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Alkali Treatment of Acidic Solution From Hanford K Basin Sludge Dissolution

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September 1998

Prepared for the U.S. Department of Energy
by the Institute of Physical Chemistry,
Russian Academy of Sciences, through the
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under the Contracts 318862-A-R5 and 318862-A-J2
with the Pacific Northwest Division of
Battelle Memorial Institute

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Summary

Nitric acid solutions will be created from the dissolution of Hanford K Basin sludge. These acidic dissolver solutions must be made alkaline by treatment with NaOH solution before they are disposed to the Tank Waste Remediation System on the Hanford Site. During the alkali treatments, sodium diuranate, hydroxides of iron and aluminum, and radioelements (uranium, plutonium, and americium) will precipitate from the dissolver solution. Laboratory tests, discussed here, were performed to provide information on these precipitates and their precipitation behavior that is important in designing the engineering flowsheet for the treatment process. Specifically, experiments were conducted to determine the optimum precipitation conditions; the completeness of uranium, plutonium, and americium precipitation; the rate of sedimentation; and the physico-chemical characteristics of the solids formed by alkali treatment of simulated acidic dissolver solutions. These experiments also determined the redistribution of uranium, plutonium, and americium from the sodium diuranate and iron and aluminum hydroxide precipitates upon contact with carbonate- and EDTA-bearing simulated waste solutions. Note: EDTA is the tetrasodium salt of ethylenediaminetetraacetate.

The results of the experiments indicate that alkali treatment of the acidic dissolver solution is best performed by precipitation and digestion at 40°C with 0.01 M NaOH excess (pH 12) using direct strike addition of NaOH solution to the dissolver solution. These conditions yield the lowest uranium concentration in the supernatant, require the least excess NaOH, and provide the highest apparent partitioning of plutonium to the carbonate-resistant Fe(III) hydroxide solid phase. However, other conditions, such as reverse strike, 80°C, have little effect on precipitate properties. The resulting supernatant solutions using the range of conditions tested here are non-TRU for both plutonium and americium. Contacting product precipitates having no Fe(III) in the solid phase with carbonate-bearing solutions can produce TRU-level plutonium and americium concentrations in solution. Alkaline solutions containing EDTA also can leach americium to near-TRU levels from iron-free solids.

Results from the specific tests are summarized below:

The alkali-treated simulated dissolver solutions were found to be non-transuranic for both plutonium and americium. Plutonium concentrations in the alkaline mother solutions were scattered and low ($\sim 2\times10^{-8}$ M versus 5.5×10^{-6} M Pu equivalent to the 100 nCi ^{239,240}Pu/g TRU waste limit). Americium concentrations in the mother solutions also were low [$(5\text{-}11)\times10^{-11}$ M versus 1.2×10^{-7} M Am equivalent to 100 nCi ^{241}Am/g] and not strongly dependent on the precipitate composition. When the NaOH concentration was increased from 0.01 to 1 M, uranium concentrations in the mother solutions increased, accordingly, from 1.5×10^{-6} to 18×10^{-6} M.

The sedimentation rates of precipitates formed by alkali treatment of a simulated dissolver solution were found to be nearly independent of the conditions of precipitation (alkali excess or direction of mixing), but did increase slightly with increasing temperature. Sedimentation rate also was independent of the dissolver solution composition. Solids volume increased with an increase of the total molar concentration of the macrocomponents (U, Fe, and Al) in the dissolver solution. The sodium diuranate precipitates were about two-fold denser than the Fe(III) or aluminum hydroxides.

The precipitates consisted of crystalline $Na_2U_2O_7$ with Fe(III) and Al(III) hydroxides generally present as amorphous species. However, some precipitates obtained by coagulation at 80°C contained crystalline Fe_2O_3 (hematite), and crystalline $Al(OH)_3$ (bayerite) also was present in one test. The $Na_2U_2O_7$ crystallite size was estimated to be 5 to 8 nm based on X-ray diffraction line width.

Crystallite size distributions were measured by a small angle X-ray scattering technique for a variety of dissolver solution compositions. In all cases, the maximum population occurred at crystallite particle sizes of 2 to 3 nm (0.002 to 0.003 microns). The particle size distribution for pure Fe(III) hydroxide was slightly lower than that of sodium diuranate. The small crystallite size guarantees intimate mixing of iron- and uranium-based neutron poisons with plutonium.

The sodium diuranate precipitate dissolves extensively if contacted with a simulated high carbonate waste solution (1 $\underline{M}$ Na_2CO_3 + 5 $\underline{M}$ $NaNO_3$). The concentrations of plutonium and americium dissolved by the carbonate leaching solutions were correlated with the amount of uranium dissolved. However, only a fraction of the plutonium, perhaps that associated with sodium diuranate, dissolved in the carbonate solution. In most tests, the fraction of plutonium leached was lower than that of uranium.

Plutonium was found to preferentially associate with Fe(III) hydroxide in the precipitates; plutonium concentrations in the carbonate leach exceeded the TRU limit (100 nCi/g or 5.5×10^{-6} $\underline{M}$) only for those solids containing no Fe(III), but approached the TRU limit and were greater than 1×10^{-6} $\underline{M}$ in all cases. No association of plutonium with aluminum hydroxide was found. Similarly, americium dissolution by the carbonate leaching solution was lowest for the solid phases highest in Fe(III) hydroxide and exceeded the TRU limit (1.2×10^{-7} $\underline{M}$) only for two tests having no Fe(III).

Leaching of the precipitates by a simulated alkaline waste solution containing a high concentration of organic complexing agent (0.1 $\underline{M}$ EDTA + 1 $\underline{M}$ NaOH + 5 $\underline{M}$ $NaNO_3$) was also tested. The uranium concentrations were about three times higher than found in the original alkaline mother solution. The plutonium concentrations in the EDTA leachates (about 2×10^{-8} $\underline{M}$) were similar to those observed in the original alkaline mother solutions and were well below the TRU limit. The precipitation conditions and compositions had little effect on the degree of uranium and plutonium dissolution in the EDTA-bearing leachates. In contrast, the americium concentrations in the EDTA leachates approached the TRU limit for solids having no Fe(III).

Acknowledgments

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1.0 Introduction

The K Basins at the U.S. Department of Energy's Hanford Site have been used since the 1970s for the underwater storage of N Reactor spent fuel elements. Over time, sludge formed by the corrosion of damaged fuel accumulated at the bottoms of the basins and in some of the storage containers. The sludge contains irradiated uranium from corroded fuel, as well as iron and aluminum hydroxides from corroded structural materials (racks, canisters), sand from sand filters, and wind-blown soil. Plans for disposal at Hanford involve separating the solid and liquid portions of the sludge. Ultimately, the liquid portion will be disposed in the Tank Waste Remediation System (TWRS) underground storage tanks and the solids in the Environmental Restoration Disposal Facility (ERDF). However, before the sludge solids can be sent to the ERDF site, the radioactive components must be removed.

Studies conducted as part of the overall K Basin cleanup effort recommend using a nitric acid treatment to dissolve the radioactive materials in the sludge, and then treating the resulting acidic dissolver solution to produce an alkaline slurry that would also be disposed in the TWRS storage tanks (Flament 1998). The dissolver solution generated from nitric acid dissolution will contain uranium, iron, and aluminum macrocomponents; small concentrations of dissolved silica; and radioactive plutonium, americium, and fission products. To be acceptable for TWRS disposal, the solution must be blended with depleted uranium and possibly iron solutions for criticality safety. The amended dissolver solution then will be treated with sodium hydroxide (NaOH) to reach a required minimum NaOH concentration of 0.01 M. The purpose of the work discussed here was to further verify the alkali treatment approach for the dissolver solution.

Treating the sludge dissolver solution with NaOH will precipitate sodium uranates and hydroxides of iron, aluminum, and other highly charged metal cations. The solid phase will coprecipitate the tracer amounts of radioactive plutonium, americium, and strontium. In designing an engineering flowsheet, it is important to understand the nature and the physico-chemical characteristics of precipitates produced by NaOH treatment under various process conditions. At the same time, the completeness of plutonium coprecipitation and its distribution in the solid phase should be determined because of nuclear criticality safety considerations. Plutonium and americium also are contributors to the transuranic (TRU) waste (i.e., they contain α-emitting isotopes with half-lives greater than 20 years). Therefore, special attention should be paid to understanding plutonium and americium behavior not only during the initial precipitation but also upon interaction of the alkaline precipitates with complexants such as carbonate and ethylenediaminetetraacetate (EDTA) present in the waste tanks.

