

**WORK SCOPE DOCUMENT FOR 'ACTINIDE MIGRATION STUDIES AT THE
ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE'**

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Significant findings of the FY 1997 study:

1. Selective leaching analysis of soil isolates taken from a region trending SE of the 903 Pad indicates: a) from 0.04 to 0.09 % of the soil-associated $^{239,240}\text{Pu}$ is 'exchangeable; b) addition of reducing agents 'solubilized' 0.1 to 5% of soil-associated Pu, suggesting that a relatively small percentage of total soil $^{239,240}\text{Pu}$ could be released from the soil matrix during prolonged periods of soil anoxia; c) the predominant phase classes for Pu are the 'organic' and 'residual' fractions. The significance of the 'organic' fraction with respect to Pu speciation is not yet clear. For example, the addition of acid peroxide solutions may release Pu through Pu reduction to Pu(III) rather than simply indicating that Pu is directly complexed to, or aggregated with (if $\text{PuO}_2(\text{s})$), the organic fraction. In addition, organic materials and associated actinides may be released during proceeding extraction steps. FY 1997 work points to the need for evaluating the release of soil component elements (e.g., Fe, Mn, Al, C) during selective extraction and anoxic K_d experiments.
2. Bulk distribution coefficients derived from $^{239,240}\text{Pu}$ desorption from soil isolates under oxic conditions range from ca. $1 \times 10^4 \text{ L kg}^{-1}$ to $1.2 \times 10^5 \text{ L kg}^{-1}$. K_d values are dependent on time of contact of solution with soil particles as well as solution composition. The data set described here provides a likely upper range of K_d values. The FY 1997 K_d values are consistent with previous solubilization work conducted on Rocky Flats soils and sediments (e.g., Cleveland *et al.*, 1976).
3. Soil-Pu solubilization studies (both K_d and selective extraction analyses) indicate that $^{239,240}\text{Pu}$ has a limited solubility (as defined by filtration via $0.45 \mu\text{m}$ filters) under oxidizing conditions and is consistent with interpretations that the primary transport process under oxidizing conditions is through mechanical erosion.
4. Yearly fluxes of $^{239,240}\text{Pu}$ to the RFETS ponds evaluated are estimated to range from 0.02 to 1.7 mCi y^{-1} depending on the pond and method of Pu inventory determination.
5. K_d values for $^{238}\text{U}(\text{VI})$ interaction with solar pond core isolates range, under oxidizing conditions, from ca. 30 to 180 L kg^{-1} .
6. Additional studies need to be initiated to expand the data set for Site Pu K_d values to cover a range of soil redox conditions from oxidizing to reducing.

The goal of the Actinide Migration Study (AMS) is to provide data in support of the development of the Site conceptual model (*A conceptual model of Pu movement through RFETS soils*, Bruce D. Honeyman and Peter H. Santschi, May 26, 1997, Document #: CSM-3-97) and site closure, including: 1) soil action levels vis-à-vis surface water quality; 2) long-term disposition of the ponds; 3) 'far-field' actinide behavior during long-term closure.

The work during this fiscal year (FY 98) centers around the role of particles in Pu and Am transport throughout Site environmental media. While work outlined below does not explicitly

consider transport or mobility, the results do address the distribution of Pu and Am between soil and solution phases under a range of redox conditions and such information is required as input for refining the Site conceptual model and mathematical models of actinide transport.

1. FY 98 Objectives.

This workplan addresses the Scope of Work for FY 1998 and covers the period of 25 October 1997 to September 30, 1998. The main objective is to provide data commensurate with the Data Quality Objectives of the Actinide Migration Study.

A wide range of work at Rocky Flats has demonstrated that particulate forms of Pu and Am make up a significant fraction of the actinide inventory in soils and suggests that surface water transport of Pu and Am is dominated by actinide associations with suspended solids. For example, observations that $^{239,240}\text{Pu}/^{241}\text{Am}$ activity ratios in soils and surface water are relatively 'fixed' at values between 7 and 4 have been invoked to support the hypothesis that Pu and Am have not been physically or chemically separated and share a common environmental fate (i.e., that Pu and Am are 'locked' together in particulate form).

