Rocky Flats Environmental Technology Site
Actinide Migration Studies
Meetings July 7-8, 1999
Advisory Group Greg Choppin, David Clark, David Janecky, Leonard Lane

Results and Discussions

Solar Ponds

The discussion of the treatability studies and the volumes of nitrate and uranium involved was very informative The isotopic data on uranium from High Resolution ICP/MS indicate that uranium really has not moved much from where it was originally deposited While uranium was initially placed in the ponds in the form of uranyl nitrate, subsequent precipitation is likely to have occurred, rendering the uranium *relatively* immobile For sample sites just below the plume extent indicated by the HR ICP/MS analyses, the value of a baseline analysis using Thermal Ionization Mass Spectrometry (TIMS) should be evaluated

Update on Redox Experiments

As part of the redox experiment studies, a hypothesis was developed regarding the potential to generate reducing conditions by microbiota Soil cores were taken from a B series pond and the interceptor ditch Pond soils showed a change in E_h ranging from +0 96 mV at the water-sediment interface to –190 5 mV at 4 inches below the interface This latter reducing potential was similar to that reached by Honeyman in laboratory redox cell experiments Sediments were sealed in columns with and without nutrients and a carbon source Four soil cores were "sterilized" using gamma radiation at Oregon State University to kill any microbiological activity and serve as experimental blanks The columns were heated to 35C to rapidly generate microbiological activity Samples were taken (nominally with sterile technique) and monitored for "operational solubility" of redox sensitive metals (Fe and Mn) as judged by 0 45um filter passing experiment

The samples were incubated for up to 24 days and then stopped The largest reducing potential was found to be –380 mV with pH values approaching 6 8 Dissolved iron "operationally defined" was observed, and Fe^{2+} was quantified using a bipyridine titration to form an Fe(II) bipyridine complex Manganese concentrations also were found to increase, but the Mn oxidation state was not quantified These experiments demonstrate nicely that one can generate reducing conditions, and that such conditions can cycle the oxidation states of Fe and Mn from pond sediments and interceptor ditch soils The observed redox cycling of Fe and Mn was anticipated from the work of Werner Stumm, and the present data illustrates that cycling can take place at RFETS Of real interest for the migration of plutonium, is whether these reducing conditions will result in the eventual release of plutonium At the July meeting, we didn't know anything about Pu concentrations, but these data will be available at the close of the project, at which time this important relationship will be known There are also some additional questions regarding experimental technique, but we feel that we should wait for the final report for a full experimental writeup

Industrial Area Strategy (Environmental Remediation)

Lane Butler gave an overview of the Industrial Area Strategy The main drivers for the strategy were future land use and protection of surface water quality There is relatively good recognition that there is a balance that needs to be found between site characterization and environmental restoration However, there are some potential pitfalls with respect to the coupling of D&D with ER activities

Conceptual Model and future developments

The Conceptual Model and its presentation on the afternoon of July 7, 1999 went well and prompted the Advisory Board to suggest to Christine Dayton to consider bring a polished version of the Conceptual Model to a web site for broader dissemination within the Site and to the public We feel this is necessary because of the central role the Conceptual Model plays in coordination of Site activities and in communicating with the public

903 Pad Characterization Results and Path Forward for Remediation

The data set obtained from field HPGe measurements and laboratory measurements of soil samples is excellent The RFETS team is encouraged to apply krigging methods to this data set to refine and evaluate the direct analysis of soil contamination and uncertainties in this area as it relates to remediation approaches and decissions

Tours: Old Landfill, 800 area

A tour was conducted for the actinide chemists of the advisory group We visited the original landfill and discussed its past history and future disposition We then visited a series IHSS sites in the 800 area Of particular interest were process waste leaks, drum storage areas, footing drain outfall, and status of sumps

Tours: Buffer Zone and Erosion Modeling sites

We visited gauging sites with water quality sampling on Woman Creek The flow is measured with Parshall flumes and pump samples are taken with and Isco pump sampler which collects water samples for determination of suspended sediment concentrations Notable were the flow gaging capacities of these sites, estimated by Win and Greg to be on the order of the 2 to 5 year return period peak discharge rates If this is the general case of flow monitoring sites, the monitoring network may be under-designed with regard to calibrating the WEPP model over a range of representative flow rates In an attempt to ascertain if this informal observation is accurate, on behalf or the Advisory Board I have asked for descriptive tables of the flow monitoring sites indicating the site description, location, period of record, mean and standard deviation of annual runoff volumes, etc Also, we request DQOs and written QA/QC procedures for the hydrologic data collection and processing activities The purpose of these tables and the data they contain is to allow an overview of the hydrologic network and its