The primary task of this investigation arises from designing the alkali treatment process and satisfying the acceptance requirements for disposal of the treated dissolver solution. The main objectives are to identify optimum precipitation conditions; measure the extent of uranium, plutonium, and americium precipitation; determine the rate of precipitate sedimentation; and characterize the physico-chemical properties (phase identity, volume, particle size) of the solids formed by alkali treatment of acidic sludge dissolver solutions (Flament 1998, Section 4.9). The secondary task involves storing and processing these and similar wastes in the underground tanks. The purpose of this secondary task is to study the possible redistribution of uranium, plutonium, and americium from the product sodium diuranate and iron and aluminum hydroxide precipitates upon contact with carbonate- and EDTA-bearing solutions. The carbonate- and EDTA-bearing solutions simulate existing tank solutions, and the tests model waste blending and process operations.

This report discusses the experiments performed to meet the objectives of the two tasks. The work was conducted in three sets of experiments that included alkali treatment parametric testing; dissolver solution composition testing; and precipitate particle size distribution, as determined by small angle X-ray scattering (SAXS). Along with the results, the report describes the materials and equipment used in the study and the experimental methods for each test series.

2.0 Materials and Equipment

The experiments were performed using standard nitrate solutions of U(VI), Fe(III), Al(III), Pu(IV), and Am(III) in chemical purity grade nitric acid and distilled water. The uranium solutions were prepared by dissolving pure $UO_2(NO_3)_2{\cdot}6H_2O$ in water. The exact solution concentration (0.9973 M) was determined by gravimetric analysis by drying aliquots in platinum crucibles and calcining the residue in air to U_3O_8. Chemical purity grade $Fe(NO_3)_3{\cdot}9H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were used to prepare 1.070 M Fe(III) nitrate and 1.909 M Al(III) nitrate solutions. These solution concentrations were also determined by gravimetric analysis by drying aliquots and calcining to Fe_2O_3 or Al_2O_3. The Fe(III) solution also contained 0.05 M free HNO_3 to prevent hydrolysis.

For these testes, Pu(IV) nitrate solutions with known concentrations of HNO_3 were prepared by the following methods. First, to ~0.05 M plutonium nitrate in ~3 M HNO_3 (purified by the common anion exchange method), H_2O_2 was added to 0.05 M concentration and the mixture heated on a boiling water bath. The sharp change of solution color from blue to brown indicated complete H_2O_2 decomposition and conversion of Pu(III) to Pu(IV). From this solution, $Pu(C_2O_4)_2{\cdot}6H_2O$ was precipitated by slow addition, with slight heating, of ~1 M oxalic acid to ~0.1 M excess. After 2 hours of coagulation, the compound was separated from the mother solution by centrifugation and washed with 1 M HNO_3 containing 0.01 M $H_2C_2O_4$. The $Pu(C_2O_4)_2{\cdot}6H_2O$ was dissolved in boiling concentrated HNO_3 and the product solution evaporated to a small volume. After cooling, the solution was diluted four-fold with 2 M HNO_3 and treated with H_2O_2 to stabilize Pu(IV) as previously described.

For determining the Pu concentration of the solutions gravimetrically, 0.1-mL aliquots of Pu(IV) stock solution were carefully (without boiling) evaporated to dryness in small platinum crucibles and the residues calcined at 800°C for about 2 hours to produce PuO_2. The free HNO_3 concentrations in the Pu(IV) solutions were determined by direct titration with 0.1 M NaOH using phenolphthalein as an indicator. In determining the HNO_3 concentration, it was assumed that 4 moles of NaOH were consumed in the course of the titration to precipitate 1 mole of Pu(IV). By this method, Pu(IV) stock solution was prepared having 0.206 M Pu and 4.35 M free acid. The tetravalent state of plutonium in the test solutions was verified by absorption spectrophotometry using a Shimadzu (Japan) model UV-3100 PC UV-Vis-NIR spectrophotometer.

The americium stock solution consisted of $1{\times}10^{-3}$ M $^{241}Am(NO_3)_3$ in 0.1 M HNO_3. Its concentration and existence as Am(III) were measured spectrophotometrically at 503 nm, and the concentration confirmed by radiometric analysis. Alpha spectrometry showed the ^{244}Cm impurity in the ^{241}Am stock to be less than $5{\times}10^{-3}$ %.

Silicate also was present in many test solutions. A standard 0.1 M Si(IV) stock solution was prepared by dissolving analytical purity grade $Na_2SiO_3{\cdot}9H_2O$ in 0.05 M NaOH. Working NaOH solutions were obtained by the dilution of 16.0 M NaOH of special purity grade. The NaOH solutions were stored in polyethylene bottles. Two separate leaching solutions of composition 1 M Na_2CO_3 + 5 M $NaNO_3$ and 0.1 M EDTA + 1 M NaOH + 5 M $NaNO_3$ were prepared from chemical purity grade Na_2CO_3 and $NaNO_3$ and analytically pure EDTA, disodium salt. All solutions were prepared with distilled water.

The crystallinity and identification of solid phases were determined by X-ray diffraction (XRD) measurements with a model ADP-10 (Philips) X-ray diffractometer using Cu $K_{\alpha 1}$ radiation and a graphite monochromator on the diffracted beam. Thermostats (U-2 model, Germany) were used to maintain solution temperatures within ±2°C in the range 20°C to 80°C. Precipitate separations from supernatant liquids were performed using medical centrifuges (model CLS-3, Russia) operated at 2500 times the acceleration of gravity. Sample weights were determined by use of a Sartorius (Germany) microbalance with a sensitivity of ±1 µg. The α-activities of plutonium and americium solutions were measured by an LS-6500 liquid scintillation counter (Beckman, USA). Solution pHs were measured by pH meter model OP-211/1 with glass electrode model OP-0808P (Radelkis, Hungary). Mössbauer spectra of the ^{57}Fe transition at 14.4 keV were taken with a spectrometer of constant acceleration "Mössbauer Laboratory" produced by KFKI (Hungary) with a 3-mCi ^{57}Co(Rh) source. A NaI(Tl) crystal with 0.05-mm thickness was used as the detector. A spectrofluorimeter (model SFL-2, Russia) was used to determine uranium concentration by luminescence. Uranium concentration also was determined by spectrophotometry using the Shimadzu model UV-3100 spectrophotometer.

Particle size was measured by SAXS using a KRM-1 instrument (Russia) over the range 0.5 to 10 degrees two theta with variable step scanning. Wide angle XRD patterns associated with the particle size measurements were gathered with a DRON-2 diffractometer (Russia) using Cu K_α radiation.

3.0 Experimental Methods

This section describes the methods used for each series of tests.

3.1 Alkali Treatment Parametric Tests

The first series of tests was performed to identify optimum conditions (temperature, excess NaOH, direction of solution mixing) for transforming the acidic dissolver solution into an alkaline slurry. The measured experimental characteristics included the settling rate, the specific volumes, and phase compositions of precipitates; the uranium and plutonium concentrations in the mother solutions; and the leaching of uranium and plutonium from the precipitates by alkaline EDTA or carbonate solutions.

The tests were conducted using a simulated dissolver solution, consisting of 1 M HNO_3, 0.096 M $UO_2(NO_3)_2$, 0.246 M $Fe(NO_3)_3$, 0.033 M $Al(NO_3)_3$, 0.001 M Na_2SiO_3, and 1.9×10^{-4} M $Pu(NO_3)_4$, that was designed to model the expected average composition of the solution resulting from nitric acid treatment. The simulated dissolver solution was prepared by mixing measured volumes of the corresponding standard solutions described in Section 2.0.

