

**Rocky Flats Environmental Technology Site: Actinide Migration Evaluation**

Meetings October 12-13, 2000

Advisory Group

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**Summary and recommendations for path forward**

ER Sampling Analysis Plan should be coordinated with the pathway analysis

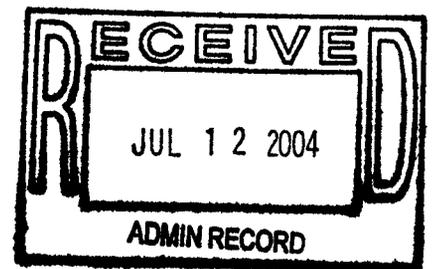
- Key point is "What is the minimum sampling intensity that will guarantee with a specified probability that no unsampled sources in the process waste lines exceed a specified level?"
- DQO's for sampling should reflect pathway analysis

Water Balance Project appears to be formulated and well planned, but must be well coordinated with the erosion modeling and final configuration with the erosion modeling and final configuration projects to avoid duplication and for consistency in qualifying pathways

We need to know, soon, what the post closure meteorological and hydrological network configuration DQO's, etc are if we are to make useful monitoring network recommendations

**Progress and integration**

The Pathway Analysis Report is progressing and we continue to see this document as a major advance in documentation of the conceptual models for actinide migration at Rocky Flats Integration of Industrial Area, Environmental Remediation and Actinide Migration Evaluation projects, plans and results are essential and discussions at this meeting were very useful



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## **Results and Discussions**

### ***Erosion and Hydromonitoring***

On Wed Oct 11, 2000 a tour of selected hydrologic monitoring facilities at RFETS was conducted for technical representatives of the CAB, AME Advisory Group, RFETS, and others. The tour of these facilities was primarily in response to review comments on the Erosion Report by Dr T E Hakonson. The tour included the following facilities and discussion leaders are shown in parentheses

- 1 Gaging Station GS01 (Squibb)
- 2 GS01 Sediment Pump Sampler (Squibb) The existing pump sampler was observed and the strengths and limitations of sampling at a fixed flow depth were discussed. Primary discussion topics included suggestions to analyze existing sediment concentration data for their particle size distribution and the possibility of including a slot sampler to collect vertically integrated sediment samples. These data are necessary for particle size analysis and actinide concentrations, by particle size, to obtain more representative sample throughout the depth of flow. Particle size data, and associated actinide concentrations, would be of benefit in further calibration and validation studies of sediment and actinide transport modeling at RFETS.
- 3 Woman Creek Diversion (Wetherbee) The main discussion topics here included channel erosion processes, channel hydraulics, erosion and sediment transport modeling, and the recently completed erodible-sediment measurement and mapping. The erosion modeling team will re-examine the HEC6T channel erosion modeling to reflect the channel erosion occurring at headcuts and in channel reaches with erodible sediments.
- 4 Gaging Station GS42 (Chromec) Detailed discussions were held at this site. The small watershed above GS42 was an important site for WEPP hillslope modeling and in situ soil particle size-actinide concentration sampling. Participants discussed the possibility of installing small runoff/sediment sampling plots on this hillslope to obtain measurements of sediment particle size distributions in overland flow and their associated actinide concentrations as functions of sediment particle size. Data such as might be collected on experimental plots here would help test the assumed sediment particle size-actinide concentration relationships used in the WEPP model.

### ***Site-wide Water Balance – J. Thomson***

The Site Wide Water Balance (SWWB) model and a work plan were presented by J Thomson of Applied Hydrology Associates, Inc (AHS). Several important topics were discussed during this presentation. Overall, the Project seemed well conceived by RFETS and well planned by AHS. Conceptual model formulation, simulation model selection, and modeling strategies were presented and discussed. The project appears to be well formulated and should be closely coordinated with the erosion modeling and site configuration projects to ensure the maximum possible use of common climate data sets, site characterization data, hydrologic monitoring, etc to avoid duplication of efforts.

and to integrate the modeling and configuration projects for consistency in pathways analysis. In addition, information exchange on strategies, methods and results should be pursued with other sites in the DOE complex, particularly with work developing in the Subsurface Contamination Focus Area.

