Rocky Flats Environmental Technology Site
Actinide Migration Studies
Meetings October 21-22, 1998
Advisory Group Greg Choppin, David Clark, David Janecky, Kirk Nordstrom

Summary and recommendations for path forward

Particulate transport continues to be the dominant transport pathway identified for the Pu and Am actinides off the Site, based on surface water characterization, soil redox reaction process experiments and erosion modeling Experimental plans for characterization of redox processes, of surface water, and of site end-state concepts were presented and discussed Microbiologic processes coupled to redox reactions in soils and an approach to define experimental constraints were also discussed, including cognizant experts to be contacted during definition of a detailed experimental plan Use of a K_d approach for the Site as the overall summary of quantitative measures for risk and release calculations was discussed extensively We have included in this report our present evaluation of the limitations and caveats of such an approach in application to the complicated and nonlinear process of actinide migration at Rocky Flats Environmental Technology Site

Recently completed uranium isotopic analysis results were presented for selected solar ponds plume and background samples This work has significantly enhanced characterization of the contamination problem, and replaced simplified assumptions with quantitative data Coupled with these improvements in characterization, the geochemical modeling effort needs to define tests for our geochemical and transport understanding

We heard discussion of end-state planning and concepts, including removal of the retention ponds and re-engineering the drainage At this time, it remains unclear if site cleanup and the conceptual end-state will remove the problem of surface-water exceedances at the Site boundary The impact and detailed operations of wetlands versus settling ponds is not clear, given the present understanding of contaminant distribution and transport via surface water The Site might need to consider not removing ponds in some or all instances, and potential enhancement of surface water quality through reconfiguration or addition of ponds at other locations

Progress and integration

Characterization of redox processes, chemical/physical contaminant signatures (Pu and Am concentrations and ratios, U isotopics) and erosion modeling have advanced during the past year Definition of workscope for FY99 includes substantial opportunities for integration (as noted below) Integration and application of results should be a focus of AMS discussions during the year to maximize their value in application to site problems

Results presented

Bruce Honeyman – soil/solution redox reactions and actinide mobility characterization

Peter Santschi – surface water actinide component size fractionation and characterization

Craig Cawdry – uranium isotopic analyses of groundwater samples from the solar ponds plume and background sites

Plans presented and discussed

Mike Peters – RFETS closure project plans and end-state summary

Keith Motyl – RFETS surface water and end-state

Greg Wetherbee – End-state roadmap and FY99 plans

Discussion of FY99 efforts

Redox Studies.

The committee found the development and application of an electrochemical cell and use of redox indicators to be a very important study that goes a long way towards answering key questions of importance to the Site These studies indicate that the "operational" solubility of plutonium appears to decrease, while the solubility of americium is unchanged under strongly reducing conditions "Operational" solubility is defined as that measured in solution after using a filter sized to separate particulates, while recognizing that small particulates are expected to be within the filtrate It is stressed that these observation are only preliminary, and need to be confirmed or revised by determination of additional data points below +164 mV and between +164 to +800 mV during the upcoming FY Intermediate Eh points where Mn and SO_4/H_2S redox reactions occur in C-2 pond and soils should be examined, and the work should be augmented with some redox state modeling

The preliminary results suggest that reducing conditions decrease the amount of plutonium in the cell It is unclear at this time whether this is the result of precipitation, hydrolysis, sorption, or some other chemical reactions However, it is well known that Pu(V) is a predominant oxidation state for plutonium in dilute ground water environments Pu(V) has a rather low charge-to-size radius ratio, and is known to form only weak complexes with ligands Plutonium(IV) on the other hand, is known to form strong complexes with most ligands, and undergoes strong hydrolysis reactions, even at pH 1 These hydrolyzed plutonium compounds are very insoluble Therefore, the decreased solubility under reducing conditions may be interpreted in terms of chemical reduction of Pu(V) to Pu(IV), although the exact oxidation states have not been determined Americium is always in the form of Am(III), and should show similar solubility over the Eh range studied here

These preliminary observations begin to provide quantitative constraints on the hypothesis of Dr Litaor that under periods of prolonged and heavy rain events, waterlogging of soil produces anoxic conditions, and that reduction of plutonium to a lower oxidation state could mobilize plutonium The present

work indicates that strongly reducing conditions result in decreased mobility of plutonium

The Influence of Microbes on Plutonium Redox State.