The alkali treatment parametric tests were performed in the following manner. First, 20 mL of the simulated dissolver solution were mixed with calculated amounts of 16.0 M NaOH to obtain an alkali excess of 0.01, 0.1, or 1 M. Mixing entailed either direct (alkali to acid) or reverse (acid to alkali) addition over 5 to 10 min in a thermostatted bath, along with intense stirring using a magnetic stirrer. The cell temperature during solution mixing and subsequent settling was maintained at either 40 ±1°C or 80 ±2°C.

The 0.01 M NaOH excess was determined by pH measurement of the supernatant solution. Before potentiometric pH measurements were made, the glass electrode was calibrated using 0.001 and 0.01 M NaOH in 2.0 M $NaNO_3$ as pH 11.00 and 12.00 standards, respectively. The $NaNO_3$ concentration used was similar to that present in the slurry after alkali treatment of simulated dissolver solution. Separate tests showed that the pH reading in 0.01 M NaOH was about 0.25 pH units higher than the reading found for 0.01 M NaOH + 2.0 M $NaNO_3$. Varying the $NaNO_3$ concentration in the range of 1.7 to 2.2 M produced no noticeable effect on measured pH values. The pH reading of 12.00 for 0.01 M NaOH + 2.0 M $NaNO_3$ at 20°C decreased to 11.85 at 40°C. The pH value of 11.85 was used subsequently to adjust NaOH concentration to 0.01 M during alkali treatment of simulated dissolver solution at 40°C. For tests at 80°C, the same amount of NaOH was used as at 40°C; the final pH of the mother solution subsequently was verified after it cooled to room temperature.

Each product suspension was collected in a graduated test tube and the precipitate volume measured as a function of time for about 1 day. The mother solution then was sampled and, after filtration (filter pore size 0.45 µm), analyzed for uranium and plutonium concentrations. The remaining precipitate and mother solution were stirred and homogenized, and were divided into two equal portions. The precipitates were separated from the mother solutions by a 10-min centrifugation, and small samples of the solid phase were taken as required for XRD and Mössbauer effect measurements. The precipitates then were weighed and mixed with 1 M Na_2CO_3 + 5 M $NaNO_3$ (one portion) or 0.1 M EDTA + 1 M NaOH + 5 M $NaNO_3$ (the second portion) at a solid-to-liquid ratio of 0.05 g/mL. The solids plus added solution were kept for a week at ~28°C. Once daily, the precipitates were suspended by stirring. After contact for

1 week, the mother solutions were filtered (pore size 0.45 μm) and the filtrates analyzed for uranium and plutonium concentrations.

The uranium in the mother solutions was determined by luminescence according to published methods (Riabchikov and Seniavin 1963). Solution aliquots (0.005 to 0.05 mL) were placed in a number of small Pt pans with 150 mg of a Na_2CO_3:K_2CO_3:NaF in weight ratio 5:5:1. To all but the first pan, aliquots of standard 10^{-5} to 10^{-3} M $UO_2(ClO_4)_2$ were added. The samples with flux were dried and then melted in a furnace at 660°C to 670°C. The melts were then cooled to room temperature, and their fluorescence to an excitation at 360 nm was measured by a spectrofluorimeter at 560 nm. The results were used to calculate the matrix-corrected uranium concentration in the test solution. The reproducibility of this technique is ±30%.

More exact uranium determinations for the same solutions were made by a spectrophotometric method based on the formation of a U(IV) complex with Arsenazo-III[a] in 4 to 6 M HCl (Riabchikov and Seniavin 1963). To remove nitrate, 2-mL aliquots of the solution to be analyzed were mixed with 0.5 to 2 mL of concentrated $HClO_4$; the mixture was heated to the appearance of white fumes. The residue was diluted to 5 mL with 4.5 M HCl and treated by zinc amalgam for 5 to 10 min to complete reduction of U(VI) to U(IV). The solution was filtered and mixed with 0.2 mL of 0.1% Arsenazo-III in water. The optical density of the solution was measured at 665 nm against a blank Arsenazo-III solution of the same concentration in 4.5 M HCl. The uranium concentration in the analyzed solution was calculated based on the molar extinction coefficient found by experiment to be 120,000 L/mol·cm. The reproducibility of such uranium determinations was about ±10%. Separate tests showed that Fe(III) and Al(III), in amounts significantly higher than their expected concentrations in analyzed solutions, do not interfere. Compared with uranium, plutonium concentrations were too low to interfere.

The U(VI) concentrations in the carbonate leaching solutions were high (~10^{-3} M). Therefore, it was possible to analyze these solutions for uranium concentration by direct measurement of their light absorption at 442-nm wavelength. The molar extinction coefficient of U(VI) in 1 M Na_2CO_3 + 5 M $NaNO_3$ was found to be 28 L/mol·cm. The error of uranium determinations in these cases was not higher than ±10%. It was shown in separate tests that NaOH concentrations of less than 0.05 M do not interfere with uranium determination by this method.

The direct plutonium analyses of the alkaline mother solutions and the EDTA leaching solutions by liquid scintillation gave only approximate results, because the sensitivity of the method was insufficient to measure such low concentrations (~3×10^{-8} M). Therefore, the plutonium was concentrated by coprecipitation with $La(OH)_3$ or $Fe(OH)_3$. In the first method, about 1 mg La(III) was introduced to 2 to 5 mL of analyzed solution previously acidified to pH ~1 with HNO_3. Excess NaOH was then added. A precipitate was formed which, after coagulation for 10 to 15 min, was centrifuged, washed twice with water and once with acetone, dried in an air flow, and dissolved in 0.2 mL of 2 M HCl. The coprecipitation of plutonium with $Fe(OH)_3$ was performed by alkaline hydrolysis of sodium nitroprusside (Krot et al. 1996). The $Fe(OH)_3$ precipitate then was washed, dried, and dissolved in 0.2 M HCl as in the case of $La(OH)_3$. The product solutions were analyzed for plutonium by liquid scintillation. Two or more samples were taken for radiometric measurements. The measurement statistical error was less than ±3%, and the reproducibility typically in the range of ±10%.

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[a] Arsenazo-III is 2,7-bis(2-arsonophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid.

3.2 Dissolver Solution Composition Tests

The second series of tests focused on the influence of dissolver solution composition on the properties of the precipitates resulting from direct strike 40°C treatment with 0.01 M excess NaOH. The measured experimental parameters were the same as in the parametric tests, except that americium concentrations in the mother solutions; americium leaching by alkaline EDTA or carbonate solutions; and precipitate particle (crystallite) size also were determined.

The tests were performed using 10 different simulated dissolver solution compositions (see Table 3, Section 4.2 for the uranium, iron, and aluminum concentrations used). Additionally, each dissolver solution contained 0.001 M Na_2SiO_3. For the tests with plutonium, 1.9×10^{-4} M $Pu(NO_3)_4$ was used. For the tests with americium, an Am:U ratio of 0.00005 was used. Although a weight ratio of Pu:U was stipulated as 0.002, a constant plutonium concentration was used instead to obtain more reliable data on plutonium coprecipitation caused by the alkali treatment. As shown in the parametric testing results (Section 4.1), reliable plutonium analyses become difficult at the low concentrations obtained under certain test conditions. On the other hand, changing the plutonium concentration at tracer levels is known to exert little effect on its degree of coprecipitation in alkali with Fe(III) hydroxide and sodium uranates (Bessonov et al. 1997).

The experimental techniques in the dissolver solution composition tests were analogous to those used in the parametric tests. In the solution composition tests, however, the low concentrations of uranium were only determined using the spectrophotometric method based on the complex formation of U(IV) with Arsenazo-III (Riabchikov and Seniavin 1963). Americium concentrations were determined by liquid scintillation.

