

Rocky Flats Environmental Technology Site: Actinide Migration Evaluation

Meetings: May 19-21, 2003

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Summary and Recommendations for Path Forward

Progress reported on 903 Pad remediation is very good. The discussion and evaluation of the technical basis for application of HPGe measurements strongly supports the existing calculation used to estimate plutonium concentrations as disposal criteria for soils being packaged for removal.

To further evaluate contamination erosion consequences around the 903 Pad, we recommend that continuous simulation modeling and 30-day averaging be used to compare with the 30-day moving average standard of 0.15 pCi/L. In addition, for flood frequency-design storm approach, we recommend a range of storm sizes from <2 year to 100 year be used in the simulation modeling.

Transition to Stewardship is a key area where Kaiser-Hill plans and actions need to be monitored and cross-walked with respect to developing DOE plans.

Lastly, a large number of samples have been analyzed for uranium isotopic composition across the site, allowing spatial evaluation of contamination relative to natural backgrounds.

Progress and Integration

Erosion modeling of the 903 Pad and Woman Creek drainage is very well developed. The Advisors commend RFETS personnel for using the soil erosion, sediment transport and actinide mobility models to assist in design and analysis of remediation activities in the 903 Pad Area. This is exactly the role of simulation modeling envisioned for Site remediation, transition to stewardship, and closure

Questions have been raised about the potential affects of carbon tetrachloride, its decomposition products and other organic contamination on mobility of radionuclides at Rocky Flats. The data amassed during AME studies is consistent with our expectations of uranium, plutonium and americium chemical behavior in the environment. The extremely low solubility of plutonium and americium results in association with colloids, particulates and solids, with no substantial reactivity. The greater solubility of uranium results in soluble transport and reactivity with ionic compounds (carbonate in particular). Carbon tetrachloride is a non-polar solvent, and is a poor solvent for charged ions. Due to the small amounts of CCl₄ present in groundwater, one would not expect an overall effect on uranium solubility.

Transition to Stewardship discussions with Kaiser-Hill, DOE, regulators, local governments and stakeholders were very interesting. In particular, the question and answer session of the public meeting indicated a broad interest in transition issues.

Results and Discussions

903 Pad remediation status and presentation

Pertinent historical data regarding the 903 pad were examined in light of ongoing 903 Pad remediation activities and to compare past assessments of the area of contamination with current findings.

From October 1958 to January 1967 the 903 Drum Storage Site at Rocky Flats was used to store drums containing waste machine cutting oil that was radioactively contaminated. Approximately 75% of the drums were plutonium-contaminated, and predominantly contained waste lathe coolant consisting of a high molecular weight straight-chain hydrocarbon oil (Shell Vitrea) and carbon tetrachloride in diverse proportions. Leakage of the oil was recognized early, and in 1959 ethanolamine was added to the oil to reduce the corrosion rate of the steel drums. The shipment of drums to the 903 Drum Storage Site ended in January 1967 when drum removal efforts began. Removal of all drums and wastes was completed in June 1968.

Drum leakage was noted at the 903 Drum Storage Site in 1964, and the contents of leaking drums were transferred to new drums and the entire area was fenced to restrict access. Based upon material balance around the drums, it is estimated that a total of 5,000 gallons containing approximately 86 g of plutonium were released into soils at the 903 Drum Storage Site.

Between November 1968 and November 1969, cleanup operations took place, which included moving contaminated soil from around the fenced area to inside the fenced area, removal of contaminated soils, addition of clean fill material, and an asphalt containment cover. In February 1970 additional road base course material was applied to soils directly east and south of the asphalt pad. The asphalt cover is approximately eight centimeters thick, and reportedly underlain by fifteen centimeters of loose gravel and eight centimeters of fill dirt.

A number of studies were conducted on soils beneath the asphalt cap, and all of these indicate inhomogeneous distribution of plutonium and americium in the soils, which appeared to be restricted to shallow depths below the original ground surface. (Dow Internal Report RFP-INV-10, Rockwell Internal Report CRD79-016, RF/RMRS-99-427.UN).

Lane Butler presented an overview of current cleanup activities at the 903 Pad. The area has been divided into 225 cells of which 96 have been completed. A total of 792 intermodals have been removed, representing 2080 tons of asphalt, and 10,960 tons of soils. The completed cells have been back-filled with offsite clean soil. Field instruments show that the contamination is very inhomogeneous as expected based on all the prior studies. The use of tents during these operations is critical for mitigating against wind dispersal of contaminated soils.