However, many questions remain that can impact approaches to remediation and strategies for long-term site disposition. More specifically, the chemical behavior of actinide-bearing particles in response to changing environmental conditions has not been investigated. Such chemical behavior includes (not an exclusive list):

- The potential for dissolution of actinides from particles, which may result in release of Pu and Am to the solution phase in ratios not identical to those of the original particles.
- Potential redox reactions of Pu within and on the surface of particles due to external or internal conditions (e.g. Pu(IV) to Pu(III)). This may also affect potential for dissolution and further reactions.
- The response of 'host' soil-phase constituents, such as Fe, Mn, Si-Al oxides and hydroxides and soil organic matter, to changes in soil redox conditions and the potential of subsequent actinide release from the host phases.

Work during this fiscal year will address a number of questions of relevance to the Site conceptual model including:

1. The distribution of Am and Pu between particle and 'solution' phases under 'normal' and 'extraordinary' soil conditions.
2. The relevance of colloidal forms of Pu and Am in surface water transport.
3. An assessment of the potential for non-particle transport under anoxic soil conditions.

The overall question that will be addressed by FY 98 analytical work is: How general is the assumption of particle transport of Pu and Am?

2. Tasks.

Task 1: Expand the K_d data set for Am and Pu to include a range of redox conditions.

2.1.1 Objectives:

- a. To extend the basic data set for Pu and Am distribution between particles and solution (parameterized as K_d values).
- b. To provide data required in the evaluation of the hypothesis that the primary process for Pu and Am movement through RFETS soils and watersheds is transport of Pu and Am by suspended particles.
- c. To provide a distribution of K_d values under a range of environmental conditions throughout the Site for the establishment of defensible modeling parameter sets.
- d. To evaluate, using selected soil samples, the mass requirements for data reproducibility.
- e. An evaluation of the 'leachable' Pu, Am fraction over several wetting cycles.

2.1.2. Justification:

Data on the particle/solution partition of Pu and Am under a range of soil conditions are needed: 1) to develop and refine the conceptual model of actinide transport at RFETS; 2) as input parameters for actinide transport models. A broad set of Site data is supportive of a model for Pu and Am fate at the Site which give primacy to low actinide solubility under 'normal' Site conditions and actinide mobility through particle transport. Examples of supporting evidence includes:

1. Apparent limited vertical transport of Pu and Am through soil horizons as ascertained through analysis of Pu and Am in soil cores or in simulated rain events;
2. The apparent relative constancy of $^{239,240}\text{Pu}/^{241}\text{Am}$ activity ratios;
3. Exploratory measurement to assess colloidal forms of Pu and Am in seep and groundwaters.

However, Site data also suggest that, under unusual conditions, Pu and Am mobility may be enhanced relative to the 'normal' conditions, particle transport model, e.g.:

1. Indications from FY 1997 selective extraction data that up to 5% of the soil Pu may be released under conditions such that sesquioxides reductively dissolved; yielding K_d values for Pu, under reducing conditions, of 5 -110 L kg⁻¹, depending on assumptions about soil bulk density, porosity, etc.
2. Measured actinide mobility after prolonged soil saturation (Litaor *et al.*, 1996) which is suggestive of actinide release from soil matrixes through the reductive dissolution of the host matrix (e.g., Fe(III) oxides and hydroxides).

Understanding the magnitude of the 'exchangeable' or 'easily soluble' fraction of particle-associated Pu and Am under a range of redox conditions is crucial for water quality issues. For example, although the fraction of Pu that is released during the K_d or selective-extraction analyses is small (1 ‰ to 1%; Honeyman and Santschi, 1997), the data suggest that the fraction potentially can have a significant impact on water quality. For example, if 1 ‰ of the ca. 1 Ci of environmental $^{239,240}\text{Pu}$ in the 903 Pad region is 'soluble' then ca. 1 mCi of $^{239,240}\text{Pu}$ is potentially available for aqueous-phase transport. At a water quality standard of 0.15 pCi L⁻¹, the 1 ‰ of soluble Pu can contaminate ca. 6×10^9 L of water ($\approx 2 \times 10^9$ gal).

2.1.3. Analytical Plan:

The basic sample set to be used this fiscal year consists of the samples taken for the FY 97 work: 903 Pad 'lip' area soil 'box cores', SID samples and pond-core materials. Possible additional sample locations include soils in the N. Walnut Creek drainage basin. At most four sampling sites soil isolates will be evaluated.

