# CHARACTERISTICS OF AQUEOUS COLLOIDS GENERATED BY CORRION OF METALLIC URANIUM FUEL[1]

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# CHARACTERISTICS OF AQUEOUS COLLOIDS GENERATED BY CORROSION OF METALLIC URANIUM FUEL

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## ABSTRACT

Metallic uranium fuel from the Hanford N Reactor was corroded in aqueous solutions and the resulting colloidal suspensions were analyzed to determine particle size, morphology, population, and radionuclide association. The experiments used a range of solution chemistry conditions including deionized water, single salt solutions, and modified groundwater from Yucca Mountain. Colloids were analyzed by inductively coupled plasma mass spectrometry, transmission electron microscopy, photon correlation spectroscopy, and synchrotron small-angle x-ray scattering. The results of these analyses indicate that stable suspensions of small (1-10 nm diameter), spherical uranium oxides are generated and aggregate to approximately 100-200 nm colloids. There is no indication that these colloids continue to aggregate to larger size. In silicate solutions, large acicular uranium silicate colloids are formed in small quantities as are large uranium-bearing smectite clay colloids. Plutonium clearly associates with colloidal particles. Large particles contain the same Pu/U ratio as the uncorroded fuel, possibly indicating that the Pu is incorporated in the particle matrix. Smaller particles are highly enriched in Pu relative to the uncorroded fuel.

## INTRODUCTION

Uranium-containing colloids arising from the corrosion of metallic uranium fuel may provide a transport mechanism for radioisotopes in a geologic repository environment such as the proposed Yucca Mountain site. Transport of sparingly soluble radionuclides is enhanced by colloids because the stable particles can achieve significantly higher solution-phase radionuclide concentrations than permitted by solubility constraints, and the highly-mobile charged colloids provide a vehicle for movement.

Corroding spent nuclear fuel may generate radionuclide-associated colloids by several mechanisms. Current colloid nomenclature distinguishes real colloids, primary colloids, and pseudocolloids based on their generation mechanism. Real colloids are generated by condensation of low solubility species, primary colloids are formed by spallation of fuel fragments and fuel oxidation products, and pseudocolloids result from adsorption of radionuclides onto pre-existing groundwater or waste package colloids. These mechanisms are discussed briefly below as they pertain to metallic uranium fuel.

As the fuel undergoes aqueous corrosion, dissolution of low solubility radio-elements, such as actinides, is followed by their hydrolysis, condensation as metal-oxo polymers, and aggregation as real colloids. Real colloids of Pu(IV) generated in laboratory experiments have been characterized as discrete particles of 1-2 nm diameter, or aggregates of discrete particles that reach considerably larger size (>10 nm, with molecular weights 4000 to several million) [1]. Nitsche [2] demonstrated that in J-13 well water, dissolved Pu(IV) is converted to solid and colloidal species as well as dissolved Pu(V). At approximately neutral pH in oxic, carbonate containing solutions, these real colloids are expected to be minor contributors to the total radionuclide-associated colloid population because carbonate complexation stabilizes actinide complexes, rendering them unlikely to polymerize and generate colloids. Furthermore, actinide real colloids undergo formation of pseudocolloids in groundwater by adsorption of real colloids onto existing groundwater colloids and thus real colloids are not expected to directly contribute to subsurface radionuclide mobility [3].

Spallation of colloid-sized fuel oxidation products has been widely observed for metallic uranium fuel. Radionuclide-associated spallation colloids may be generated both by cleavage of nano-scale fuel corrosion products with engulfed radionuclides, and by subsequent adsorption of radionuclides onto spalled corrosion products. Thus, radionuclides can be embedded in the colloid substrate or sorbed to its surface or both. In general, embedded radionuclides are considered to be irreversibly sorbed and hence transportable over the entire transit path of the colloid, while surface-sorbed radionuclides may be reversibly or irreversibly sorbed. Reversible sorption of a sparingly soluble radionuclide results in precipitation of that element when solubility limits are exceeded, and thus a shorter transit than expected for irreversibly sorbed radionuclides.