903 Pad Area Erosion Modeling and Actinide Transport Study

Ian Paton presented a summary of the WEPP – Actinide Mobility - HEC6T modeling activities being used to assist remediation efforts in the contaminated areas around the 903 Pad lip area and on the hillslopes upstream of the South Interceptor Ditch (SID), Pond C2, and the POC at GS01 on Woman Creek at Indiana Avenue. Simulation results for the “existing conditions”, using a large storm (120 mm of precipitation in 5.5 hours), resulted in simulated instantaneous Pu concentrations well above the 30-day moving average standard of 0.15 pCi/L at GS01. Analysis of remediated hillslopes in the 903 pad area and the same large storm suggested that aerially extensive remediation efforts would be required to meet the 0.15 pCi/L standard. However these simulation results are only indicative and not definitive because instantaneous concentrations from the modeling were compared with a weighted 30-day average concentration as specified in RFCA and because the large storm (120 mm in 5.5 hours) may not represent the appropriate design storm to use in the analyses. The Advisors recommend that continuous simulation modeling and 30-day averaging be used to compare with the 30-day moving average standard of 0.15 pCi/L. In addition, if a flood frequency-design storm approach is also used, then a range of storm sizes from <2 year to 100 year be used in the simulation modeling. Finally, the Advisors commend RFETS personnel for using the soil erosion, sediment transport and actinide mobility models to assist in design and analysis of remediation activities in the 903 Pad Area. This is exactly the role of simulation modeling envisioned for Site remediation, transition to stewardship, and closure.

Pu/Am ratio discussion and residual contamination

A discussion of plutonium and americium relationships was held among personnel from the Site, CDPHE and the AME advisors. Concepts and data discussed included first principle calculation of americium in-growth, field measurements and uncertainties for soils from the 903 Pad and published literature, as well as comparison to water and air sampling results. In particular, data from the paper by Ibrahim et al. (1996) was discussed with respect to geographic position and depth in the soils. The discussion and analysis of the data was extensive and further data necessary for evaluation of 903 Pad remediation was identified. A white paper on the subject is forthcoming.

Uranium contamination data

A “white” paper, being prepared by R. Peterson and I. Paton on “Uranium in Surface Water and Groundwater at RFETS” was discussed. Data from water samples at a large number of locations within the RFETS were analyzed for U concentrations and isotopic ratios. The isotopic ratio data can allow classification of the uranium as natural or anthropogenic (introduced by former RFETS operations).

The isotopic measurements seek information on four uranium isotopes: ^{234}U , ^{235}U , ^{236}U , and ^{238}U . Anthropogenic depleted uranium is deficient in ^{234}U and ^{235}U . Weapons grade U is depleted in ^{238}U with very much higher relative levels of ^{234}U and ^{235}U than natural uranium. All anthropogenic sources of uranium within the DOE complex contain traces of ^{236}U , making ^{236}U a unique fingerprint for anthropogenic uranium in RFETS environs.

The surface and groundwater data, which have been collected, are consistent in showing levels of total uranium concentrations well below the regulatory compliance levels for Woman and Walnut Creeks. The presence of ^{233}U and/or ^{236}U in a narrow set of samples is accepted as evidence that an anthropogenic source contributes to the uranium in specific industrially contaminated areas. Additional data collection was used to obtain comparisons of techniques for both total concentration and isotopic ratios for uranium with ultimate sensitivity.

We note that two sites are well outside of the influence of industrial activities at Rocky Flats – one in the northern area of RFETS and the second in the southern area. At the first site, the uranium has been identified as natural/background by the absence of ^{236}U , even though uranium concentrations are naturally high. While a definitive determination of natural background has not been conducted in the southern site, there have been a number of isotopic measurements performed just south of the industrial area. In these studies, the majority of samples showed no ^{236}U , demonstrating that much of the uranium observed south of the industrial area is in fact due to natural sources.

This project has collected and analyzed a large number of samples spread over the entire RFETS. This allows useful spatial mapping of contamination vs. natural background for uranium at RFETS.