***D&D Planning / Pu in Concrete Studies – J. Stevens (with supporting documentation from S. Conradson)***

**X-ray Absorption Spectroscopy of RFETS Samples.** X-ray absorption measurements were performed at Stanford Synchrotron Radiation Laboratory by Dr. Steve Conradson and co-workers on a series of well-characterized standard compounds, followed by samples of RFETS contaminated concrete and soils. There are principally two kinds of information that can be obtained from these sophisticated measurements. By looking at changes in the energy of the x-ray absorption, one can extract valuable information on the oxidation state of plutonium. This is done by a technique known as X-ray Absorption Near Edge Structure (XANES) spectroscopy. By careful analysis of the fine structure that appears in the x-ray absorption spectrum, one can deduce the local structure around the plutonium atom by determination of the local bond distances, and therefore determine a great deal about the chemical form of plutonium. This latter technique is referred to as X-ray Absorption Fine Structure (XAFS) spectroscopy. When both phenomena are examined together, the X-ray absorption techniques provide a very powerful speciation tool for environmental samples. One caveat is that this technique is not well suited for dilute samples, which is typically the case in the RFETS environment. This means that one must find RFETS samples with enough plutonium present to actually perform the studies. So far, this technique has provided some valuable information about the oxidation state and chemical form of plutonium in soils from the 903 Pad, and from contaminated concrete samples from some buildings.

**Oxidation state determination using XANES spectroscopy.** In X-ray absorption spectroscopy, there are characteristic energies where x-rays are strongly absorbed by the sample. It is these characteristic energy regions (referred to as absorption edges) where x-rays are strongly absorbed that we use in x-ray absorption spectroscopy. These absorption peaks will vary in energy as a function of plutonium oxidation state, and will show fine structure changes as a result of chemical bonding changes. For plutonium studies, researchers prefer to use the L<sub>III</sub> edge, which appears near 18,060 eV because it has the highest absorption intensity. However, in RFETS environmental samples there are many other elements present which interfere. Therefore, the plutonium x-ray absorption studies were performed instead at the L<sub>II</sub> edge, which appears near 22,270 eV. This absorption edge has a lower intensity than the L<sub>III</sub> edge, making the RFETS samples even harder to study using x-ray absorption spectroscopy. A calibration experiment was run using plutonium standards in oxidation states 0, III, IV, V, and V, which showed the expected increase in edge energy position.

with increasing oxidation state. The  $L_{III}$  and  $L_{II}$  XANES spectra were nearly identical, giving high confidence in the use of the  $L_{II}$  edge for RFETS samples. RFETS soil and concrete samples were measured along with the standards, and concrete samples that were "spiked" with Pu(IV) and Pu(VI) standards. The Pu XANES spectra of the soil and concretes samples were not only clearly consistent with Pu(IV), but were identical within the experimental uncertainties to the  $PuO_2$  standard. Of interest to many in both the scientific and local communities is the recent report of a new form of plutonium oxide,  $PuO_{2+x}$ . An authentic sample of composition  $PuO_{2.2}$  was also examined by XANES spectroscopy, which revealed the presence of a mixture of Pu(IV) and Pu(V). Of relevance to RFETS is the fact that this XANES spectrum is very different in energy than either  $PuO_2$ , the soil or the concrete samples. The XANES measurements on RFETS soils and concretes clearly show that the oxidation state of plutonium is Pu(IV), and the XANES spectral signatures are very similar to that of  $PuO_2$ .

**Local Chemical Structure Determination Using XAFS** The X-ray Absorption Fine Structure (XAFS) data can be curve-fit to extract the number of near-neighbor atoms at different bond distances in order to determine chemical structure information. As an example, consider that from the crystalline structure of  $PuO_2$ , there are eight Pu-O distances at 2.33 Å, and 12 Pu-Pu distances at 3.86 Å. This is precisely the kind of information that can be extracted from fitting of the XAFS data, although for dilute environmental samples, the amount of uncertainty in the actual number of atoms at a given distance is of less value than the bond distances themselves. The actual XAFS data and fits can be examined in two primary ways. One method is to compare the actual oscillatory waveforms of each sample, to the waveform that is calculated from the curve fit to the data. This method has been used for the standards and the RFETS samples, but is too complex to really describe in a simplified form here. From such a comparison it is clear however that the standards are all different from one another, and that the RFETS soils and concrete samples are nearly identical to the XAFS waveform of  $PuO_2$ . For non-experts, a more useful and intuitive way to examine the data is to look at the Fourier transform of the data and the fit. The Fourier transform gives a distinct peak for each interatomic distance in the sample. In the example of  $PuO_2$ , the Fourier transform and fit both show peaks for Pu-O at 2.33 Å, and Pu-Pu at 3.86 Å. This is unique for  $PuO_2$ . Other samples show peaks at different distances making it fairly easy to see how the XAFS of different compounds will show different numbers of peaks and at different interatomic distances. This is a very powerful tool for determining the chemical form of an environmental contaminant.