3.3 Precipitate Particle Size Distribution

The size distributions of the primary crystallites arising from alkali treatment of the 10 simulated dissolver solutions and of a simple Fe(III) nitrate solution were determined by the SAXS method. Samples for the SAXS measurements and for XRD patterns were prepared by methods similar to those used for the tests with plutonium and americium spiking. First, 10 mL of simulated dissolver solution, but without plutonium or americium spike, were treated with 16 M NaOH under the selected precipitation conditions: 40°C temperature, 0.01 M excess NaOH, and alkali-to-acid addition. The product precipitate was coagulated for 24 hours at 40°C, separated from the mother solution by a 10-min centrifugation, and washed three times with five-fold volumes of water. The washing was carried out to decrease nitrate concentration to ~0.015 M (measured by spectrophotometry at 301 nm). Further washing caused unacceptable precipitate peptization. The washed precipitate was mixed with an equal volume of C_2H_5OH, and the uniform suspension was applied as thin 1 cm x 2 cm layers on a Mylar film (thickness 0.02 mm). After the layers were dried to a paste, fresh layers of the suspension were placed on the same film. The layering was repeated three to five times to obtain a final deposit containing 350 to 500 mg over the 1 cm x 2 cm surface. Such layers provided optimum attenuation of the X-ray beam. A Mylar film was put over the sample to avoid further drying.

The SAXS measurement results were corrected to account for parasitic scattering by the instrument and by the Mylar film. The sample background also was subtracted from the main scattered intensity by published methods (Ruland 1974). The background is especially significant on the external part of the scattering indicatrix.

A special method (Plavnik 1994) was used to derive the particle volume distribution function f(R) from experimental data

$$f(R) = N(R) \cdot V(R)$$

where V(R) is the volume of a particle with radius R and N(R) is the number of such particles. The method eliminates collimation distortions and significantly reduces interparticle interference (Plavnik 1986).

The radii of gyration, R_g, are characteristic of the linear sizes of the particles

$$R_g^2 = (\int_v R^2 dV)/\int_v dV$$

The R_g parameter may be evaluated for particles of arbitrary form, including irregular or asymmetric shapes. Regularly shaped solids follow simple relations for R_g. For cubic particles, $R_g = \ell/2$ where ℓ is the length of the cube edge; for spherical particles, $R_g = (3/5)^{1/2} R_{sphere}$.

4.0 Results and Discussion

The results from each set of experiments are discussed below.

4.1 Alkali Treatment Parameters

The sedimentation data of precipitates produced by NaOH treatment of simulated acidic dissolver solution are graphed in Figures 1 through 3. These data show that sedimentation is not complete in 24 hours. The process, in fact, proceeds slowly for several more days. It is convenient to characterize the sedimentation rate by measuring the time ($\tau_{1/2}$) required to decrease the precipitate volume to the mean value between its initial and 24-hour volumes. The results shown in Table 1 indicate that $\tau_{1/2}$ has no regular dependence on alkali excess and mixing direction, and increases slightly with increasing temperature. It is more likely that the stirring intensity (shear rate) and local supersaturation determined the particle and particle agglomerate size and, consequently, the solids sedimentation rate. Near-wall effects also can influence the sedimentation rate. Though a constant speed magnetic stirrer maintained shear rates, the actual transmitted shear may have been more difficult to control because of the high viscosity of the NaOH solution.

In contrast to the sedimentation rate, the data on precipitate volumes are more reproducible and less scattered (Table 1). After 24 hours of coagulation, the precipitate volumes are about half the volume of the initial suspension. The precipitate volumes decrease slightly with increasing temperature at the precipitation and coagulation. The order of solution mixing (direct or reverse strike) and the amount of excess alkali do not significantly influence the precipitate volumes.

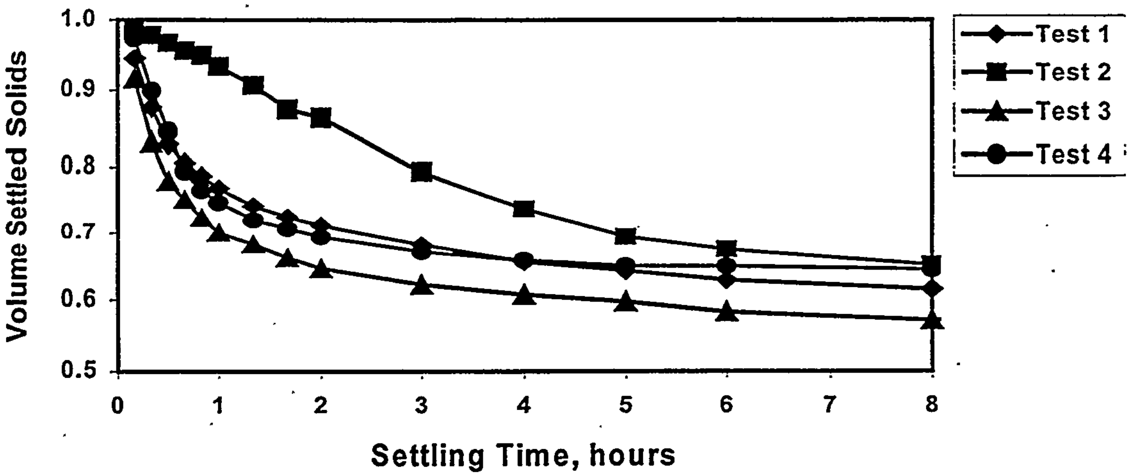

Figure 1. Settling for Precipitates from Tests 1, 2, 3, and 4 at pH 12 (Table 1)

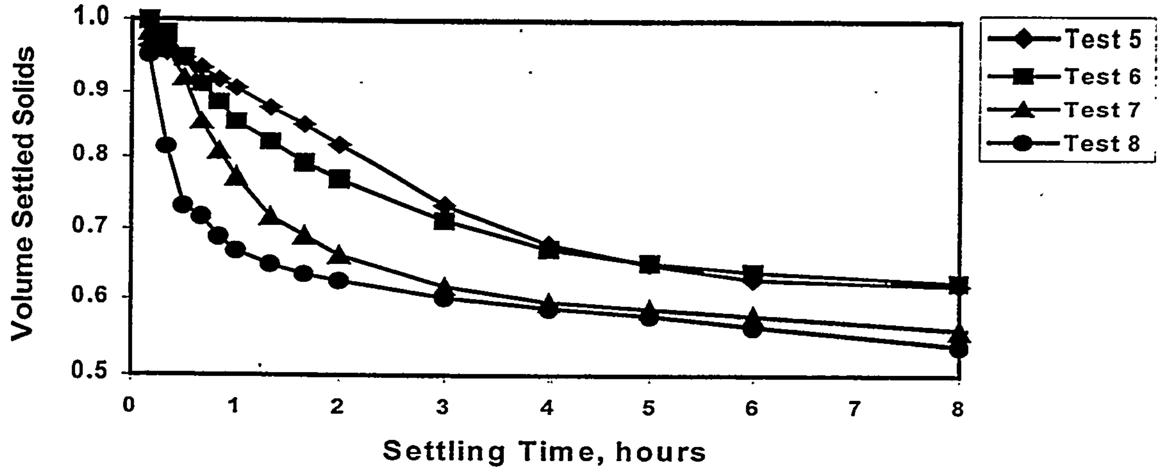

Figure 2. Settling for Precipitates from Tests 5, 6, 7, and 8 at 0.1 M NaOH (Table 1)

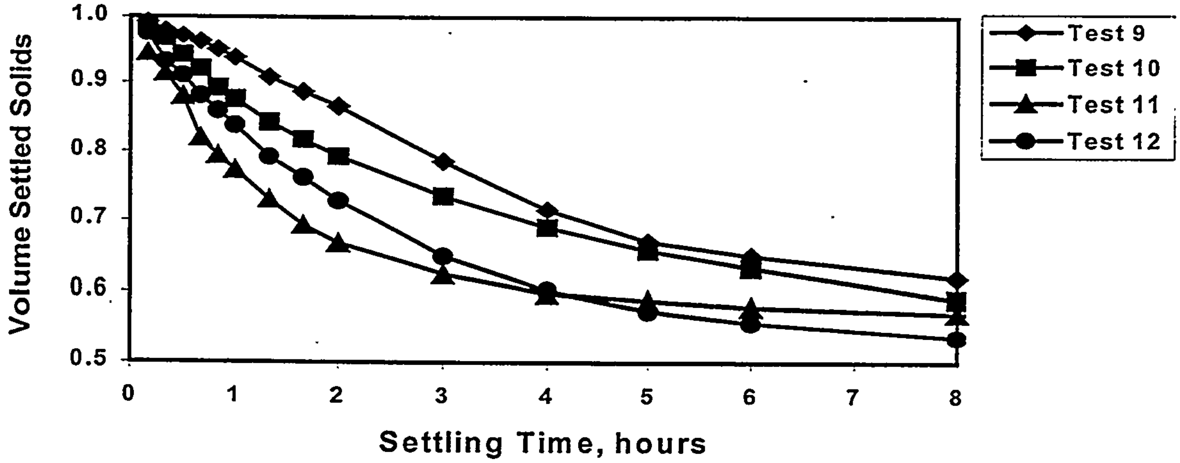

Figure 3. Settling for Precipitates from Tests 9, 10, 11, and 12 at 1 M NaOH (Table 1)

As seen in Table 1, plutonium concentrations in the mother solutions obtained by NaOH treatment of acidic dissolver solutions, though somewhat scattered, are low (~3×10^{-8} M) and are practically independent of the precipitation conditions. The scatter perhaps is caused by the presence in the mother solutions of very small plutonium-bearing particles that are not removed by 0.45-µm filtration.