Effect of Organic Groundwater Contamination (e.g. CCl_4) on Uranium, Plutonium and Americium Solubility and Mobility at RFETS

Carbon tetrachloride (CCl_4) has been observed in soils, surface water and ground water in areas adjacent to the 903 Pad, under the Pad itself, and in a ground water plume south of building 771 where it originated from an underground storage tank. These observations have raised questions, as to whether carbon tetrachloride or its decomposition products would alter the solubility and mobility characteristics of uranium, plutonium and americium at RFETS. The purpose of this discussion is to address these recent questions.

Background. Organic liquids contaminated with radioactive materials were generated at the Rocky Flats Plant through various manufacturing processes. In the early days of operation, the volumes of organic liquids were very low. Changes in weapon design and manufacturing processes significantly increased the amount of waste oils that were generated, and in 1958 an outside plutonium contaminated oil drum storage area was established. These drums generally contained plutonium-contaminated waste lathe coolant containing a

high molecular weight hydrocarbon oil and carbon tetrachloride. Eventually, a carbon tetrachloride recycle system was established at the Site.

What we can learn from Studies of the 903 Pad. A good deal of insight into the relationship between organic solvents and actinide mobility is already available through data collected at the 903 Pad. When the original drums stored at the 903 Drum Storage Site failed, the plutonium (and its associated americium from radioactive decay) contaminated oils leaked into the soils. Since the metal particles were extremely small (they were sieved with a 100 micron sieve), they would be expected to oxidize rather quickly from plutonium metal to plutonium dioxide upon exposure to the environment. The plutonium oxide formed in this way would be expected to contain americium through in-growth mechanisms. Plutonium metal particles have been shown to react with carbon tetrachloride/methanol mixtures in the laboratory to generate plutonium chlorides. Uranium, plutonium, and americium dioxides are also known to react with CCl_4 to form metal chlorides under harsh conditions imposed by high temperature gas-phase reactions. For example, UO_2 will react with gaseous CCl_4 vapor at $550\text{ }^\circ\text{C}$ to form UCl_4 , and PuO_2 will react with gaseous CCl_4 vapor at $450\text{ }^\circ\text{C}$ to give PuCl_3 . (Katz, Morss, Seaborg, *Chemistry of the Actinide Elements*, 2nd Edition, 1986) Rocky Flats personnel (see Crisler, 1974, RFP-2181, or Kazanjian, 1972, RFP-1945) conducted much of this early work. Since plutonium metal can react directly with CCl_4 , it is possible that small quantities of plutonium trichloride could have formed in the drums themselves. This trivalent compound would also be expected to oxidize upon exposure to the environment, either in the leaking drums or adjacent soils, and convert to the more stable PuO_2 . Based on our fundamental understanding of plutonium chemistry, one would predict that the oil/plutonium mixture stored in drums would penetrate the soil until chemical conversion (either metal or chloride) to PuO_2 occurred, at which time the PuO_2 would be expected to remain relatively stationary due to its propensity to stick to soil and mineral particles. The organic residues however would be expected to continue to migrate and mix with the groundwater. All of the data collected at the 903 Pad over the years of study support this assessment. The plutonium and americium contamination has remained largely in the surface soils, and the chemical form has been definitively identified as hydrous PuO_2 . By contrast, the organic plume containing carbon tetrachloride has continued to migrate. These observations suggest that the CCl_4 in groundwater will have no effect on the mobility of plutonium and americium.

Chemical Characteristics of UO_2 , PuO_2 , and AmO_2 . The dioxides of uranium, plutonium and americium are solid compounds with extremely strong metal-oxygen bonds, and infinite solid-state crystalline structures. These solids are insoluble in water, carbon tetrachloride, and all other common solvents. They are very refractory materials. Chemists use this term in its true sense of "obstinate and unyielding" because they are extremely difficult to dissolve by any technique. This is particularly true for plutonium dioxide. In the laboratory, one must resort to extremely harsh chemical conditions such as boiling, concentrated nitric and hydrofluoric acid mixtures (HNO_3 -HF) to dissolve PuO_2 . When PuO_2

has been treated at high temperatures (high-fired), the solubility decreases even further, and this is generally attributed to an annealing of the crystalline lattice, to a more highly ordered (more refractory) crystalline state. In fact, heat-treating plutonium residues to form high-fired PuO_2 has become the Defense Nuclear Facility Safety Board (DNFSB) standard (DOE 3013 Storage Standard) for stabilization of nuclear materials for long-term storage.

