

**PROJECT SPECIFIC PLAN
FOR THE ANALYSIS OF HOW URANIUM IS SORBED AND
PARTITIONED ON GREAT MIAMI AQUIFER MATRIX SEDIMENTS**

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1.0 INTRODUCTION

This Project Specific Plan (PSP) serves as the controlling document for conducting an analysis of how uranium is adsorbed and partitioned on Great Miami Aquifer (GMA) sediments. Detailed information on how uranium is adsorbed or partitioned within aquifer matrix material is not available. Of interest is the uranium fraction that is readily exchangeable or bound with carbonate minerals, metal oxides, metal hydroxides, organic matter, clay minerals, refractory minerals, and residual solids.

Uranium that is present on the surface of sediment components may be able to participate in adsorption/desorption reactions. Uranium that is present in individual sediment grains at depths of 10's on nanometers or greater is either structurally bound or present as co-precipitates that have been encapsulated as the coating of the grain grew. If the uranium is encapsulated, then it is sequestered more or less permanently within the grain.

Groundwater cleanup predictions to date have assumed the aquifer was in equilibrium with respect to sorption and desorption of uranium (e.g. the adsorption rate is assumed to be equal to the desorption rate). Under assumed equilibrium, the partitioning coefficient, K_d , can be used to represent the proportion of contaminant sorbed onto the aquifer matrix compared to the amount of contaminant dissolved in groundwater. Operational experience with the remedy suggests the equilibrium assumption may not be valid and that sorption and desorption reaction rates for uranium in the aquifer may not be equal. A disequilibrium approach may be required in order to improve the accuracy of cleanup predictions.

The modeling code used for the FEMP Groundwater Remediation Project has been enhanced to allow for modeling a system in disequilibrium. Instead of representing mass partitioning in the model by a single partition coefficient, K_d , the enhanced model provides for four reaction rate parameters: 1) a chemisorption coefficient α_C , 2) a desorption coefficient α_D , 3) a precipitation coefficient, and 4) a dissolution coefficient. In the GMA, uranium concentrations are not high enough to result in significant precipitation/dissolution reaction rates. Therefore, only the α_C and α_D , parameters are of interest.

The work outlined in this PSP will provide additional measurements of K_d as well as information that can be used to gain a better understanding of α_C . Since K_d is related to α_C , and α_D , a measurement of K_d and α_C will fix the value for α_D . Refinement in the value of K_d and a determination of α_C , will improve model predictions of aquifer remedy performance.

All of the laboratory work discussed in Section 3 of this PSP will be conducted at Sandia National Laboratories in Carlsbad, New Mexico or the University of New Mexico in Albuquerque New Mexico. An outline of the scope of work is provided below.

Outline of Scope of Work

- Sediment samples will be collected from the Great Miami Aquifer (GMA) in areas where the uranium plume exists.
- Collected sediment samples will be analyzed for total uranium.
- The sediment samples with the highest measured uranium concentration will be sieved into different size fractions and the uranium concentration of each size fraction will be measured.
- Sieve fraction samples with the highest measured uranium concentration will undergo sequential leaching. The leachate will be analyzed for uranium to measure the uranium associated with various sediment components (i.e., mineral fractions, organic matter, clay minerals, residuals, metal oxides, and metal hydroxides).
- Mineral grains selected from the sieved samples will undergo microanalysis to determine how the uranium is partitioned on and within the grains.

2.0 MANAGEMENT AND ORGANIZATION

The U.S. Department of Energy (DOE) Operable Unit 5 Team Leader is responsible for:

- Acting as the point of contact within DOE and for the regulators and stakeholders for all communications concerning work carried out under this PSP.

The Aquifer Restoration/Wastewater Project (ARWWP) Manager is responsible for:

- Providing overall project management and technical guidance
- Ensuring the necessary resources are allocated to the project for the efficient and safe completion of PSP activities
- Overseeing and auditing PSP activities to ensure that the work is being performed efficiently and in accordance with all regulatory requirements and commitments, DOE Orders, site policies and procedures, and safe working practices.