Table 1. Characteristics of Alkali Treatment of the Simulated Dissolver Solution[(a)]

Test	Precipitation Conditions			Mother Solution		Precipitate	
	[NaOH], M	T, °C	Mode	[U], 10^{-6} M	[Pu], 10^{-8} M	$\tau_{1/2}$, h	V, mL
1	0.01	40	Reverse	2.0	1.9	0.83	12.9
2	0.01	40	Direct	2.0	2.0	3.9	13.6
3	0.01	80	Reverse	1.5	2.0	0.52	11.8
4	0.01	80	Direct	0.5	3.2	0.67	12.9
5	0.1	40	Reverse	5.8	0.8	2.4	12.7
6	0.1	40	Direct	8.1	3.2	1.8	12.8
7	0.1	80	Reverse	6.4	5.1	1.1	11.3
8	0.1	80	Direct	5.8	2.4	0.55	9.6
9	1.0	40	Reverse	20	5.0	3.1	13.2
10	1.0	40	Direct	24	4.6	2.5	12.7
11	1.0	80	Reverse	18	5.1	0.95	13.1
12	1.0	80	Direct	12	6.4	1.8	11.9
(a) 20-mL starting acid dissolver solution treated with 16 M NaOH.							

In contrast to plutonium, the uranium concentrations in the mother solutions increase with increasing NaOH concentration. The higher uranium concentrations are caused by the increased solubility of sodium diuranate with increasing NaOH concentration. The existence of uranium in true solution is confirmed by the fact that uranium concentration in the mother solution is not changed by ultrafiltration. As in the case of plutonium, however, temperature and direction of mixing have no influence on uranium concentration.

Prior studies in our laboratory showed that Pu(IV) is uniformly distributed in precipitates of Fe(III) hydroxide and sodium diuranate generated from NaOH treatment of separate homogeneous acid solutions of Fe(III) and U(VI) (Fedoseev et al. 1998). Considering these findings, the data in Table 1 indicate that, in the alkali treatment of simulated dissolver solution, Pu(IV) must primarily be associated with Fe(III) hydroxide, because the plutonium concentrations in the mother solutions do not depend on the completeness of uranium precipitation.

According to XRD analyses, the precipitates in each test consist of a crystalline $Na_2U_2O_7$ phase and a primarily amorphous Fe(III) hydroxide. However, for precipitates formed and coagulated at 80°C, generally with direct strike NaOH addition (Tests 4, 7, 12, and especially 8 in Table 1), α-Fe_2O_3 (hematite) was observed (Figure 4).

The diffraction lines of $Na_2U_2O_7$ are diffuse and broad, indicating the very small crystallite size of the compound. In contrast to $Na_2U_2O_7$, the α-Fe_2O_3 lines are narrow, which means that α-Fe_2O_3 is well crystallized and has relatively large crystals compared to $Na_2U_2O_7$. However, little of the amorphous Fe(III) hydroxide transformed into crystalline oxide under the present test conditions. The crystallization to form α-Fe_2O_3 changed the precipitate color from dark brown to light brown. The color change did not proceed near the test tube wall and was observed only by stirring the suspensions.

The chemical form of amorphous Fe(III) hydroxide in the precipitates was studied using Mössbauer spectrometry. A Mössbauer spectrum of the precipitate from Test 3 (Table 1) is shown in Figure 5. The

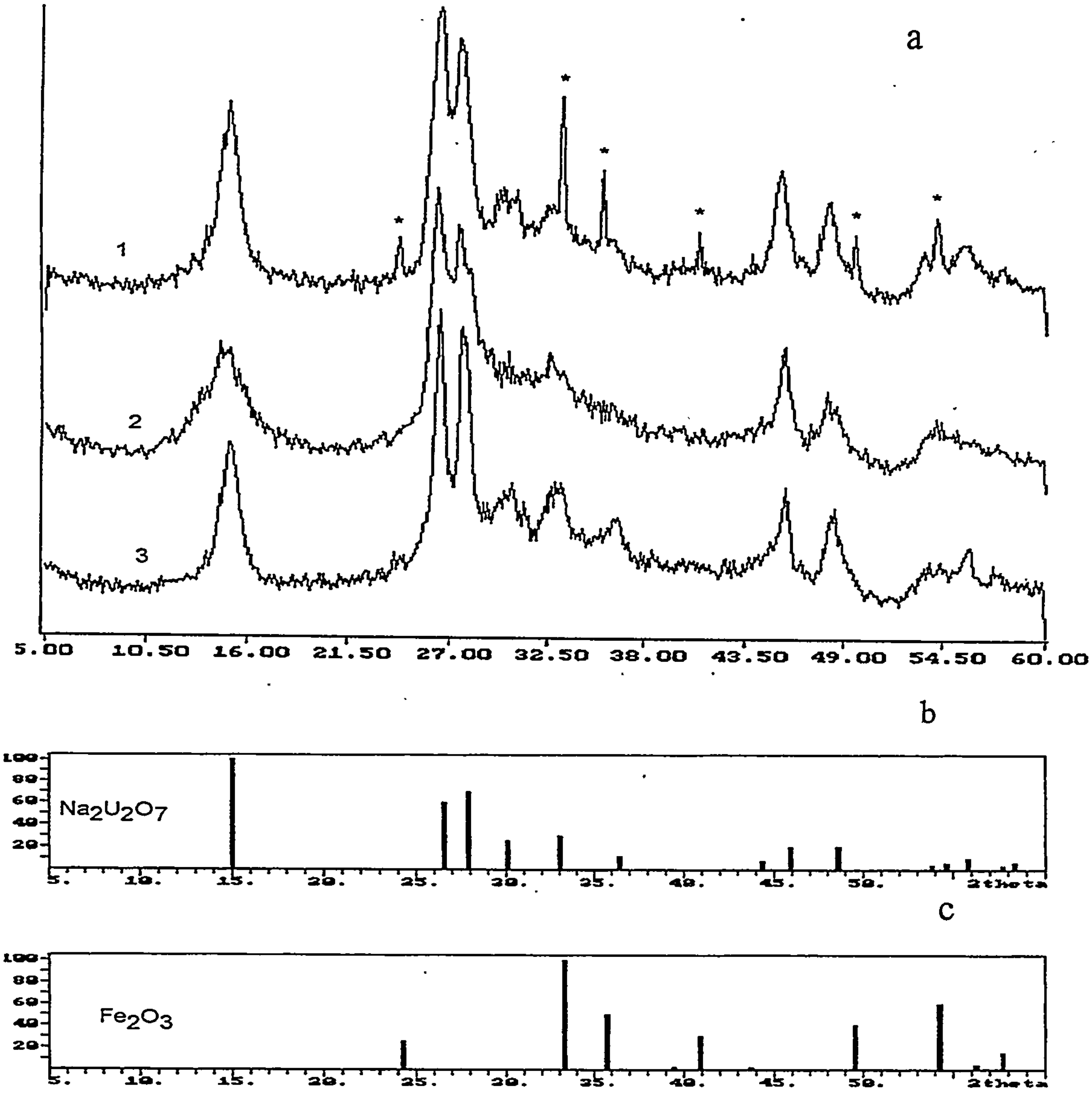

Figure 4. XRD Analyses of Precipitates from Alkali Treatment Parametric Tests
a. Powder XRD patterns for the precipitates
1 - Test 8
2 - Test 2
3 - Test 3 in Table 3 (see Section 4.2)
* - lines of α-Fe_2O_3
b. Stick diagram for $Na_2U_2O_7$ [from JCPDS powder diffraction database]
c. Stick diagram for α-Fe_2O_3 [from JCPDS powder diffraction database]
Note: JCPDS is the Joint Committee on Powder Diffraction Standards.

isomer shift (δ) in the spectrum was determined at room temperature relative to sodium nitroprusside, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$. Zero velocity in Figure 6 (see Section 4.2) corresponds to the centrum of the sodium nitroprusside doublet; that is, to zero δ. The spectrum was computer fit by a least squares method based on a Lorentz line shape approximation. The reproducibilities of the isomer shift and quadrupole splitting (Δ) values were about 0.01 to 0.02 mm/s.