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adequacy for monitoring a sufficient time series of runoff rates and volumes and sediment concentration/yield data to assist in calibration of the WEPP soil erosion model

Additional sites such as the diversion ditch below Pad 903 and the A, B, and C series of ponds were observed and their role in trapping sediment and associated contaminants was discussed Maps of the site showing these facilities were obtained and will be used to raise further questions on the erosion and transport modeling as appropriate

Introduction to D&D and Concrete Leaching Studies (Industrial Area Strategy)

The strategy for D&D activities in the Industrial Area was presented for the 2006 closure plan The integration and handoffs between D&D and ER are getting some attention, and we will continue to evaluate this interface One area raised by during the D&D presentation is the stability of contaminated concrete, particularly for plutonium This problem is parallel to the plutonium in soils and sediments question on which the Actinide Migration Evaluation group has spent considerable effort Review of the BNFL report on the behavior of buried contaminated concrete indicates two major knowledge gaps (1) the crystallinity of plutonium solid phase is a crucial unknown factor in determining the mobility and solubility, and (2) all of the collected previous laboratory experimental work has determined solubility from supersaturation and for fresh precipitates of aqueous plutonium Freshly precipitated plutonium as hydroxide and/or oxyhydroxide results in solubilities identical to those reported in the BNFL report on the order of 10^{-9} moles/L (approximately $2x10^{4}$ pCi/L), while the thermodynamic solubility of crystalline PuO_2 is approximately 10^{-17} moles/L ($2x10^{-4}$ pCi/L) [Efurd and others, 1998, ES&T v32, p3893] At least two sources of plutonium contamination of concrete can be identified at Rocky Flats (particulate transport during fires and solution spills), and all of the material has aged substantially in a relatively uncontrolled environment The chemistry and state of these plutonium contaminants can be evaluated using state of the art spectroscopy, supported by other conventional laboratory and material science characterization tools, to provide information on the detailed structural and spatial distribution of actinide and cement products

Documents provided to advisory group

- Solar ponds plume viewgraphs
- Water quality-monitoring memo of June 21, 1999
- Industrial area characterization and remediation strategy view graphs
- Notes on experimental work of Ranville and Honeyman
- Harnish, McKnight and Ranville (1994) USGS WRI Report 93-4175
- Summary of 2006 Rocky Flats closure project baseline A brief overview
- Response to Kirk Nordstrom data action items identified on May 12, 1999
- A literature review on the behavior of buried contaminated concrete over time and relevance to plutonium, americium and uranium contamination at the Rocky Flats Environmental Technology Site BNFL, Inc report submitted to RMRS

Documents and information requested for advisory group

- For surface water monitoring data from 3/23/94 to 10/28/97, we have previously received plutonium and americium concentrations and uncertainty data from the RFETS databases Is there corresponding flow rates, flow volumes, and TSS data for these samples and locations that can be provided electronically?
- For surface water monitoring data since 10/28/97, a similar data set by location, date, and sample number for plutonium, americium, flow rates, flow volumes, and TSS (amount and uncertainty) is requested

Participants in AMS technical meetings

Name	Organization
Mike Peters	RMC/QA
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Lane Butler	Kaiser-Hill

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Plutonium Speciation and Distribution in Soil Samples from the Rocky Flats Environmental Test Site

Los Alamos National Laboratory Report

Principal Investigators: Mary Neu, Wolfgang Runde
Investigators: M.A. Lin, D.M. Smith, S.D. Conradson, A. Wong

June 15, 1999

Background:

The DOE is currently conducting cleanup activities at its nuclear weapons development sites, many of which have accumulated plutonium in soils for 50 years To properly control Pu migration in soils within Federal sites and onto public lands, better evaluate the public risk, and design effective remediation strategies, a fundamental understanding of Pu speciation and environmental transport is needed The key scientific goals of the EMSP project we are conducting are to determine Pu concentrations and speciation at a contaminated DOE site, to study the formation, stability, and structural and spectroscopic features of environmentally relevant Pu species, to determine the mechanism(s) of interaction between Pu and Mn/Fe minerals and the potential release of Pu via redox cycling, and to model the environmental behavior of plutonium Our long-term goal is to use characterization, thermodynamics, mineral interactions, and mobility data to develop better models of radionuclide transport and risk assessment, and to enable the development of speciation-based decontamination stategies