Effect of organic groundwater contamination on plutonium, americium and uranium Solubility at RFETS. In view of the extreme insolubility of, PuO_2 , AmO_2 and UO_2 in all solvent systems except concentrated boiling acids, or high temperature gaseous CCl_4 vapor, organic contaminants in groundwater should have little to no effect on actinide (plutonium, americium, uranium) solubility or mobility in RFETS soils. All the data collected at the 903 Pad is consistent with this expectation, and this scenario is expected to be the same for other areas at RFETS (such as south of building 771) where organic contaminants have been found in the subsurface. Moreover, these organic contaminants are present in minute amounts, typically measured in quantities of micrograms/Liter. Thus the organic contaminants are themselves minor impurities to the system, much like the plutonium. Uranium can also exist in a higher oxidation state (VI). Because uranium(VI) forms compounds of much greater solubility, uranium can be transported as a soluble species in the environment. Water owes its ability to dissolve charged ions due to its highly polar nature and its ability to undergo auto ionization to hydroxide and hydronium species. Carbon tetrachloride is a non-polar solvent, and is a poor solvent for charged ions. In this regard, uranium(VI) complexes that are soluble in water would be expected to have a lower solubility in CCl_4 . Due to the small amounts of CCl_4 present in groundwater, one would not expect overall effect on uranium solubility.

Carbon tetrachloride decomposition. It is known that carbon tetrachloride can decompose in the environment. Field studies reveal that even under very reducing conditions (where the kinetics are favorable – see *Applied Geochemistry*, **2003**, *18*, 503), heavily CCl_4 -contaminated groundwaters are typically in the range pH 6-7.5, a pH range that would have no effect on actinide (uranium, plutonium, americium) solubility. We reiterate, that in the laboratory, it requires strong inorganic acids (nitric, hydrochloric, etc.) and harsh conditions (boiling acids, high acid concentrations) to get the actinide oxides to dissolve.

One of the potential decomposition products of carbon tetrachloride degradation is the generation of the chloride anion, Cl^- . Plutonium ions can form complexes with the chloride ion, but these are exceedingly weak complexes. Chloride complexation is so weak, that in dilute concentrations, as have been observed at RFETS, chloride complexation cannot compete with water to form hydrous plutonium dioxide.

Actinide Environmental Behavior at RFETS. The data amassed during AME studies is consistent with our expectations of uranium, plutonium and americium chemical behavior in the environment. Because of the extremely low solubility of plutonium and americium, these elements are predominantly

associated with solids. They are either strongly sorbed, or attached to soil or sediment particles, or precipitated as oxides. These solubility characteristics are not altered by presence of CCl_4 in groundwater. The oxides only become soluble under extremely harsh chemical conditions. Uranium can also exist in a higher oxidation state (VI). Because uranium(VI) forms compounds of much greater solubility, uranium can be transported as a soluble species in the environment. Water owes its ability to dissolve charged ions due to its highly polar nature and its ability to undergo auto ionization. Carbon tetrachloride is a non-polar solvent, and is a poor solvent for charged ions. In this regard, uranium(VI) complexes that are soluble in water would be expected to have a lower solubility in CCl_4 . Due to the small amounts of CCl_4 present in groundwater, one would not expect overall effect on uranium solubility.

Transition to Stewardship strategy and concepts

A public meeting was held at the Broomfield City Hall from 4:30 to 6:30 on Tuesday, May 20, 2003. At this public meeting a presentation entitled "Transition to Stewardship at RFETS" was given. The question and answer period indicated a broad interest in transition issues. The main points of the presentation are summarized below:

Overall Goal: Protect human health and the environment.

- A transition to stewardship is already happening and will benefit from a high level of planning and discussion.
- The transition from Site remediation to long-term stewardship should be a continuum, not an abrupt change.
- A well defined conceptual model is needed for transition to stewardship to help guide and focus Site activities from now into the stewardship.
- A science-based method is necessary to manage Site activities in the transition to stewardship. (We recommended an adaptive management approach).