In a prior study, samples of homogeneously coprecipitated Fe(III) and Pu(IV) hydroxide were found to have (at 80 K) the same isomer shift (δ), 0.71 mm/s, as amorphous Fe(III) hydroxide (Fedoseev et al. 1998). However, they have a quadrupole splitting (Δ) about 0.09 mm/s larger than found in Fe(III) hydroxide (0.66 mm/s). The earlier study also showed that the amorphous Fe(III) hydroxide has the same Mössbauer spectrum as α-FeO(OH) (göthite), thus suggesting that amorphous Fe(III) hydroxide consists of small crystallites of α-FeO(OH) and is a precursor to this compound. The earlier findings showed that the effective charge on the central Fe(III) ion is the same, but the environment of this ion becomes less symmetric, in the Fe(III)-Pu(IV) mixed hydroxides. In other words, Pu(IV) interacts with Fe(III) in the mixed hydroxide.

Tests were performed to check if a similar interaction could take place in the mixed U(VI)-Fe(III)-Al(III) system studied in the present work. The Mössbauer spectrum parameters obtained for U(VI)-Fe(III)-Al(III) precipitates ($\delta = 0.70$ and $\Delta = 0.62$ mm/s) are similar to those observed for pure amorphous Fe(III) hydroxide. Therefore, it is reasonable to conclude that Fe(III) hydroxide shows no noticeable interaction with sodium diuranate, at least to the extent that is observed for mixed Fe(III) and Pu(IV) hydroxides. This conclusion cannot be extended to Al(III) hydroxide because aluminum in amorphous Fe(III) hydroxide would have little effect on the Fe(III) Mössbauer spectrum.

The results of uranium and plutonium leaching from the precipitates by carbonate and alkaline EDTA solutions are presented in Table 2.

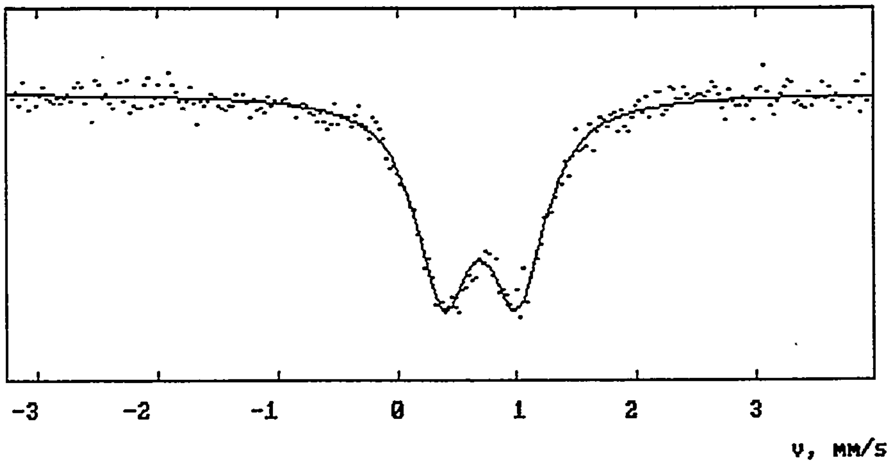

Figure 5. Mössbauer Spectrum (at 80 K) of the Precipitate Prepared in Test 3 (Table 1)

Table 2. Uranium and Plutonium Concentrations in Carbonate and EDTA Leach Solutions in the Parametric Tests

Test	Precipitation Conditions			Carbonate Leaching		EDTA Leaching	
	[NaOH], $\underline{M}$	T, °C	Mode	[U], $10^{-3}\underline{M}$	[Pu], $10^{-6}\underline{M}$	[U], $10^{-6}\underline{M}$	[Pu], $10^{-8}\underline{M}$
1	0.01	40	Reverse	8.5	5.2	7.8	4.7
2	0.01	40	Direct	6.7	3.8	9.0	4.3
3	0.01	80	Reverse	4.5	5.0	9.5	3.1
4	0.01	80	Direct	3.0	4.2	8.5	1.4
5	0.1	40	Reverse	7.1	6.7	12.	3.9
6	0.1	40	Direct	7.0	4.5	9.0	3.8
7	0.1	80	Reverse	2.8	10.	8.8	1.5
8	0.1	80	Direct	1.8	4.8	8.7	1.6
9	1.0	40	Reverse	1.4	3.3	11.	2.3
10	1.0	40	Direct	1.3	1.8	6.8	2.2
11	1.0	80	Reverse	0.34	0.40	7.4	2.0
12	1.0	80	Direct	0.27	0.34	5.8	1.9

A number of conclusions can be drawn from these data.

1. The maximum uranium dissolution by the carbonate leachant was ~55% from the Test 1 solids. The varying extent of uranium dissolution could be caused by slow dissolution kinetics or by low solubility of the double salt $Na_4UO_2(CO_3)_3$ caused by the salting-out effect of sodium. Separate tests showed that, at 30°C, $Na_4UO_2(CO_3)_3$ solubility is over $5x10^{-2}$ $\underline{M}$ in the mixed 1 $\underline{M}$ Na_2CO_3 + 5 $\underline{M}$ $NaNO_3$ leach solution. This concentration is higher than observed in any test. Therefore, the observed incomplete uranium leaching must be attributed to variable and low dissolution rates.

2. Uranium concentrations in the carbonate leach solutions decrease noticeably, under otherwise equal conditions, with increasing precipitate coagulation temperature. Increased $Na_2U_2O_7$ crystallinity and the consequent decrease of its dissolving rate can explain the decreased concentration.

3. The degree of uranium leaching by the carbonate solution markedly decreases with increase in the NaOH excess used to prepare the precipitate. The decreased leaching likely is caused by retention of NaOH mother solution in the precipitates. The excess NaOH would displace carbonate from the U(VI) and thus inhibit dissolution of the uranium as carbonate complexes.

4. The amounts of plutonium and uranium dissolved by the carbonate solution seemingly are correlated. It is reasonable to assume that only plutonium that is associated with sodium diuranate is dissolved.

5. In 9 of 12 tests, the fraction of plutonium leached by the carbonate solution is lower than that of uranium. This confirms the previously stated assumption that plutonium associates with sodium diuranate to less extent than with Fe(III) hydroxide. The Pu/U ratios in the carbonate leach solutions range from 0.0006 to 0.0036 versus 0.002 in the original precipitate. The lowest ratios are observed for Tests 1, 2, 5, and 6 in which 0.01 or 0.1 $\underline{M}$ excess NaOH and 40°C precipitation conditions were used.

6. Uranium and plutonium concentrations found in the alkaline EDTA leach solution (0.1 M EDTA + 1 M NaOH + 5 M $NaNO_3$) are similar or slightly lower than found in the original mother solutions (Table 2). The precipitation conditions have little effect on the degree of uranium and plutonium dissolution in the EDTA leachant.

Based on these data, the conditions chosen for further testing on the effects of dissolver solution composition were precipitation and digestion at 40°C using 0.01 M NaOH excess added by direct strike (alkali-to-acid). These conditions yield the lowest uranium concentration in the supernatant, require the least excess NaOH, and provide the highest apparent partitioning of plutonium to the carbonate-resistant Fe(III) hydroxide solid phase.