$^{239,240}\text{Pu}$ and ^{241}Am release for soil matrixes, $^{239,240}\text{Pu}/^{241}\text{Am}$ activity ratio and K_d determination:
Bulk Am and Pu K_d values will be determined using the experimental protocol applied to the determination of Pu K_d values for RFETS soils (Honeyman and Santschi, 1997, and relevant Appendixes). Pu activity will be determined through α -counting. If Am activity in the soils is sufficiently high, Am activity will be measured with HPGe detector and analyzed through gamma spectroscopy; alternatively, Am activity will be determined through alpha spectroscopy.

The strategy is to place soil isolate homogenates in closed analytical vessels in contact with solutions of defined initial composition (e.g., redox buffer and pH buffer activity). The mass concentration will depend on the total soil activity. System conditions (e.g., pe, pH) will be regulated by a means to be selected in consultation with, and approval by, members of the Actinide Advisory Group. 'Particulate' and 'soluble' Am and Pu will be operationally determined via filtration with 0.45 μm filters. Solution-phase Fe, Mn, Al and C will be evaluated in support of data analysis.

Data quality and uncertainty:

Rocky Flats Environmental Technology Site Analytical Services Division Modules RC01-B.2 (Isotopic determinations by alpha spectroscopy) and GR01-B.1 (General laboratory requirements) will provide guidance, where appropriate, for QA/QC protocols. Documentation of FY 97 work will follow procedures to be established through discussions between CSM, TAM and Site QA/QC personnel. The Data Quality Objectives outlined in the Actinide Migration Study Data Quality Objectives final document will serve as the framework of recording and reporting the results of these investigations (i.e., PARCC requirements).

Limits on data uncertainty will correspond to the required margin of uncertainty specified for final computed parameters, as outlined in the data quality objectives (DQO). With respect to the outlined task, there are three major sources of error contributing to overall parameter uncertainty: 1) accuracy with respect to instrument calibration; 2) random analytical error; 3) sample representativeness. Errors 1 and 2 will be minimized through standard laboratory protocols for instrument calibration and replicate sample analysis. Fundamental to the successful completion of this task is development of a strategy to determine the sample size (error 3) that will permit the baseline reproducibility required to meet the specified margins of uncertainty (e.g., $\pm 10\%$ uncertainty in phase distribution).

2.1.4. Expected results:

1. K_d values for Am and Pu and selected Rocky flats soils over a range of pe conditions.
2. Evaluation of $^{239,240}\text{Pu}/^{241}\text{Am}$ solution-phase activity ratios over a range of pe conditions: do Am and Pu track each other?
3. Evaluation of the reproducibility of K_d values.

4. The response of 'host' soil-phase constituents, such as Fe, Mn, Si-Al oxides and hydroxides, to changes in soil redox conditions and the potential of subsequent actinide release from the host phases.

Task 2: Phase speciation studies.

2.2.1. Objectives:

- a. To evaluate the question of the chemical differentiation of Am and Pu in Rocky Flats environmental media (i.e., controls on variations in the $^{239,240}\text{Pu}/^{241}\text{Am}$ activity ratios).
- b. To use selective chemical attack to evaluate the geochemical controls on Pu and Am transport by particles.
- c. To ascertain the conditions under which particle transport of Am and Pu may no longer be dominant.
- d. To assess the inventory of actinides associated with operationally-defined soil components.

2.2.2. Justification:

It has long been assumed that the initial condition for Pu in the 903 Pad environs is $\text{PuO}_2(\text{s})$. Constancy in $^{239,240}\text{Pu}/^{241}\text{Am}$ activity ratios has been invoked as evidence that transport by particles is the dominant process contributing to Am and Pu mobility: transport either as $\text{PuO}_2(\text{s})$ and associated ^{241}Am in-growth or that both Pu and Am are closely-associated and in a constant isotopic ratio on environmental particles.

There is a need to challenge the Site's understanding of the relative contribution of the different actinide transport pathways and mechanisms embodied in the conceptual model of the Site and to understand the geochemical conditions under which the various contributions change within the context of the conceptual model.