As discussed above, pseudocolloids generated by the interaction of radionuclides with groundwater colloids may be significant in radionuclide transport. However, groundwater pseudocolloids are not discussed in this paper as the scope is limited to real and primary colloids generated directly by metallic uranium fuel.

This paper discusses uranium-containing colloids that were generated and characterized in a series of aqueous corrosion experiments with irradiated and unirradiated metallic uranium fuel. The experiments used a range of solution chemistry conditions including deionized water, single salt solutions, and modified groundwater from Yucca Mountain. Colloids were analyzed by inductively coupled plasma mass spectrometry (ICPMS), transmission electron microscopy (TEM), photon correlation spectroscopy (PCS, and synchrotron small-angle x-ray scattering (SAXS). The results of these analyses are presented in this paper.

## EXPERIMENTAL METHODS

### *Metallic Uranium Fuel*

Small coupons (0.1 to 1 gram) of both unirradiated and irradiated fuel from the Hanford N-Reactor were tested. The fuel was prepared by de-cladding and cutting into rectangular coupons. Immediately before the start of a corrosion test, the coupons were polished with 600 grit alumina and sonicated briefly in deionized water.

### *Solution Composition*

Solution compositions included deionized water, 1 mM $Na_2CO_3$, 1 mM $NaSiO_4$, 1 μM $Fe(NO_3)_3$, and modified groundwater. The carbonate, silicate, and iron concentrations were selected to be approximately the same as in the modified groundwater which is “tuff equilibrated” USGS J-13 well water from Yucca Mountain, referred to as EJ-13.

### *Test and Analysis Methods*

Unirradiated metallic uranium fuel coupons were corroded in each of the leachant solutions in static, batch corrosion tests for a period of 5 months. Each solution was adjusted to pH 4 or 8 at the start of the batch test. Temperature was maintained at 30ºC in a water bath. Colloids were observed directly in the supernatant at several analysis times using an *in situ* photon correlation spectroscopy (PCS) technique. Glass sample vials were moved from a bench-top water bath to the water bath of the photon correlation spectrometer in the same laboratory and particle light scattering was monitored without change in temperature, sample removal or any preparation. In addition to the *in situ* measurements, aliquots of sample were removed periodically for filtration and analysis by other techniques.

In hydrologically unsaturated tests, irradiated uranium fuel coupons were placed on gold mesh filters suspended in the path of dripping/injected EJ-13 groundwater. The water contacted the coupon and drained into a stainless steel receptacle beneath the gold mesh. Twice weekly, injections of air and 0.75 mL EJ-13 were made. The vessels were sealed air tight and maintained at 90ºC. Vessels were opened periodically and all liquid removed for analysis.

Colloids generated during these tests were characterized by a series of complementary analytical techniques. Unfiltered and filtered aliquots of solution were analyzed by ICPMS to quantify the uranium and plutonium content of each particle-size fraction and the dissolved fraction. Unfiltered samples were examined by PCS to determine colloid population and size distribution, by TEM to determine size, morphology, and identity, and by SAXS analysis to determine colloid morphology and dimensions. The SAXS analysis was performed at the Advanced Photon Source, Argonne, using the pinhole camera with a 3 m flight path. A high-energy incident beam (17.1 keV), approximately 50 eV below the U-$L_{III}$ edge, was used to ensure that the small-angle scattering was due only to the uranium.

## RESULTS & DISCUSSION

### *Colloid Size and Morphology*

Colloids were generated in the corrosion of metallic uranium fuel under all conditions tested. Most corrosion conditions and leachant solutions produced abundant nanophase $UO_2$ colloids which are characterized by a nearly spherical morphology and small size. Figure 1 shows results of $UO_2$ characterization by TEM and PCS. As seen in Figure 1a, the $UO_2$ colloids consist of discrete particles approximately 1-10 nm in size that agglomerate to form larger colloidal associations of approximately 100-200 nm. The particles are identified by electron diffraction (Fig. 1b) as $UO_2$. It should be noted that the PCS size distribution shown in Figure 1c is intensity weighted. This results in large scattering peaks for large colloids but does not imply that the larger colloids are more abundant. In fact, the intensity of light scattering is proportional to the square of the particle radius in the PCS technique, and thus large particles result in high intensity scattering and large peaks while small particles may be significantly more abundant and generate only a small intensity peak. Nevertheless, the *in situ* PCS technique permitted non-disruptive determination of the particle size distribution throughout the testing period and correlated well with TEM determination of particle size.

