica Acta*, 89 (10): 613-617.
- ⁸ S. M. Loyland, S. E. Herbison, S. M. Lamont, and S. B. Clark (2000), "Study of Plutonium Partitioning to Contaminated Sediments", *Radiochimica Acta*, 88(9), 793-798.
- ⁹ Clark, S. B.; Johnson, W. H.; Malek, M. A.; Serkiz, S. M.; Hinton, T. G. *Radiochim. Acta* **1996** 74, 173.

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- ¹⁰ H. Kurosaki, S. M. Loyland Asbury, J. Navratil, and S. B. Clark (in press), "A Flow-through Sequential Extraction Approach Developed from a Batch Extraction Method", *Environmental Science & Technology*.
- ¹¹ Keon, N. E.; Schwartz, C. H.; Brabander, D. J.; Harvey, C.; Hemond, H. F.; *Environ. Sci. Technol.* **2001** *35*, 2778-2784.
- ¹² Ahnstrom, Z. A. S.; Parker, D. R.; *Environ. Sci. Technol.* **2001** *35*, 121-126.
- ¹³ Dollar, N. J.; Souch, C. J.; Filipelli, G. M.; Mastalerz, M. *Environ. Sci. Technol.* **2001** *35*, 3608-3615.
- ¹⁴ G. A. Smith, Fractionation of Actinide Elements in Sediments Via an Optimized Protocol for Sequential Chemical Extractions, Masters Thesis, Florida State University, 1998
- ¹⁵ Schultz, M. K.; Burnett, W. C.; Inn, K. G. W. *J. Environ. Radioactivity* **1998** *40(2)*, 155-174.
- ¹⁶ Schultz, M. K.; Inn K. G. W.; Lin, Z. C.; Burnett, W. C.; Smith G.; Bielgalski, S. R.; Filliben, J. *Appl. Rad. Isotopes* **1998** *49(9-11)*, 1289-1293.
- ¹⁷ Schultz, M. K.; Bielgalski, S. R.; Inn, K. G. W.; Yu, I.; Burnett, W. C.; Thomas, J. L. W.; Smith, G. E. *J. Environ. Monitoring* **1999** *1(2)* 183-190.
- ¹⁸ National Research Council, 1999. *Groundwater and Soil Cleanup*. Washington DC, National Academy Press.
- ¹⁹ Phelps CL, Smart NG, Wai CM, "Past, present, and possible future applications of supercritical fluid extraction technology", *JOURNAL OF CHEMICAL EDUCATION* **73** (12): 1163-1168 DEC 1996
- ²⁰ H. Kurosaki, S. Lamont, R. Filby, S. B. Clark, and D. R. Peterman (in press), "Developing Combined Fission Track Analysis and Alpha Track Analysis to Study the Spatial Distributions of U and Pu Sorbed to Environmental Particles", *Journal of Nuclear Science and Technology*.