This research will fill important gaps between basic actinide science and the problems impeding site clean-up, plutonium disposition, and accurate risk assesment Information gained will allow for the development of technologies and clean-up approaches targeting particular plutonium contaminants and improved assessment of risks associated with actinide migration, site remediation, and decontamination By combining very specific study of plutonium at the Rocky Flats Environmental Test Site (RFETS), a well-characterized contaminated site, with laboratory studies on the most important plutonium and mineral component systems, we will provide essential knowdege of contaminant characteristics and distinguish critical geochemical processes and mechanisms Herein we report summarize our results on characterizing samples from RFETS

Technical Description of Work:

To determine Pu concentrations and speciation at RFETS we are using Thermal Ionization Mass Spectrometry (TIMS) to measure the isotopic $^{240}Pu/^{239}Pu$ ratio and identify the plutonium as originating from global fallout or site activities For those water and soil samples having the highest concentrations we are using x-ray absorbance spectroscopy to determine the oxidation state and local coordination geometry (speciation) of the Pu For particular samples we are performing physical separations and radionuclide counting to determine the characteristics of fractions containing portions of the Pu to determine overall concentrations, for example, size fractionation to determine the grain/soil size having the highest Pu concentration—macroscopic localization We are using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) to determine the morphology of components within samples, degreee of microscopic localization, and association of Pu with other elements in soil samples   And we are using x-ray absorbance spectroscopy (XAS, EXAFS) to determine the oxidation state and coordination environment of Pu in environmental samples

Samples from the RFETS which are most concentrated in Pu provide an opportunity to determine the speciation and other chemical and physical details of the contaminant Pu present   We have size fractionated soil samples from the 903 Pad area and analyzed each fraction using radionuclide decay counting, SEM, EDX, XAS, and decay radiography SEM secondary electron images showed that the Pu in the soil fractions was delocalized down to at least the 100Å scale   EDX analysis showed the samples were predominantly alumino silicates and that Pu was not correlated with any other elements (Al, Si, K, and O dominated the spectra, other elements were absent or present in only some spots at trace levels)   Particle track images are consistent with the SEM data, radiographs showed dispersed, omnidirectional tracks

X-ray absorbance experiments were difficult because the 'standard' L_{III} spectra were not informative due to the presence of elements which absorb in the same energy range Data were therefore obtained using the L_{II} absorption edge   Two of the fractions were sufficiently concentrated in plutonium to yield high quality spectral data   The near edge region of the spectrum has an absorbance maximum and edge indicative of Pu(IV)   In fact, just after this measurement we measured the L_{II} absorbance of pure solid PuO_2 and found the two spectra had the same features (edge, maximum, no near-edge 'shoulder' indicative of Pu(V) or Pu(VI)) at the same energies   Analysis of the EXAFS data for the more concentrated of these two samples indicates there are approximately eight nearest neighbor atoms at a distance of 2 33 Å from the Pu in the soil sample, consistent with PuO_2

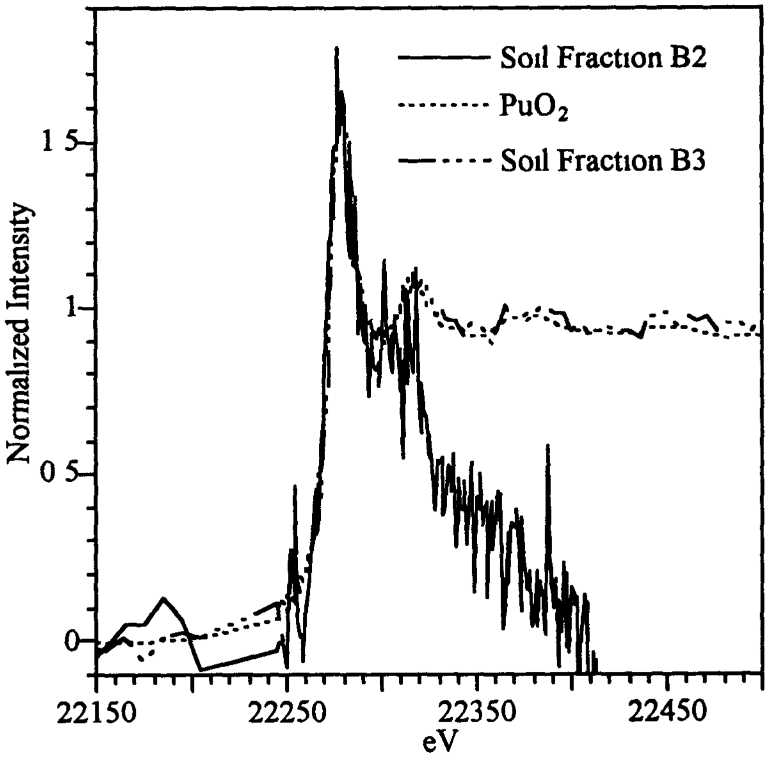
Not only is this the first definitive spectroscopic data on Pu in an environmental sample, but the data show the Pu in the most concentrated samples from the RFETS is in a highly stable and immobile form, the dioxide   The data also show that Pu is most concentrated in the 0 01-0 02 inch fractions, is dispersed on macroscopic and microscopic scales, and is not highly associated with any other particular element   These results should be very powerful and useful to RFETS personnel tasked with addressing concerns regarding plutonium migration from the site and for those tasked with remediating the site