Colloid Presentation

Dr. Annie Kersting presented a summary of the technical knowledge base on colloids and radionuclide transport in the environment, with particular emphasis on implications for Rocky Flats. Natural colloids are small particles that are less than 1 micron in size, and are ubiquitous in geologic systems. Plutonium can sorb to natural mineral colloids or exist as its own intrinsic colloid. Field studies highlight the importance of local geology in determining the extent of colloid formation and mobility. At moderate pH, colloids are the dominant mechanism for transport of plutonium and americium in water.

At Rocky Flats, colloids represent a portion of the particle-size spectrum, are therefore have already been incorporated into the pathway analysis whenever particulates are discussed. Physical (particulate and colloidal) transport is the dominant mechanism for plutonium and americium migration in Kaiser-Hill Company, LLC.

water and soils. As documented previously, and reviewed in the site-wide water balance study, surface and shallow groundwater are linked. Insolubility of these actinides does not equate to immobility, and mobility does not equate to solubility. Therefore, the association of plutonium and americium with particles and colloids is the key to ultimately predicting their migration and distribution from contamination releases.

Documents Provided to Advisory Group

- Honeyman, B.D. & Ranville, J.F. (2002) Colloid properties and their effects on radionuclide transport through soils and groundwaters. In *Geochemistry of Soil Radionuclides*. Soil Science Society of America Special Publication **59**, 131-163.
- 903 Pad Update, May 2003 – Lane Butler
- Viewgraphs – draft White Paper: Uranium in surface water and groundwater at the Rocky Flats Environmental Technology Site; GIS maps of surface water and groundwater data for uranium concentration and isotopes – Rachael Peterson & Ian Paton
- Viewgraphs – Status report on erosion modeling for 903 Pad area and Woman Creek – Ian Paton
- Ibrahim, S.A., Schierman, M.J., & Whicker, F.W. (1996) Comparative distribution of ^{241}Am and $^{239,240}\text{Pu}$ in soils around the Rocky Flats Environmental Technology Site. *Health Physics* **70**, 520-526.
- Kaiser-Hill White Paper – Calculating Pu-239 activity for 903 Pad soils from measured Am-241 value
- US EPA-R-8 white paper, 22 April, 2003 – Plutonium / Americium ratio as a function of depth at the Rocky Flats 903 Pad
- Kersting, A. – Colloids and Radionuclide Transport: Implications for Rocky Flats presentation
- Clark, D.L. & Janecky – 903 Pad Remediation and Actinide Transport presentation
- Lane, L. & AME advisors – Transition to Stewardship at RFETS presentation

Documents and Information Requested for Advisory Group

- Kaiser-Hill plans and actions for Transition to Stewardship, and cross-walk with developing DOE plans for Long-Term Stewardship
- Further detailed info on 903 pad remediation and resulting data – depth distribution, pictures of cell floor at lift stages and comparison with HPGe
- Site configuration design strategy and documentation

Requests for Future Presentations and Information

- 903 pad remediation – Actinide and VOCs contamination characterization; structure observations and strategic approaches
- Information on air and site monitoring for solar ponds area, and revegetation activities
- Information on revegetation time scale & schedule, ecology group + species composition, coupled with climate + wind processes + water erosion (latter two with year sequence processes) – this is critical to planning for 903 pad + lip + other areas
- Further detailed info on 903 pad remediation and resulting data – depth distribution, pictures of cell floor at lift stages and comparison with HPGe

estimates of intermodal numbers as a function of Pu/Am ratios (8, 7, 6.5, 6, 5.7)

Continuous simulation for erosion and actinide migration, especially 30-day moving averages and storm/baseflow sequence scenarios for the Woman Creek drainage.

Participants in AMS technical meetings

<u>Name</u>	<u>Organization</u>
Chad Blake	K-H
Lane Butler	K-H
Greg Choppin	Florida State
David Clark	Los Alamos
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Rick DiSalvo	DOE/RFFO
Bob Duraski	US EPA
Steve Gunderson	CDPHE
David Janecky	LANL
Mike Keating	K-H
Annie Kersting	LLNL
Gary Kleeman	US EPA
Leonard Lane	Tucson
Russell McCallister	DOE/RFFO
Robert Nininger	K-H
Ian Paton	WWE
Rachael Peterson	WWE
John Rampe	DOE/RFFO
Tim Rehder	US EPA
David Shelton	K-H
John Stover	DOE/RFFO

Future Meetings

August meeting canceled, to be replaced by telephone conferences as necessary