4.2 Dissolver Composition

The effects of dissolver solution composition on precipitate properties were investigated by separate tests having plutonium and americium spikes. Results of the precipitate sedimentation rate testing are presented in Figures 6 through 10 for Tests 1 and 2; 3 and 4; 5 and 6; 7 and 8; and 9 and 10, respectively, for the two data sets and are summarized in Table 3. The data show no apparent dependence of sedimentation rate on precipitate composition. The sedimentation rates are slow and comparable to the rates observed in the parametric tests.

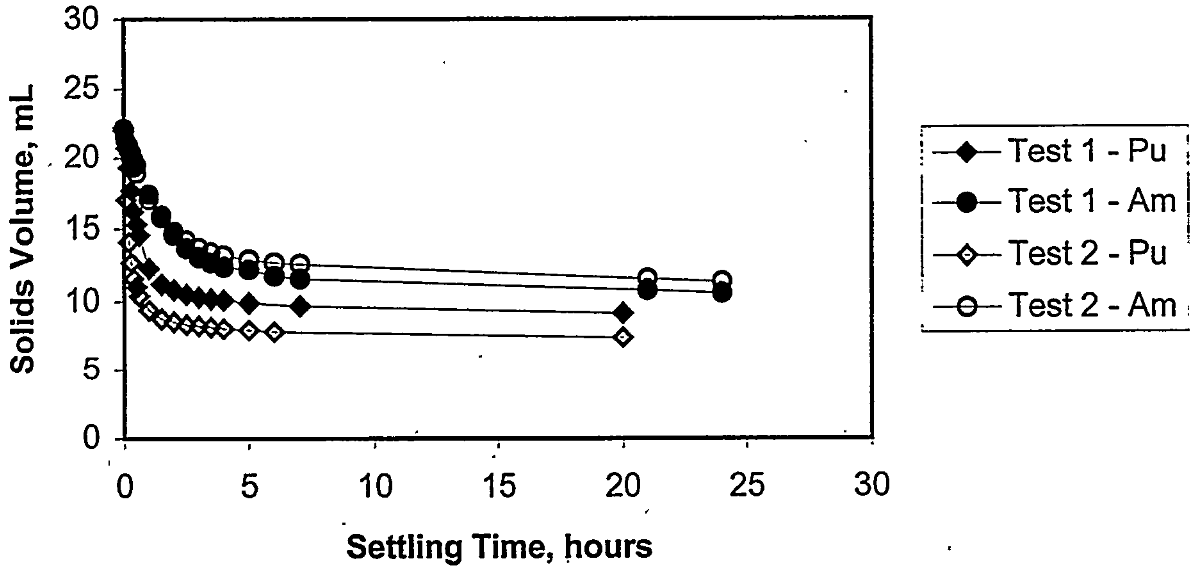

Figure 6. Settling Rate Curves for Precipitates from Tests 1 and 2 (Table 3)

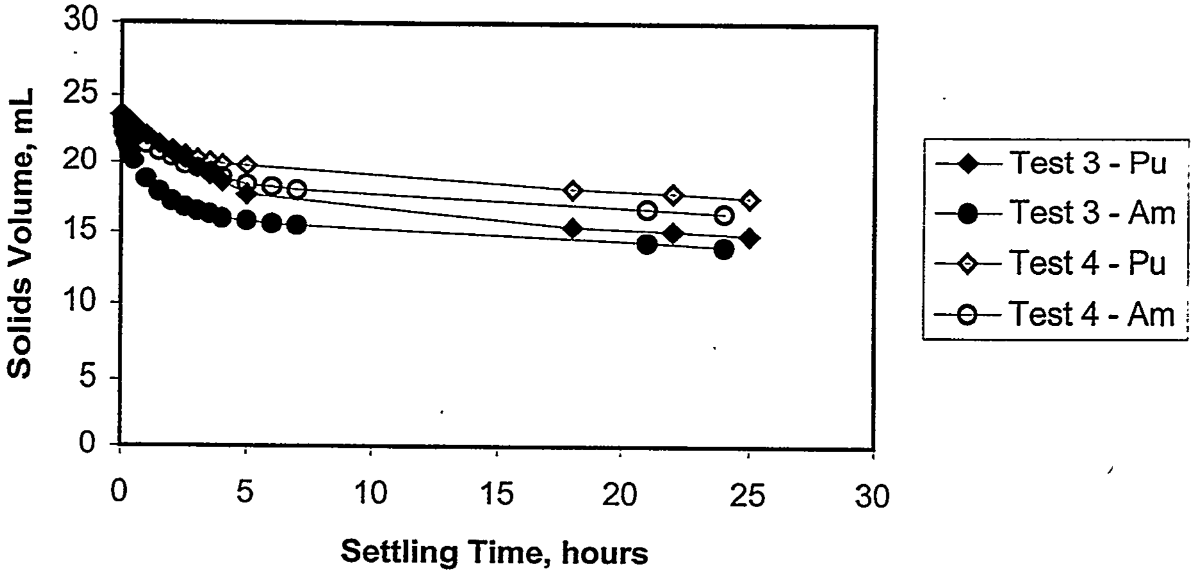

Figure 7. Settling Rate Curves for Precipitates from Tests 3 and 4 (Table 3)

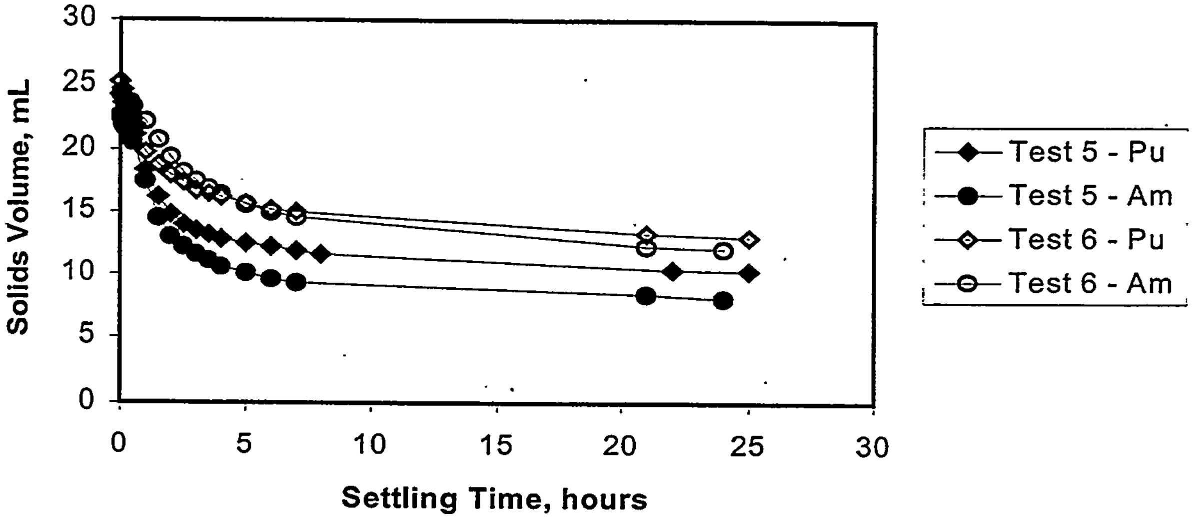

Figure 8. Settling Rate Curves for Precipitates from Tests 5 and 6 (Table 3)