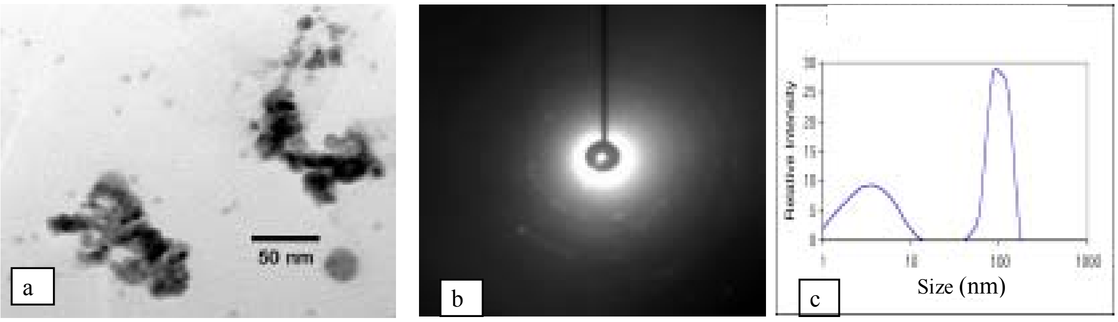

Figure 1. $UO_2$ colloids generated from corrosion of metallic uranium N Reactor fuel in EJ-13 groundwater. 1a) transmission electron micrograph of agglomerations of discrete 5-10 nm particles; 1b) crystallographic identification of colloids as $UO_2$ by Selected Area Electron Diffraction; 1c) particle size distribution determined by photon correlation spectroscopy.

Individual $UO_2$ particles appear roughly spherical in TEM micrographs. Data from SAXS experiments also indicate spherical uranium-containing colloids of 3 nm diameter in silicate solutions (Fig. 2) and approximately 30 nm diameter in carbonate solution. This corroboration is significant for a number of reasons. In complex colloidal systems such as waste package corrosion environments and groundwater, colloids of several minerals can co-exist and potentially interact. While TEM images provide *ex situ* information about colloid size and shape, it is not always possible to obtain mineralogical identification of the particles in the mixture. The SAXS technique enables *in situ* characterization, and in this analysis, use of x-ray energy 50 eV below the U-$L_{III}$ edge ensured that scattering resulted only from uranium-containing particles. This result was confirmed by analyzing control samples of the silicate and carbonate solutions (i.e. replicate tests performed with no uranium present). Thus, the SAXS technique provided corroborating evidence of the size and shape of uranium-containing colloids that were identified by TEM as $UO_2$.

While extended stability studies of these colloids were not performed, suspensions of these colloids were observed to persist for 1.5 months after removing the coupon from the liquid phase. During that period, the particle size distribution broadened such that a single broad peak included the two peaks previously seen for $UO_2$ colloids at approximately 1-10 nm and 100-200 nm. The suspensions were not monitored after 1.5 months, so it is not known how long the colloids remained stable.

Colloids generated in 1 mM $NaSiO_4$ were typically much larger than the $UO_2$ colloids and are characterized by a broad distribution from 100-1000 nm. These colloids included a small number of long acicular colloids (Fig. 3) and a larger quantity of spherical, globular, and plate-like aggregates. Several different phase compositions were observed. Irradiated U metal fuel corroded for 8.5 months in EJ-13 groundwater contained smectite clays with associated U (Fig. 4). The U was a minor component and the nature of its association (i.e. sorption vs. incorporation) is not known.