A proposal was made to "incubate" a soil sample for a month, and then determine if microbial action would reduce plutonium to a lower oxidation state While this proposal has merit, it has not been well thought out Due to the complications of working with microbes, and the relative failure of bioremediation applied to actinides in general, we feel that such an undertaking should only be carried out after consultation with a microbiologist familiar with actinide chemistry issues A recommendation was made to first consult with Dr A J Francis (Brookhaven), and Betty Strietelmeier or Dr Jim Brainard (Los Alamos) If these microbiological experts feel that such an experiment has merit and are willing to help design such an experiment, it should be pursued If these experts can not envision a simple and meaningful experiment, then we recommend that this endeavor not be pursued

Filtration Studies.

By employing operational definitions of solubility as determined by filter-passing experiments, it was determined that that there is very little "dissolved" plutonium in solutions collected at gauging station GS03 Of particular importance is the observation that the majority of plutonium activity in solutions was found associated with particulate material, and that the concentrations of "dissolved" plutonium were only in the femto-molar range (10^{-15}M) Femto-molar concentrations of "dissolved" plutonium are similar to global fallout concentrations as measured around the world The observation of very small quantities of "soluble" plutonium in this surface water at RFETS provides quantitative information that "dissolved" plutonium is only of minor importance as a migration pathway, and that efforts should be focused on particulate and colloid-facilitated transport in surface waters at RFETS Preliminary analyses indicate that these particulates contain a high amount of organic carbon, consistent with the notion of colloidal material The determination of such ultra-low concentrations should be accompanied by QA/QC documentation to demonstrate the ability to determine such low concentrations of actinides using radioactive counting techniques This documentation can be developed between sampling campaigns

Conceptual Model Development.

The initial conceptual model document is now complete and has been released The Site is to be congratulated on completion of this important milestone The conceptual model is needed to serve as a guide to direct future research, and to help focus efforts on the needs of the Site in general, and on surface water quality in particular

Erosion Modeling.

The erosion modeling effort appears to be moving forward at a reasonable pace It is clear that when all the bugs are worked out, and the different hillside models are coupled together, it will be a valuable tool with which to probe various erosion scenarios Based on the observations of the ultra-filtration and redox studies in FY98, it appears "dissolved transport" may be quantitatively defined as a minor pathway in the conceptual model, shifting focus to primarily particulate transport pathways in FY99 The erosion model will be crucial for examining different particulate transport scenarios, and the possible effects of heavy rain events over many years This model will also be important in coming up with an independent prediction of the amount of plutonium that migrates on the 903 hillside during a heavy storm event This prediction should be compared with Dr Litaor's results and estimate that 0 5Ci of plutonium moved across the 903 hillside during a heavy storm events during May 1995

Uranium Geochemistry.

Jim Ball – Uranium geochemical modeling

The data available for evaluation of geochemical processes and transport (attenuation) modeling for the solar ponds plume was presented and discussed Gaps in water quality data and in the sampling well distribution were described The advisor's charge to the geochemical modeling investigators is to define tests based on the AMS thermochemical and transport network modeling conclusions It is expected that this could include new sampling locations and needs for sample component analyses at new and existing sampling locations, as well as proposal of coupled, reactive transport modeling for components of the hydrologic and plume systems

Craig Cowdery for Annette Primrose – results of uranium isotopic analyses on selected solar ponds plume and background samples

Results from an initial set of background and solar ponds plume samples, selected for ICP/MS analysis, were presented The implementation of isotopic analyses is an excellent step forward in characterizing the site and quantitatively defining extent and remediation requirements for the solar ponds plume This is how the integration of DOE remediation activities and research developments from Environmental Science Management Program (EMSP) are supposed to work We would like to see plans for further characterization analyses and information on how these results are impacting remediation actions and plans

RESRAD Modeling using K_d Values

There are major concerns associated with the use of K_d values, measured by Honeyman and Santschi, in the RESRAD model First, there are major uncertainties about these values, partially due to the use of data from simple extraction experiments The solution phase concentration includes PuO_2^+ and $Pu(OH)_m^{4-m}$ dissolved species as well as $PuO_2 \bullet nH_2O$ colloidal and/or particulate species whose relative amounts and significance are unknown