The XAFS Fourier transforms for the standards are all different from one another as expected. The XAFS Fourier transforms of the RFETS soils and concrete samples are nearly identical with that found for  $PuO_2$  with one small exception. In addition to interatomic distances of 2.33 and 3.86 Å, the RFETS

soil and concrete data show some small peaks at intermediate distances between 2.33 and 3.0 Å which are consistent with additional Pu-OH or Pu-OH<sub>2</sub> interactions expected for hydrated PuO<sub>2</sub> in the environment. This was verified experimentally by examining the XAFS of a number of laboratory-prepared samples of hydrated PuO<sub>2</sub>. The appearance of these additional peaks is expected for PuO<sub>2</sub> in the environment, and is consistent with association with water. It is essentially identical to the everyday use SiO<sub>2</sub> (silica gel) to absorb water by placing SiO<sub>2</sub> packets in camera cases and other optical equipment. The SiO<sub>2</sub> absorbs water to form SiO<sub>2</sub>·xH<sub>2</sub>O. The process is reversible with heating. It is important to note that the ability to associate water in SiO<sub>2</sub> or PuO<sub>2</sub> does not alter the solubility. It is also important to note that XAFS of PuO<sub>2</sub> and the PuO<sub>2</sub> found in soil/concrete samples is uniquely different from the XAFS of the standards. Of interest to the site and the public is the question of whether this XAFS could be consistent with the recently reported PuO<sub>2+x</sub>. The XAFS of PuO<sub>2.2</sub> was radically different from that of PuO<sub>2</sub>. In particular, the PuO<sub>2.2</sub> shows an additional Pu-O peak at 1.84 Å that is not present in PuO<sub>2</sub>.

From comparison of the XANES and XAFS of the standards, the RFETS soil/concrete samples, and the spiked samples, it is clear that plutonium in RFETS soil and concrete analyzed to date is in oxidation state IV, and that the chemical form is that of a hydrated PuO<sub>2</sub>. It is also clear that plutonium in these RFETS soils and concrete is NOT in the form of PuO<sub>2+x</sub>. This is an important experimental confirmation of our expectations of plutonium behavior in the environment.

### ***IA Strategy – L. Norland***

The approach being used to develop the functional design criteria, which can lead to establishing the significant parameters for a model of the final design, for the Rocky Flats Site was described. It was stressed that adequate data on actinide migration, water balance, etc. is needed to allow initial work on a conceptual design for the site by FY 2002. A major driver is protection of the water to meet the defined end state (0.15 pCi/L at present). The strategy as described, is to clean to action levels and, then, ensure that the cleaned area cannot be recontaminated through the use of barriers, dams, removal of sources, etc.

It was stated that pipes of process, drains, etc. lines may be removed to some undefined depth below which the residual pipes would be capped and left in place. In answer to questions, it was stated that these residual lines could be flushed to remove remaining contamination. However, residual plutonium contamination may not be fully removed by such flushing. Consequently, as described in this presentation, it is not clear that such capping would not leave in place contaminated pipes with unknown levels of contamination and which constitute sources of future releases as the pipes corroded over hundreds of years.

Either all the buried lines should be removed or a program put in place to clean the pipes to be left in place and the amount of residual contamination determined prior

to final capping of these pipes Leaving capped, buried pipes with unknown levels of plutonium contamination does not seem to be an acceptable policy