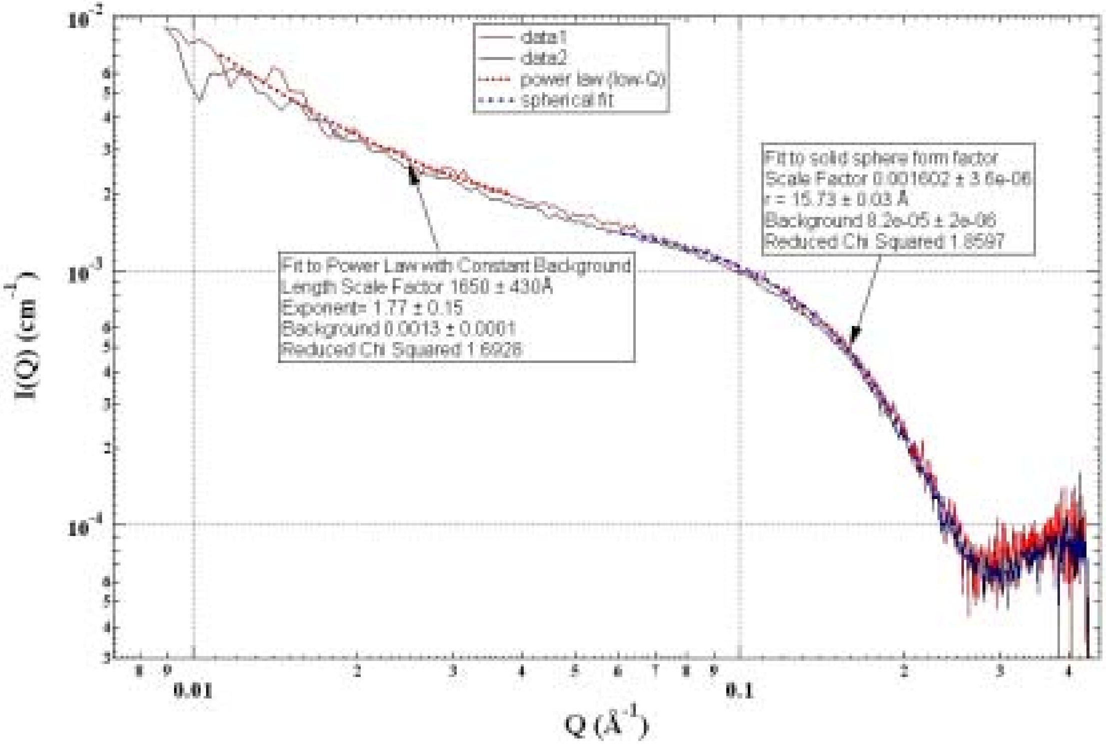

Figure 2. Small-angle x-ray scattering from $UO_2$ colloids generated by corrosion of unirradiated N-reactor fuel in silicate solution. Results indicate spherical scatterers of 1.6 nm radius.

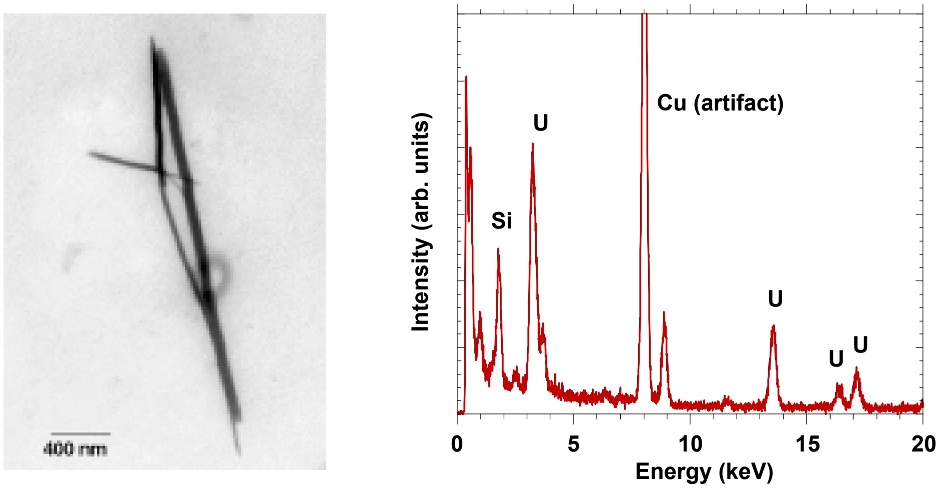

Figure 3. Acicular uranyl silicate colloids generated in EJ-13 and silicate solutions. These particles are a minor colloidal product of both unirradiated and irradiated N Reactor fuel.