The ARWWP Hydrogeology Team Coach/Project Lead is responsible for:

- The safe and prompt completion of work as outlined in the PSP
- Oversight and programmatic direction of sampling activities
- Providing a technical lead for the collection and interpretation of sampling data

- Establishing and maintaining the scope, schedule, and cost baseline
- Reporting to the DOE Operable Unit 5 Team Leader and ARWWP Manager on the status of PSP activities and on the identification of any problems encountered in the accomplishment of the PSP
- Obtaining the necessary funding to complete the sampling and data analysis activities.

The ARWWP Hydrogeology Technical Lead is responsible for:

- Reporting to the ARWWP Hydrogeology Project Lead on the progress of PSP activities and on the identification of any problems encountered in the accomplishment of the PSP
- Providing technical guidance and assisting field personnel as required to complete work described in this PSP
- Interpretation of data collected in the field
- Interfacing with off-site analytical facilities regarding the status and quality of the analyses.

The Environmental Monitoring (EM)/Water Monitoring Section Team Coach is responsible for:

- Collecting sediment samples from the cores for sieving.

The key project personnel contacts are listed below:

KEY PROJECT PERSONNEL

Title	Primary	Secondary
DOE Operable Unit 5 Team Leader	Rob Janke	
ARWWP Manager	Dave Brettschneider	
ARWWP Hydrogeology Team Coach/Project Lead	Bill Hertel	Ken Broberg
ARWWP Safety Lead	Keith Lanning	Andy Cleeter
ARWWP Hydrogeology Technical Lead	Ken Broberg/Rich Abitz	Bill Hertel
EM Water Monitoring Section Team Coach	Karen Voisard	
Field Oversight Contact	Jon Walter	Karen Voisard
Laboratory Contact	Brenda Collier	
Environmental Compliance Contact	Frank Johnston	
Quality Control Contact	Mike Hoge	Frank Thompson

3.0 ACTIVITIES

Activities will include:

- The collection of sediment samples
- Total uranium analysis of sediment samples
- XRD Analysis of sediment samples to determine mineralogy.
- Sieving of the sediment samples
- Total uranium analysis of the sieved sediment fractions
- Sequential leaching of the sieved sediment fractions and analysis of the leached aliquots for total uranium
- Detailed microscopy of select mineral grains from the selected sieved sediment fractions.

3.1 THE COLLECTION OF SEDIMENT SAMPLES

The collection of sediment samples needed to support Kd work, will be coordinated with the installation of extraction, re-injection, or groundwater monitoring wells. A rotosonic-drilling rig will be used to collect a core sample of aquifer material as a well is being drilled. Some sediment samples have already been collected and have been archived for use on this project. Individual PSPs will be prepared to drill and install future wells and those PSPs will reference back to this PSP for sediment collection requirements for the Kd study.

A minimum of four sampling locations will be targeted for samples in order to provide data across a wide area of the uranium plume. The four locations are:

1. The South Plume
2. The western edge of the South Field plume in the vicinity of the former Inactive Flyash Pile
3. The eastern edge of the South Field plume in the area where uranium concentrations are greatest
4. The Pilot Plant Drainage Ditch plume.

Up to a dozen samples of sediment will be selected from the core obtained at each drilling location. Exact depths to be targeted cannot be defined until the exact drilling location has been selected. Once the exact drilling location has been identified, the ARWWP Hydrogeology Technical Lead will provide target intervals for the collection of samples from the core. The zone of highest dissolved uranium contamination will be targeted. The vadose zone just above the water table elevation that is encountered

at the time of drilling will also be targeted to determine if uranium might be present; left in the sediment from past transport events that took place when water levels were higher.

Two liter samples will be containerized in either glass or plastic jars. The jars will be filled as much as possible to reduce headspace above the sample. The jars will be sealed and clearly identified with a well number and depth interval. Samples from all four locations will be sent to Sandia National Laboratory (SNL) in Carlsbad New Mexico in one large batch. It is estimated that no more than 48 samples (12 from each location) will be sent to SNL.