Selective chemical attack of soil isolates and the concomitant analysis of $^{239,240}\text{Pu}/^{241}\text{Am}$ activity ratios in the 'solubilized' fractions will provide the means of systematically evaluate the hypothesis that Am and Pu are 'locked' into the same particle form and therefore subject to transport by the same processes. Am and Pu data will be supported with analysis of solubilized soil solid-phase constituents (Fe, Mn, Al, C, etc.).

2.2.3. Analytical Plan:

The strategy is to selectively attack soil host phases with chemical amendments which serve as chemical 'probes' for the phase associations of the target actinides. The phase speciation protocol of Yong *et al.* (1993: *Can. Geotech. J.*, **30**, 834-847) will serve as the basis of the FY 98 work. 'Soluble' $^{239,240}\text{Pu}/^{241}\text{Am}$ ratios will be determined in each extraction step. As will be the case for the K_d determinations, 'particle-' and 'solution-phase' Pu and Am activities will be operationally defined using 0.45 μm filters. Soluble Fe, Al and Mn will be determined for each extraction step. Variations in the Yong *et al.* protocol will be by consensus of the Actinide Advisory Group.

Data quality and uncertainty:

Rocky Flats Environmental Technology Site Analytical Services Division Modules RC01-B.2 (Isotopic determinations by alpha spectroscopy) and GR01-B.1 (General laboratory requirements) will provide guidance, where appropriate, for QA/QC protocols. Documentation of FY 97 work

will follow procedures to be established through discussions between CSM, TAM and Site QA/QC personnel. The Data Quality Objectives outlined in the Actinide Migration Study Data Quality Objectives final document will serve as the framework of recording and reporting the results of these investigations (i.e., PARCC requirements).

Limits on data uncertainty will correspond to the required margin of uncertainty specified for final computed parameters, as outlined in the data quality objectives (DQO). With respect to the outlined task, there are three major sources of error contributing to overall parameter uncertainty: 1) accuracy with respect to instrument calibration; 2) random analytical error; 3) sample representativeness. Errors 1 and 2 will be minimized through standard laboratory protocols for instrument calibration and replicate sample analysis. Fundamental to the successful completion of this task is development of a strategy to determine the sample size (error 3) that will permit the baseline reproducibility required to meet the specified margins of uncertainty (e.g., $\pm 10\%$ uncertainty in phase distribution).

2.2.4 Expected results:

1. Evaluation of the hypothesis that Pu and Am transport is through the particle transport 'pathway' of the conceptual model.
2. 'Soluble' $^{239,240}\text{Pu}/^{241}\text{Am}$ ratios as a function of phase-'extraction' and deduction, to the extent permitted by the data, of Pu and Am phase association.
3. Support by data on the 'solubilization' of other redox-active species (e.g., Fe and Mn).

Task 3: Phase speciation of surface water at GS03.

2.3.1. Objectives:

1. To determine the association of Pu and Am with: 1) particulate, 2) colloidal and 3) dissolved phases.
2. To determine the chemical nature of the carrier phase (e.g., Fe, Mn, C, Al, etc.)
3. To provide data needed for to meet the DQO of the watershed erosion modeling efforts.

2.3.2 Justification:

The phase speciation of Pu and Am during the May and June 1997 surface water exceedances is unknown. It is possible that Pu and Am during periods of elevated activity could have been in the colloidal state (i.e., $<0.45\mu\text{m}$), which is considered to be not very bioavailable and where metal species complexed by functional groups of microparticles and macromolecules might have a limited lifetime (Wen et al., 1997a). Therefore, experimental determination of phase speciation of Am and Pu, and chemical characterization of the respective carrier phases, will provide the needed information for modeling surface water fate (i.e., speciation) and transport of Pu and Am.

Cross-flow ultrafiltration, CFUF, provides the means to extend our understanding of Pu and Am size distribution to the size realm of microparticles and macromolecules, and to confirm that the truly dissolved fraction of Pu and Am ($<1\text{ kDa}$), e.g., $\frac{\text{Pu}_{\text{dissolved}}}{\text{Pu}_{\text{T}}}$, is small relative to other size fractions. CFUF experiments will also be used to follow up on the ultrafiltration experiments of Harnish *et al.* (1996) who showed that Pu/Am ratios in well and surface waters in different size

fractions were the greatest in the 10-100 kDa and less than 10 kD fractions (i.e., ≈ 10), and were lower, ranging from 2-7, in all other fractions. The enhancements of Pu over Am in the small colloidal and <10kDa fractions was ascribed by these authors to fulvic acid complexation of Pu.