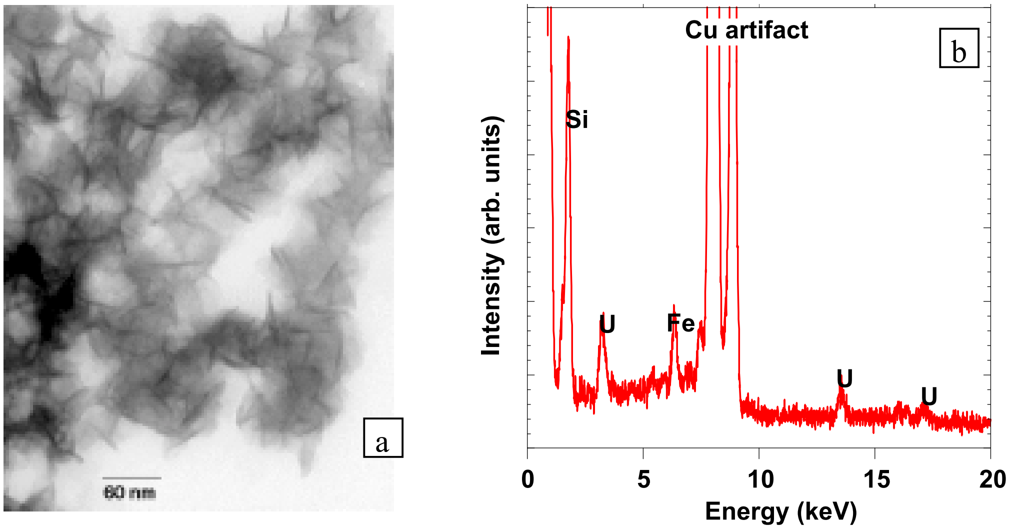

Figure 4. Uranium containing smectite clay colloids generated by reaction of fuel sludge with EJ-13 groundwater for 8.5 months at 90˚C. 2a) TEM image of agglomerated smectite clay; 2b) EDS spectrum indicating U association with the clay.

*Colloid Quantitation*

Colloid quantitation was performed by solution filtration followed by ICPMS analysis. The method determines the quantity of uranium and plutonium that passes through each filter pore size. The distribution of uranium-containing colloids was found to be dependent on the initial solution composition and pH. Results for unirradiated uranium metal corrosion in deionized water, silicate, carbonate, ferric iron, and EJ-13 groundwater solutions at pH 8 and 30˚C are summarized in Table I and discussed below. Results for irradiated samples are discussed in the next section.

Table I indicates that the fractional distribution of uranium-containing species in the EJ-13 and silicate solutions is similar. However, the quantity of uranium in the large particulate (> 450 nm) and in the dissolved + smallest colloid fraction (< 5 nm) is approximately a factor of 10 greater for the silicate than for the groundwater solution. This implies either that silicate (in the absence of groundwater cations) stabilizes dissolved uranium, or that very small (<5 nm) uranium silicate colloids are formed in the silicate solution but not in the groundwater solution. The former explanation is considered unlikely, however there is no evidence from TEM analysis that small uranium silicate colloids are present. To the contrary, the uranium silicate colloids identified by TEM are large (> 500 nm) acicular, plate-like, and globular structures. However, PCS and SAXS do provide evidence of very small colloids. Colloids in the 1-10 nm range are observed at long reaction times by PCS, and 3-nm diameter spherical uranium-containing colloids are indicated by SAXS analysis of the same silicate solution (Fig. 2). Thus, it is possible that in the absence of groundwater cations, uranium silicate forms and slowly aggregates over several months to generate the very small colloids indicated by filtration-ICPMS, PCS, and SAXS.