3.2 MEASUREMENT OF URANIUM CONCENTRATION IN THE SEDIMENT SAMPLES BY ICPMS

Portions of the sediment samples sent to SNL will be blended and undergo a total digestion per the alpha spectrometry digestion Method 4508 (Uranium Isotopic Determinations by Alpha Spectrometry). The blended samples will be analyzed for total uranium using ICPMS, Method 5501 (Determination of Isotopic Uranium by ICPMS) with a method detection limit of 250 micrograms per kilogram ($\mu\text{g}/\text{kg}$). The objective will be to determine which samples have the highest measured uranium concentrations. Each sediment sample will also be analyzed using XRD to determine the gross mineralogy.

3.3 SIEVING OF SEDIMENT SAMPLES

Two of the sediment samples submitted for each location will be selected for sieving at SNL. The two sediment samples will be the ones with the highest measured uranium concentrations. The samples with the highest measured uranium concentration will be selected to maximize the probability of having uranium concentrations that are large enough to measure in subsequent stages of the testing program. Efforts will be made to select one sample from the vadose zone and one sample from the area contained within the dissolved plume at each location.

Each sieve sample will be run through a minimum of the following different meshes (Sieve Number 10, 20, 40, 60, 100, and 200). Sieve screens will be blown with air before and after each use to minimize cross contamination between samples. Each individual sieve fraction will be saved for further analytical work.

3.4 TOTAL URANIUM ANALYSIS OF SIEVED URANIUM SEDIMENT FRACTIONS

Uranium analysis of each sieve fraction will be conducted at SNL. The samples will undergo a total digestion per the alpha spectrometry digestion Method 4508 (Uranium Isotopic Determinations by Alpha

Spectrometry). The samples will be analyzed for total uranium using ICPMS, Method 5501 (Determination of Isotopic Uranium by ICPMS) with a method detection limit of 250 µg/kg.

3.5 SEQUENTIAL LEACHING OF THE SIEVED SEDIMENT FRACTIONS

Four sieve samples from each location will be selected to undergo a semi-qualitative chemical extraction for the purpose of measuring soluble uranium concentrations. Sequential leaching of the 16 sieve fractions will be conducted at SNL. Eight of the 16 samples will be split and analyzed in duplicate.

An aliquot of each of the 16 samples will be ground to less than 200 mesh, and analyzed by x-ray defraction (XRD) to determine a qualitative mineralogy. Aliquots of each sample will be analyzed using a carbon analyzer, to determine both organic and inorganic carbon contents. Sub-samples will then be treated with a sequential leach procedure to determine the distribution of uranium in the mineral phases constituting the sediments. The semi-selective chemical extraction is summarized below and in Table 1. The procedure consists of the following steps.

Step 1 targets the exchangeable uranium fraction on cationic species. Washing the sediment with a magnesium-rich solution will remove uranium present as readily exchangeable adsorbed cationic species.

Step 2 targets the exchangeable uranium fraction on anionic species. Washing the sediment with a sulfate-rich solution will remove uranium sorbed as anionic uranyl-carbonate species.

Step 3 targets the uranium fraction bound to carbonate minerals. Acetic acid will be used to dissolve carbonate minerals, which commonly sequester uranium through adsorption or co-precipitation.

Step 4 targets the uranium fraction bound to amorphous iron, aluminum, manganese, and silicate oxides and hydroxides. Oxalic acid will be used to remove amorphous or poorly crystalline iron, aluminum, manganese oxides and hydroxides. These phases commonly constitute the majority of the surface area in natural samples, and usually contain a significant fraction of any uranium that might be present.

Step 5 targets uranium fraction bound to organic components of the sample. Peroxide will be used to digest organic components of the sample. Uranium complexes strongly with humic and fulvic acids, and is commonly concentrated in organic detritus in soils.

Step 6 targets the uranium fraction bound to crystalline ferric, iron oxides, and hydroxides. Dithionite will be used to release uranium bound in crystalline ferric iron oxides and hydroxides.

Step 7 targets the uranium fraction bound to clays and uranium oxides. A strong acid will be used to digest clays, uranium oxides, and some refractory minerals (phosphates and oxides).