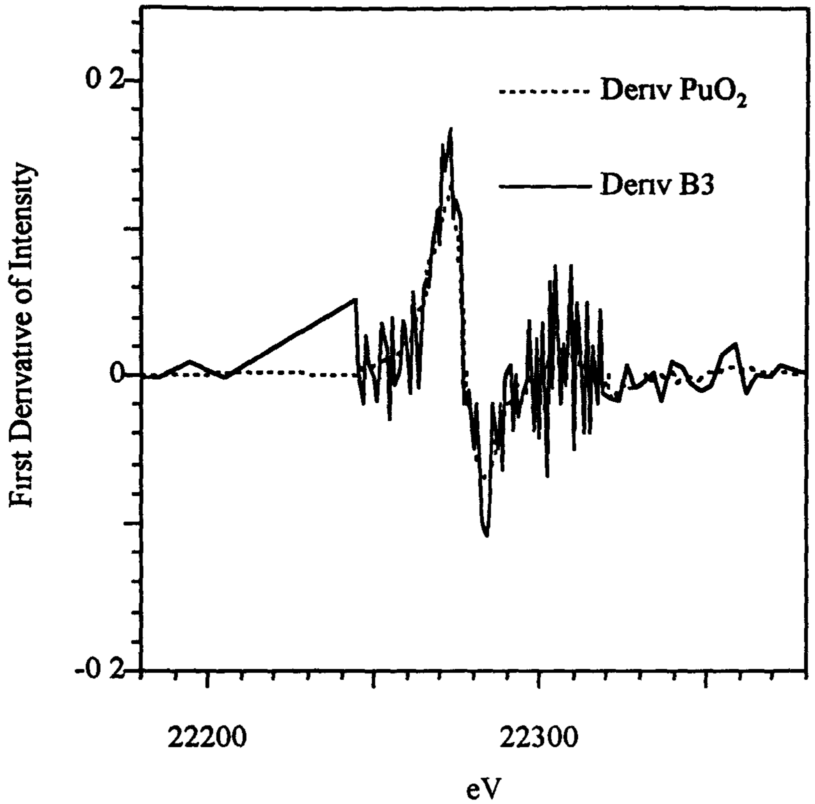
We attempted to determine the oxidation state and speciation of plutonium in several other samples, but in all other cases the concentration of Pu relative to other absorbing species was too low to obtain reliable, meaningful data   For example, a sample from a core from pond B-1 had a relatively high concentration of Zr or another element which has an absorption edge very close in energy to the Pu edge   (Zirconium has an absorption edge at 17999 35 eV, plutonium species have absorption edges of 18056, 18058, 18060 and 18061 eV for Pu III-VI, respectively)   We did not observe an absorption edge corresponding to the Pu in this soil sample   We may attempt to measure the x-ray absorption of samples in this concentration range after a pre-concentration step

Table 1   Fractionations of soils from the RFETS and Gross Gamma Counting Results

	Size	Net CPS/g

		gross gamma 241Am
A1	> 0234 inch	
A2*	0 0234-0 0164 inch	8 995
A3	0 0116-0 0164 inch	22 97
A4	>0 0116 inch	8 832
B1	> 0234 inch	
B2	0 0234-0 0164 inch	30 2
B3	0 0116-0 0164 inch	41 71
B4	>0 0116 inch	78 19




First Derivative of Intensity
0 2
0
-0 2
Deriv PuO2
Deriv B3
22200
22300
eV