**Table I. Average Uranium Concentration (mg/L) in Each Particle Size and Percent of Total Uranium in Particle Size Range.**

| Particle (P) Size Category | EJ-13 Groundwater | | Silicate (1 mM) | | Carbonate (1 mM) | | Ferric (1 µM) | | Deionized Water | |
|---|---|---|---|---|---|---|---|---|---|---|
| | mg/L | % | mg/L | % | mg/L | % | mg/L | % | mg/L | % |
| P > 450 nm | 7 | 13 | 70 | 19 | 8 | 11 | 1 | 4 | 2 | 30 |
| 220 nm <P< 450 nm | 1 | 3 | 1 | 0 | 12 | 16 | 0 | 0 | 0.4 | 7 |
| 5 nm <P< 220nm | 6 | 13 | 7 | 2 | 36 | 52 | 11 | 51 | 2 | 36 |
| P< 5 nm and Dissolved | 29 | 71 | 261 | 79 | 18 | 21 | 10 | 46 | 2 | 27 |
| Total | 39 | 100 | 290 | 100 | 74 | 100 | 21 | 100 | 6 | 100 |

The distribution of uranium corrosion products in 1 mM carbonate solution is very different. Table I indicates that the greatest quantity (52%) of uranium is in the colloidal size range between 5 and 220 nm and an additional 16% is in the colloidal range between 220 and 450 nm. While anionic carbonate complexes of U(VI) account for approximately 90% of total U(VI) at near-neutral pH [4], the dissolved + smallest colloid fraction of uranium in these corrosion tests represents only 21% of the total uranium. This is explained by the oxidation state of uranium in the corrosion experiments and the solution redox potential. Metallic uranium corrodes to $UO_2$ and $UO_{2+x}$ which spall from the solid surface as colloidal particles and large “sludge” particles. The oxidation state of this material is primarily U(IV). While oxidation of U(IV) to U(VI) occurs in oxic solutions, the redox potential of the carbonate solutions was observed to decrease from approximately 300 mV vs. NHE initially to 150 mV after 4 months in test. Although still an oxidizing solution, the oxidative driving force was greatly diminished. This potential decrease was observed in all carbonate solutions and not in any of the other solutions tested. As a result, stable U(IV) colloids remained abundant in solution and the expected carbonate complexation of U(VI) occurred only to a small extent.

The 1 µM Fe(III) solution resulted in the release of approximately half as much uranium from the fuel as in the EJ-13 solution. Essentially all of the uranium was found in the smallest size fractions, i.e. < 5 nm, and colloids between 5 and 220 nm.

### *Colloid-Radionuclide Association*

Plutonium association with colloids was studied in the hydrologically unsaturated tests performed with irradiated N Reactor fuel. Two fuel samples were corroded with EJ-13 for a period of 315 days. The tests were sampled multiple times during that period with ICPMS analysis of filtered and unfiltered leachate at each sampling time. In addition, the vessel walls were leached with $HNO_3$ to release sorbed material at each sampling. The concentration of U was above the method quantitation limit (MQL) of the ICPMS method (0.1 ng) for 100% of the samples analyzed. For Pu, 85% of the samples analyzed were above the MQL (0.1 ng). However the low solubility of Pu resulted in measurable Pu concentrations in only 40% of the dissolved fraction samples.

Comparison of the ratio of Pu/U present in each particulate and dissolved fraction is useful in determining the association of Pu with colloids from the spent fuel. The ratio in the fuel at the start of testing is $Pu/U \approx 1.7 \times 10^{-3}$. Table II summarizes the Pu/U ratios determined using data from two unsaturated corrosion tests (replicate tests sampled on different test days). Several features are immediately apparent: (1) on average, the U-containing particles > 450 nm have approximately the same ratio of Pu/U as the starting material; (2) Pu is highly concentrated relative to its original Pu/U in or on colloids that are 5 – 450 nm; 3) in general, there is very little Pu in the fraction < 5 nm; and (4) sorbed material has approximately the same ratio of Pu/U as the starting material.