### ***ICP/MS Uranium Results – S. Singer***

The results of uranium isotopic analyses were presented during the Stakeholder Meeting Clear differentiation of natural uranium in comparison to RFETS contamination uranium has been demonstrated with this data set In addition, evaluation of duplicate and QA/QC samples analyses indicates very good consistency in the results The diversity of potential sources and use of both depleted and enriched uranium at the site makes evaluation of processes and mixtures among the three components (enriched, depleted and natural) difficult based simply on isotopic data on GIS maps of the site provide a better approach, however, a series of simplified maps needs to be generated using all of the data Recommended plots are 1) simple differentiation of contaminated sample well locations based on  $^{236}\text{U}$  results with dot size proportional to total  $^{236}\text{U}$  concentration and 2) differentiation of sample well locations by amount of  $^{236}\text{U}$  and enriched, depleted or natural  $^{235}\text{U}/^{236}\text{U}$  concentrations In addition, locations of wells that were not sampled or that have not yet been analyzed should be identified No well numbers should be plotted on these maps The results of these mapping plots will allow evaluation of isotopic and concentration trends, as well as, identification of sample gaps due to both selection of existing wells and gaps in well locations

### ***Uranium History / Use Update – L. Gregory-Frost***

This presentation reported on the initiation of an effort to review records and to interview long term and former Rocky Flats staff to develop an understanding of uranium usage at Rocky Flats, in which buildings was it handled, what forms and amount were released to the environment of the site and where did such releases occur This is a large task whose results could be of significant value to the uranium transport modeling, characterization of the type and amount of UBC of uranium, and in developing plans for monitoring during Deactivation & Decommissioning activities However, this could be a very large and lengthy task but if the information is to be used as proposed above, the data must be available within a year Therefore, it is suggested that a useful screening process be developed and used immediately to set priorities on what records, etc to pursue more intensively in order to produce a useful database within the time limitations If it is not possible to place such a screening process into use, more personnel must be put on this task or if it is not sufficiently important to justify additional FTE's, it should be abandoned Such data will be of use only if it is available for use in planning R&D, redemption, etc within the closure schedule

### **Documents provided to advisory group**

Geochemical Modeling of Solar Ponds Plume Groundwater at the Rocky Flats Environmental Technology Site - USGS - James Ball  
FY01 Actinide Migration Evaluation Draft Proposal - Peter H Santschi, Texas A&M University, 10/5/00  
Air Transport and Deposition of Actinides for the Actinide Migration Evaluation at the Rocky Flats Environmental Technology Site - FY00 Report  
Air Transport and Deposition of Actinides - FY00 Report Radian International  
Water Balance View Graphs  
Site Wide Water Balance Work Plan, 8/8/2000 (EDDIE)  
Status of Plutonium Chemistry in the Environment, The LANL Study, J Stevens, 10/12/00  
Report on Soil Erosion and Surface Water Sediment Transport Modeling for the Actinide Migration Evaluation at the Rocky Flats Environmental Technology Site, 8/2000 - T E Hakonson - Technical Review of Report  
Preliminary Outline (8/30/00) / Technical Appendix - Actinide Pathway Analysis Report  
Figure 22 - Draft Original Process Waste Lines  
Figure 24 - Original Process Waste Lines, New Process Waste Lines, Sanitary Sewer System and Storm Drains  
Figure 1 - Industrial Area Groups  
Potential CSM Investigations at RFETS FY 2001 - J F Ranville, B D Honeyman, Colorado School of Mines, Golden, CO 80401  
Final Report on Phase Specification of Pu and Am for 'Actinide Migration Studies at the Rocky Flats Environmental Technology Site' Peter H Santschi, 9/29/2000

### **Documents and information requested for advisory group**

Model Code & Scenario Selection Report for Water Balance Project  
DHI Presentation materials and web connections  
XAFS report of October 10, 2000  
Sampling and Analysis Plans (draft) for IA and Buffer Zone  
Comprehensive Risk Analysis Methodology  
OPWL, NPWL, sanitary, storm drains maps

### **Requests for Future Presentations and Information**

Laura Brooks - stewardship - request for presentation at future meeting  
Lane Butler - IA strategy (continue discussions and presentation of information)  
Solar Pond archive samples to define potential source term, information on other U sites and problems

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## Participants in AMS technical meetings

<u>Name</u>	<u>Organization</u>
Greg Choppin	FSU
David Clark	LANL
David Janecky	LANL
Kirk Nordstrom	USGS
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Rob Smith	RMRS
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Rick Roberts	Kaiser-Hill
Win Chromec	RMRS
Laurie Gregory-Frost	E2
Chris Hawley	International Engineering
John Corsi	Kaiser-Hill
Jim Thompson	Applied Hydrology
Bob Prucha	Applied Hydrology
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Jeff Stevens	Kaiser Hill
Bob Scheck	MacTec

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