Step 8 targets the uranium fraction bound to non-reactive silicates, oxides, (quartz and feldspars,

zircon, allanite, etc.) and clay minerals not digested in Step 7. The remaining residual will be analyzed by hydrofluoric acid digestion.

The effluent generated in each step of the sequential extraction will be analyzed for the selected major and trace elements by ICPMS, ICP, and/or AA.

3.6 DETAILED MICROSCOPY OF SELECT MINERAL GRAINS FROM THE SIEVED SEDIMENT FRACTIONS

After conducting the sequential extractions, the sediment samples will be characterized by microanalysis. Most of this work will be done at the University of New Mexico, Department of Earth and Planetary Sciences. A maximum of 16 samples (approximately four from each location) will be targeted for microanalysis. Samples will be embedded in epoxy, cut and polished for Scanning Electron Microscope (SEM) analysis. Each sample will undergo SEM analysis to identify uranium-bearing minerals. If possible, the distribution of carbonate minerals and /or iron oxides will also be determined.

Further analysis will depend upon the results of the sequential extractions and SEM analysis. Sediment samples will be impregnated with epoxy, and cut and polished for SEM analysis. If uranium is present as discrete uranium phase's visible by SEM, these will be identified by SEM energy dispersive x-ray (EDX) analysis or by electron microprobe. The distribution of iron oxides and carbonate minerals in the sediments, as discrete grains, or as mineral coatings, will be documented.

Uranium associated with carbonate minerals or iron oxides will subsequently be evaluated using High Resolution Transmission Electron Microscopy (HRTEM). The HRTEM can provide the identification of phases present in a specimen by either electron diffraction or spectroscopic chemical analysis techniques.

If uranium is identified in carbonate or iron oxide mineral grain coatings, then samples will also be analyzed by Secondary Ion Mass Spectrometry (SIMS). SIMS is a surface analytical technique that uses an ion beam to remove material from a surface. Although the SIMS has a limited spatial resolution (approx. 20 μm beam size), it can be used in a profiling mode, in which the beam is used to ablate vertically through a sample. In this mode, the vertical resolution can be as high as a few nanometers. The distribution of uranium in mineral coatings can thus be determined with great accuracy. This will provide relative information on the mobility of the uranium.

3.7 SCHEDULE

It is most cost effective to submit all of the samples to SNL in one batch. It is anticipated that the samples will be collected in the late spring and early summer of 2002. SNL has informed us that upon receipt of the samples at their lab, they will require approximately 28 weeks to conduct all of the required testing.

Schedule

Task	Activity	Schedule (Elapsed weeks)
<i>Phase 1</i>		
Bulk analysis for U (92 samples)	Crushing, dissolution	0-3
	Analysis, data sent to Fluor-Daniel	4
Pre-test Characterization	XRD analysis	5-6
	Carbon analysis	5-7
Sequential Leaching		5-9
Report/Data Analysis		9-12
<i>Phase 2</i>		
SEM Analysis	Sample Preparation	13-15
	Analysis	15-17
HRTEM analysis	Sample Preparation	17-19
	Analysis	19-21
SIMS	Sample Preparation	21-23
	Analysis	23-25
Report/Data Analysis		25-28

4.0 EQUIPMENT DECONTAMINATION

Decontamination of any sampling equipment shall be performed to fulfill the Level I specification of the Sitewide CERCLA Quality Assurance Project Plan (SCQ) (reference Section K).

5.0 WASTE DISPOSAL

Small volumes of groundwater, decontamination water, and contact wastes may be generated during the collection and sampling of the cores. Generation of water and contact waste will be minimized whenever possible. Contact waste generation will be minimized by limiting contact with sample media, and by only using disposable materials that are necessary.

6.0 HEALTH & SAFETY

EM personnel and project subcontractor personnel shall conform to precautionary surveys performed by the personnel representing the utility engineer, industrial hygiene, and radiological control. Concurrence with applicable safety permits (indicated by the signature of personnel assigned to this project) is expected from all project personnel in the performance of their assigned duties.