**Table II. Ratio of $^{239}Pu/^{238}U$ ($\times 10^3$) in Irradiated N Fuel Leachate Samples**

| Test Day | P[a] >450 nm | 5 nm < P[a] < 450 nm | P[a] < 5 nm | Sorbed |
|---|---|---|---|---|
| 7 | 0.5 | 3.5 | <MQL[b] | 1.5 |
| 9 | 0 | 1.6 | <MQL[b] | 1.3 |
| 23 | 1.2 | 8.9 | 0.3 | 0.6 |
| 26 | 2.1 | 14.3 | 0.4 | 1.5 |
| 61 | 1.1 | [U]=0; [Pu]=9 ng[c] | <MQL[b] | 0.9 |
| 86 | 2.0 | 7.9 | <MQL[b] | 0.8 |
| 122 | [U]=0; [Pu]= 1 ng[c] | 0.03 | 0.1 | 0.5 |
| 125 | 1.5 | 20.7 | <MQL[b] | 1.2 |
| 227 | 0.8 | [U]=0; [Pu]=9 ng[c] | 0.1 | 1.3 |
| 315 | 0.8 | [U]=0; [Pu]=3 ng[c] | <MQL[b] | 1.0 |
| Average | 1.1 | 8.1 | 0.1 | 1.1 |

[a] P = particle size

[b] [Pu] < method quantitation limit (0.1 ng)

[c] No U in size fraction, but measurable Pu present.

The fact that the original ratio of Pu/U is maintained in large particles implies that the Pu in the irradiated fuel is incorporated in the spalled oxidation products. This is consistent with the solid state oxidation mechanism for metallic uranium [5].

In the colloidal phase, Pu/U is increased by a factor of 5 on average, and a factor of 12 was observed on Day 125. This concentration effect of Pu in the colloidal phase is significant because these particles are expected to be highly mobile in the Repository subsurface environment. It should be noted that the actual quantity of Pu in this size fraction typically represents 10% or less of the total Pu, but has been observed to be as high as 50% of the total Pu. The quantity of colloidal U represents about 5% of the total U with a maximum of 30% observed in one test. Thus the Pu/U concentration effect is due not only to the increase in the quantity of Pu present in the colloidal range, but also to the decrease in the quantity of U. While it is not possible to state the nature of the Pu association with these colloids, it is likely, based on the Pu enrichment and the colloid size and morphology, that the Pu is both incorporated in the colloid matrix and adsorbed on its surface.

In contrast, Pu content in the dissolved and smallest colloid fraction (<5nm) was generally extremely low, consistent with the low solubility of Pu. It accounts for <5% of the total Pu in most samples and was below method quantitation limit for 6 of 10 samples. This fraction may include real Pu colloids, but the small Pu content present in these tests did not permit distinction of dissolved Pu from real colloids. When sufficient Pu was present in these samples to be quantified, the ratio of Pu/U was significantly lower than the initial fuel ratio.

The leachate fraction with the highest Pu content is the sorbed component. This fraction includes both dissolved and colloidal materials that sorbed to the stainless steel vessel walls. It typically accounts for 40-90% of the total Pu released from the fuel in soluble or colloidal form. The ratio of Pu/U in the sorbed material is approximately the same as in the uncorroded fuel.

## SUMMARY

Uranium-containing colloids were generated from metallic uranium fuel under all solution conditions tested. The most abundant colloids appear to be small, spherical particles of $UO_2$. Individual colloids are typically 1-10 nm in diameter but aggregate to stable configurations of 100-200 nm length. Several other compositions of uranium-containing colloids were observed in smaller quantities. These include long (>500 nm), acicular uranium silicates, uranium-containing smectite clays, and large plate-like and globular particles containing primarily uranium and silicon.

The distribution of uranium-containing colloids generated in EJ-13 groundwater was most closely reproduced in 1 mM silicate solution. While uranium-colloids were also generated in carbonate and ferric iron solutions, the size distribution, morphology, and composition of those colloids did not provide a strong match to those in the modified groundwater.

Plutonium was associated with colloids in all size fractions, however the Pu concentration in the dissolved fraction was typically negligible. In large suspended particles (> 450 nm), the Pu/U ratio is approximately the same as in the uncorroded fuel matrix. This suggests that the Pu is incorporated in the colloid particle matrix. In the colloid fraction with dimensions between 5 and 450 nm, the Pu concentration is enriched relative to the original Pu/U ratio. While it is not possible to definitively state the nature of the Pu association with these colloids, it is likely, based on the Pu enrichment and the colloid size and morphology, that the Pu is both incorporated in the colloid matrix and adsorbed on its surface.

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