Similarly, the mechanism of association of Pu with the soil is unknown, e g is dissolved Pu chemisorbing via ion exchange and/or is colloidal Pu physically sorbing to the soil Where Pu can be identified as being associated with particles, the composition of this phase needs to be cogently discussed – the oxide phase, PuO_2, is often used in the soils context without detailed characterization information The simple oxide is both a significant oversimplification for Pu chemistry in aqueous systems and unlikely given the observed complex behavior of Pu in these soils Multiple reservoirs of Pu in the soils are possible and likely, resulting in reactive inventories which are less than the total concentration in the soil during these desorption/dissolution experiments Which sites of the soil are involved in these various sorption processes and what are the concentrations of the sorbing soil sites in units per square centimeters Finally what is the active total surface area of the soil samples? All these parameters must be known in order to use the K_d values with confidence for different soil samples, or at a minimum to constrain site-specific K_d values

Similar problems of unawareness about parameters to be used in any realistic modeling exist For example, are the same species sorbing in the unsaturated, compact soil as in the shaken lab experiment of dispersed soil? Are the concentrations of sorbing sites per cm^2 the same in the compacted, unsaturated soil? Is (almost certainly not) the surface area per unit mass the same for the compacted soil as for dispersed soil? Of major concern is that the lab experiment reflects the K_d for a single theoretical plate in the transport path whereas in the bulk soil, it is probable that thousands of theoretical plates are associated with the actinide transport This is actually a critical aspect of how RESRAD and other modeling codes implement the use of information from simplified experiments such as these While this may be a conservative factor, a non-conservative aspect of the modeling, that must be evaluated, is the treatment of an unsaturated soil as if it were saturated It is reasonable that all the compacted soil not in the saturated pathway would not be involved in the sorption process and cannot be included in the modeling calculations This may lead to a significant underestimation of the migration rate

Water Budget

During discussions on Keith Motyl's presentation on surface water conditions for closure, some of the components of a water budget were tabulated to explain water flow allotments from natural and anthropogenic sources This tabulation however, was not given within the context of a water budget We suggest that all discussions of water fluxes and reservoirs should be given within such a context The water budget for the site is a fundamental part of the conceptual model that underlies surface water transport, groundwater transport, recharge, storage, and discharge It should be consistently used as a framework of reference for those groups working on mass loadings, erosion, groundwater contamination, and surface water contamination It would be helpful if the water budget could be summarized on a single page, and made available for comment and for reference In addition,

estimates are needed for how closure will affect the water budget For example, large caps, the loss of ponds, and the gain of wetlands will all affect the water budget and water flow paths A second reference page outlining any significant changes in the water budget and flow paths that result from alternate remedial actions should also be provided Finally, estimates should be made for the uncertainty associated with the components of the water budget How much uncertainty is involved and how much uncertainty is acceptable?

Air Transport Modeling

Connection between erosion modeling and surface water particulate size analyses was discussed These components of the AMS work are addressing parallel problems and complementary questions Based on the short writeup provided prior to these meetings, the AMS Advisory Group requests that further information on the level of dose expected and/or possible for the contaminant resuspension and distribution be presented at an upcoming meeting As results become available, the investigators should be encouraged to examine integration issues and conclusions

Aseptic Groundwater Well Installation and Evaluation

The advisory team had a brief discussion about the rationale and approaches to validating the conceptual model conclusion that groundwater contamination by actinides observed in monitoring wells is the result of drilling and not transport through the system The value of drilling aseptic wells, in which entrainment of contaminated surface soils is carefully avoided, was accepted Priority sites are on the 903 Pad and in it's directly associated contaminated soil area

Documents provided to advisory group

Loading analysis for the actinide migration studies at the Rocky Flats Environmental Technology Site, RF/RMRS-98-277 UN Rev 0, September 1998

Actinide content and aggregate size analyses for surface soil in the Walnut Creek and Woman Creek watersheds at the Rocky Flats Environmental Technology Site, RF/RMRS-98-281 UN, September 1998

Conceptual model for actinide migration studies at the Rocky Flats Environmental Technology Site, October 1998