7.0 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

7.1 PROJECT REQUIREMENTS FOR SELF-ASSESSMENTS, SURVEILLANCE

Self-assessment of work processes may be undertaken to assure quality of performance. Surveillance of activities may be performed by the Project Lead and field contacts identified in Section 2.0 of this PSP, and shall encompass technical and procedure requirements. Such self-assessment may be conducted at any point in the project.

Independent assessment may be performed by the Fluor Fernald Quality Assurance organization by conducting surveillances. At a minimum the surveillance will consist of monitoring/observing ongoing project activities and work areas to verify conformance to specified requirements. Surveillances shall be planned and documented in accordance with Section 12.3 of the SCQ.

7.2 CHANGES TO THE PROJECT SPECIFIC PLAN

Prior to the implementation of changes, the Project Lead and/or Technical Lead shall be informed of the proposed changes. Once approval has been obtained from the Project Lead and/or Technical Lead and Quality Assurance representative for the changes to the PSP, the changes may be implemented. Variances shall be processed per Section 15.3 of the SCQ.

TABLE 1
SELECTIVE EXTRACTION REAGENTS AND DETAILS

Solid to Solution	Reagent	U fraction measured	Details
5g to 40 ml	0.1 M Mg(NO ₃) ₂ @ neutral pH	Exchangeable cationic species	Agitate for one hour at room temp.
Wash 15 minutes with 20 ml DI water, centrifuge and add to Mg nitrate extract			
5g to 40 ml	0.1 M Na ₂ (SO ₄) @ neutral pH	Exchangeable anionic species	Agitate for one hour at room temp.
Wash 15 minutes with 20 ml DI water, centrifuge and add to sulfate extract			
5g to 40 ml	1 M NaOAC adjusted to pH=5 with acetic acid	Carbonate Minerals	Agitate for four hours at room temp. Shouldn't release Fe, Al, or Mn. If it does, then dissolution of amorphous oxides may have occurred.
Wash 15 minutes with 20 ml DI water, centrifuge and add to acetate extract			
5 g to 200 ml	10.9 g/L oxalic acid [0.12 M] + 16.1 g/L amm. Oxalate [0.11 M]; pH~3	Amorphous Fe, Al, Mn, Si oxides	Agitate in the dark for four hours at room temp.
Wash 15 minutes with 30 ml DI water, centrifuge and add to oxalate extract.			
5g to 40 ml	Mix 15 ml of 0.02 M nitric acid and 25 ml of 30% H ₂ O ₂ later add ammonium acetate/nitric acid	Organics	Heat to 85°C for two hours, add 25 ml more of 30% H ₂ O ₂ and heat to 85 C for three hours. Add 40 ml of 1 M ammonium acetate/nitric acid to pH = 2, shake for 30 minutes, and extract.
Wash 15 minutes with 30 ml DI water, centrifuge and add to peroxide extract			
5 g to 200 ml	Mix 0.3 M trisodium citrate, 0.2 M NaHCO ₃ , 1 g/g sample sodium dithionite; pH ~8.3 to keep from dissolving Mn.	Crystalline ferric iron oxides, oxyhydroxides	Stir for 30 minutes at 85°C; repeat extraction (total 2 times combine leachate)
Wash 15 minutes with 60 ml DI water, centrifuge and add to dithionite extract			
5g to ~50 ml	8 M HNO ₃	Clays, U oxides	Add 50 ml of 8 M HNO ₃ , mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 ml of concentrated HNO ₃ , replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO ₃ , repeat this step (addition of 5 ml of conc. HNO ₃) until no brown fumes are given off by the sample indicating the complete reaction. Allow the solution to evaporate to approximately 25 ml without boiling or heat at 95°C ± 5°C without boiling for two hours. Remove the acid extract after solids settle.
Wash 15 minutes with 15 ml DI and add to nitric acid extract			
0.2 g in 10 ml 1:1 HNO ₃ , 15 ml HF.	Conc. HF plus 1:1 conc. HNO ₃ : DI water	Residuals (quartz, zircon, etc)	Oven dry to get wt. Crush, digest in 15 ml conc. HF plus 10 ml 1:1 HNO ₃ . Allow to go to near dryness, redissolve in 1 M HCl for analysis.