2.3.3 Analytical Plan:

This task consists of two sub-tasks: 1) CFUF evaluation (e.g., model compound filtration efficiency) and 2) surface water sampling. The sampling site will be monitoring station GS03 (Walnut Creek at Indiana Street), the site where $^{239,240}\text{Pu}$ activity was measured in excess of the Site discharge standard in the Spring and Summer of 1997, during a planned Pond A-4 and/or Pond B-5 discharge into Walnut Creek in the spring (April/May). Grab samples will be collected by bailing water from the stream using a stainless-steel beaker followed by compositing the water into clean 15 to 20 L Nalgene carboys for processing and analysis at CSM.

CFUF is not a standard analytical tool. As such, defensible data must rely on thorough system calibration. About 30% of the task effort will be devoted to calibration issues. The protocols of Guo and Santschi (1996,1997) and Wen *et al.* (1996, 1997b) will be followed for isolating colloidal and particulate phases of metals such Pu, Am from surface waters by CFUF will be followed. Chemical parameters to be measured include total organic carbon (TOC), dissolved organic carbon (DOC), colloidal organic carbon (COC), particulate organic carbon (POC), pH, alkalinity, Al, Fe and Mn of the water, and % organic carbon, Al, Fe and Mn in the colloidal and particulate phases, according to Benoit *et al.* (1994), Guo and Santschi (1997) and Wen *et al.* (1997b). These measurements will be conducted on the isolated aqueous solution phases or on resolubilized freeze dried material, or both.

2.3.4. Expected results:

1. Phase speciation (particulate, colloidal and dissolved) of Pu and Am in surface waters.
2. Elemental composition of phases (e.g., Fe, Al, C).

Task 4: Meetings.

Three two-day meetings at RFETS with two days prior to the meetings set aside for the review of meeting-related documents.

3. Quality Assurance/Quality Control.

The use of plutonium and americium at the Colorado School of Mines and Texas A&M University is regulated by the states of Colorado and Texas, respectively. Training of personnel is governed by each of the university's radioactive materials licenses. Worker Health and Safety at CSM and TAM is governed by the respective university health and safety department.

Rocky Flats Environmental Technology Site Analytical Services Division Modules RC01-B.2 (Isotopic determinations by alpha spectroscopy) and GR01-B.1 (General laboratory requirements) will provide guidance, where appropriate, for QA/QC protocols. Documentation of FY 97 work will follow procedures to be established through discussions between CSM, TAM and Site QA/QC personnel. The Data Quality Objectives outlined in the Actinide Migration Study Data Quality Objectives final document will serve as the framework of recording and reporting the results of these investigations (i.e., PARCC requirements).

The margin of uncertainty on computed parameters will correspond to those specified on the final AMS DQO document.

4. Schedule and deliverables.

Task	Time requirement	Target completion
1. Extension of K_d data set	4 months	15 June 1998
2. Phase speciation: soils	4 months	31 July 1998
3. Phase speciation: pond surface water	2 months calibration, 1 month/sampling + 2 months for processing	31 July 1998
4. QA/QC	2 months throughout the project	14 August 1998

Reports:

Draft Final Project Report due at Kaiser-Hill for internal review: 14 August 1998

Receipt of comments on Draft Final Report: 1 September 1998

Final Project Report due at Kaiser-Hill: 30 September 1998

[The 30 September 1998 date is contingent upon receipt of report comments on 14 September 1998. An extension of 1 day will be provided for each day from 14 September 1998 that the report comments are received.]

The Final Project Report will contain the following sections:

- **Methods and Procedures.**

Complete descriptions of methods used such that the work could be reproduced by personnel of similar qualifications and resources.

- **Results and Discussion.**

This section will present and describe the results of the FY 1998 work. The results will be related to findings of previous investigations. The results will also be discussed in terms of their applicability to the data needs of the conceptual model.

- **QA/QC.**

Analytical data for both target environmental samples and QA/QC samples with uncertainties, MDA's, and a clear description of the methods for calculating the MDAs and uncertainties; an analysis of data quality as pertains to Data Quality Objectives.

6. References.

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