Triay, I R , and Loge, G W , Batch experiments for desorption of plutonium and americium in contaminated soil from the Rocky Flats Plant, LA-UR-94-1165

Kung, K S , Lu, N , Triay, I R , Motyl, K M , and Roushey, W J , Chemical extraction of plutonium and americium for contaminated Rocky Flats soil Radiochimica Acta 80, 13-21 (1998)

Santschi, P H Draft final report on phase speciation of Pu and Am for 'Actinide Migration Studies at the Rocky Flats Environmental Technology Site', 15 October 1998

Keith Motyl, viewgraphs on Actinide Migration Study, Surface Water Endstate for RFETS Closure

Greg Wetherbee, viewgraphs on Endstate for RFETS Closure and AMS FY99 directions and final products

Air Modeling in Support of Actinide Migration Study (attached)

Evaluation of anthropogenic and naturally-occuring uranium in SPP groundwater (Draft 9/25/98)

Tour of Individual Hazardous Substance Sites in the Perimeter Area and Map

Documents requested for advisory group

Source Control Alternatives Analysis

Accelerating Cleanup Path to Closure of RFETS, June 1998 *[dkn has copy and has provided it to other members of advisory group]*

Summary of existing data on actinides at RFETS (Annual RFCA Report?) *[Win will provide]*

Participants in AMS technical meetings

Ball, Jim	Honeyman, Bruce	Peters, Mike
Choppin, Greg	Janecky, David	Roberts, Rick
Chromec, Win	McCallister, Russell	Santschi, Peter
Clark, David	Motyl, Keith	Shelton, Dave
Corsi, John	Nordstrom, Kirk	Wetherbee, Greg
Cowdery, Craig	Paton, Ian	

AMS Participants in public meeting

Ball, Jim	Honeyman, Bruce	Shelton, Dave
Choppin, Greg	Janecky, David	Wetherbee, Greg
Chromec, Win	McCallister, Russell	
Clark, David	Nordstrom, Kirk	
Corsi, John	Santschi, Peter	

Participants in RFETS Protected Area Tour

Ball, Jim	Janecky, David	Wetherbee, Greg
Clark, David	Mewes, Jackie	
Corsi, John	Moore, LeRoy	
Gregory-Frost, Laurie	Nordstrom, Kirk	
Honeyman, Bruce	Santschi, Peter	

Air Modeling in Support of Actinide Migration Study
(provided by site to DRJ prior to meeting)

A confirmed significant pathway for off-site emissions from Rocky Flats (RFETS) is via the air Monitoring data at the fenceline and downwind of significant fugitive source areas show ambient impacts that appear relatively well correlated with the sources of those emissions

Resuspension factors have been empirically developed for RFETS that represent the gross relationship between surface soil contamination and air concentrations downwind of that contamination However, the role of wind-blown resuspension has not been examined to understand the influence that larger airborne particles may have on the redistribution of contaminants in the environment Fine airborne particles are readily carried many kilometers in the atmosphere and have been measured Larger particles, on the other hand, may typically fall out within a few tens to several hundreds of meters These larger particles will have the effect of replenishing surfaces previously eroded, and will contribute in some amount to the contaminant levels in a water channels and surface impoundments The significance of these contributions is unknown

The proposed air modeling is expected to contribute to our understanding of near-term effects on surface contaminant distributions during and immediately following an event with significant airborne emissions (such as an environmental restoration project) In addition, and in the longer view, the modeling will help to understand and map out the consequences of gradual airborne erosion on both soil contaminant distributions and changes in expected public dose for various fixed receptor locations

In addition to the question of relative contribution to the water pathway, the following discussion suggests how air modeling may contribute to the actinide migration study Simple dispersion modeling of windblown resuspended, contaminated soils has been performed The results show that a small area of highly Pu-contaminated soils near the 903 Pad contributes about 30 percent of the dose received by a receptor at 96th and Indiana Somewhat surprisingly, very low levels of Pu contamination from a somewhat larger area immediately adjacent to that same receptor can contribute a similar dose Extending that observation, long-term redistribution (dilution, if you like) of the contamination from RFETS may not result in a significantly reduced dose to a typical receptor, but could actually lead to an increase in the average dose to more distant receptors, compared to present day estimates This suggests the importance that air modeling could play in determining the focus and extent of cleanup efforts at the Site

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