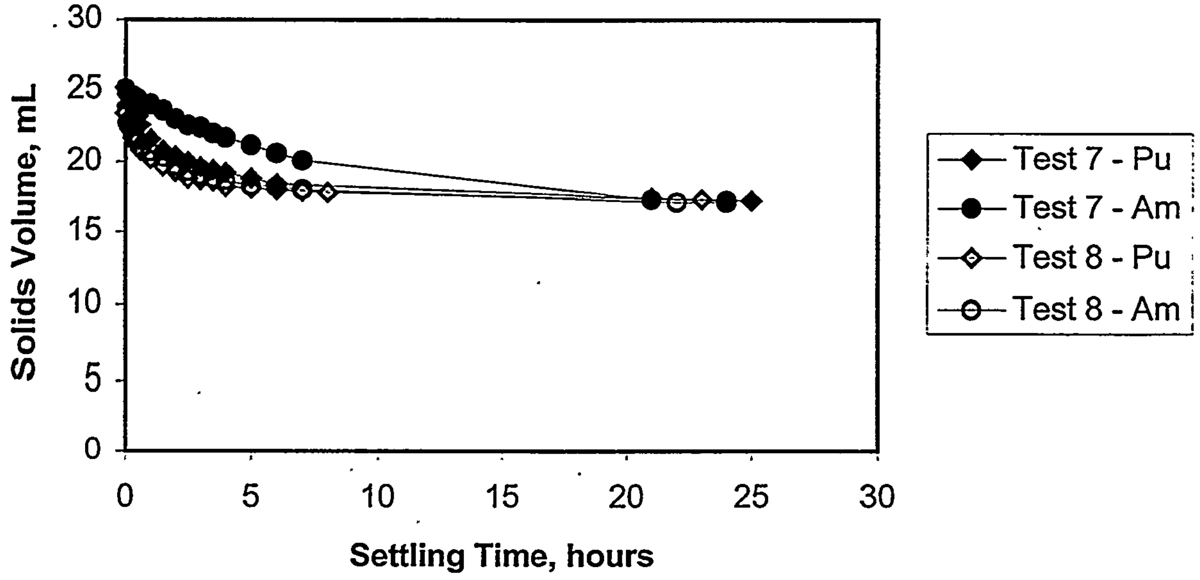

Figure 9. Settling Rate Curves for Precipitates from Tests 7 and 8 (Table 3)

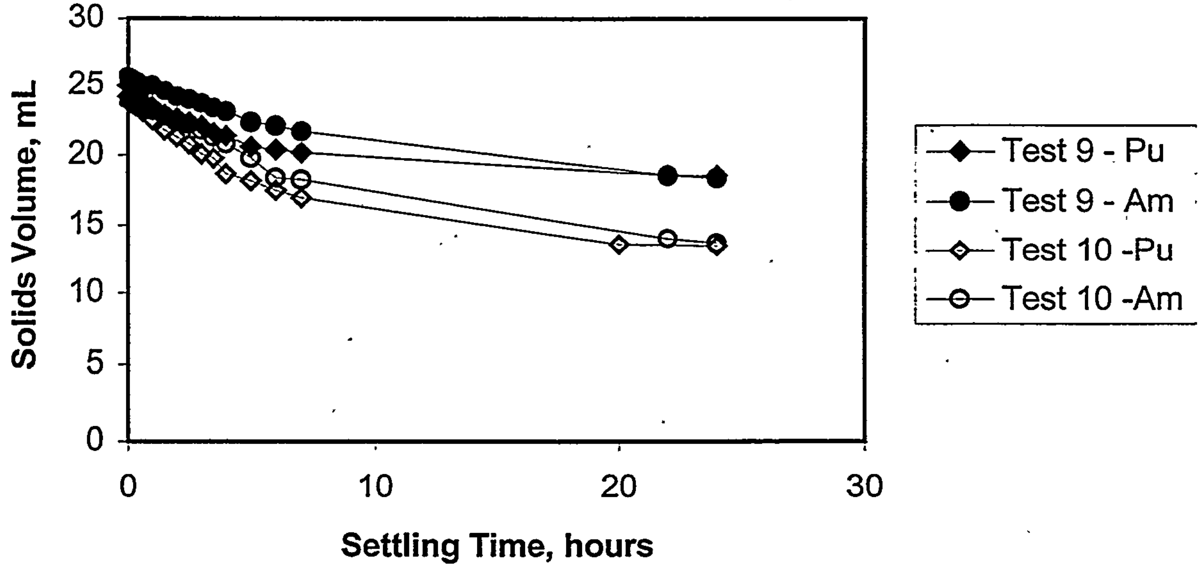

Figure 10. Settling Rate Curves for Precipitates from Tests 9 and 10 (Table 3)

Table 3. Characteristics of the Alkali Treatment of Varied Simulated Dissolver Solutions

Test	Element Concentration, g/L			Mother Solution			Precipitate	
	U	Fe	Al	[U], 10^{-6} M	[Pu], 10^{-9} M	[Am], 10^{-11} M	$\tau_{1/2}$, h	V, mL[(a)]
1	37.5	0	0	1.7, 2.2	12	9.8	0.5, 1.4	9.1, 10.6
2	33.7	3.8	0	4.5, 1.7	8	9.8	0.15, 1.1	7.4, 11.4
3	18.8	18.8	0	2.5, 1.4	6	6.6	3.2, 1.0	15.0, 14.0
4	3.8	33.7	0	0.9, 3.9	15	6.4	2.3, 2.4	17.6, 16.4
5	30.0	0	7.5	3.2, 4.2	5	11.0	1.2, 1.4	10.3, 8.1
6	18.8	0	18.8	2.2, 3.9	12	7.0	1.3, 2.4	13.1, 12.1
7	7.5	0	30.0	1.5, 4.4	12	5.8	1.3, 5.7	17.2, 17.2
8	3.8	30.0	3.8	1.6, 1.9	7	5.9	0.4, 1.2	17.2, 17.1
9	3.8	3.8	30.0	3.9, 4.6	7	5.6	3.2, 6.8	18.6, 18.4
10	12.5	12.5	12.5	3.5, 5.0	6	5.1	4.3, 6.8	13.5, 13.7

(a) 20-mL starting acid dissolver solution treated with 16 M NaOH.
Paired uranium concentration and precipitate settling and volume data are for tests with Pu and Am, respectively.
NOTE: TRU level is 5.5×10^{-6} M Pu or 1.2×10^{-7} M Am.

To a first approximation, the precipitate volumes after 24 hours of settling can be predicted based on the linear combination of the individual U, Fe, and Al component solids volumes. Thus, the gravity-settled precipitate volume, as a fraction of the initial acid dissolver solution volume, is

precipitate volume = 2.70 [U] + 1.35 [Fe] + 0.67 [Al] (concentrations in M), or
precipitate volume = 0.0114 [U] + 0.0241 [Fe] + 0.0248 [Al] (concentrations in g/L).

Based on these equations, the precipitate volume predicted for the parametric test solution prepared under the given precipitation conditions (i.e., Test 2, Table 1) is 0.61 of the initial dissolver solution volume, whereas 0.68 (13.6 mL/20 mL) was observed. It is emphasized that these equations are only valid within the studied range of U, Fe, and Al concentrations and do not extend to large process vessels where hydrostatic solids compaction can occur. The second equation does show, however, that under the reference conditions, uranium forms a precipitate that is about 2.1 times denser than the precipitates formed by either iron or aluminum.

As shown in Table 3, plutonium concentrations in the mother solutions produced by NaOH treatment of the dissolver solutions range moderately from $(0.5\text{-}1.5) \times 10^{-8}$ M and are independent of precipitate composition. It may be that plutonium is associated with very small solid particles that can pass through the filter. The uranium concentration data also are somewhat scattered, ranging from about $(1\text{-}5) \times 10^{-6}$ M (Table 3) and may be influenced by very fine suspensions of $Na_2U_2O_7$ particles. Nevertheless, the plutonium and uranium concentrations in the mother solutions are similar to those observed in the analogous parametric tests and in related studies of simulated reprocessing plant acid waste solution treatment with NaOH conducted at the Savannah River Site (Hobbs 1997). In the Savannah River Site tests, with 1.2 M excess NaOH, plutonium concentrations were about three times lower [$(2\text{-}4) \times 10^{-9}$ M] and uranium concentrations about three times higher [$(3\text{-}20) \times 10^{-6}$ M] than observed in the present studies.

According to XRD analyses, all precipitates in the dissolver solution composition tests contained crystalline sodium diuranate and primarily amorphous Fe(III) and/or Al(III) hydroxides (Figures 11 through 13). However, the crystallinity of the $Na_2U_2O_7$ depended on the precipitate composition. Crystallinity degraded with increasing mole fractions of iron and aluminum hydroxide in the solids. The powder diffraction pattern of the precipitate from Test 4 [which contained a high Fe(III) mole fraction] produced narrow lines characteristic of α-FeO(OH) (göthite). The Test 10 solids contained some crystalline α-Al(OH)$_3$ (bayerite).

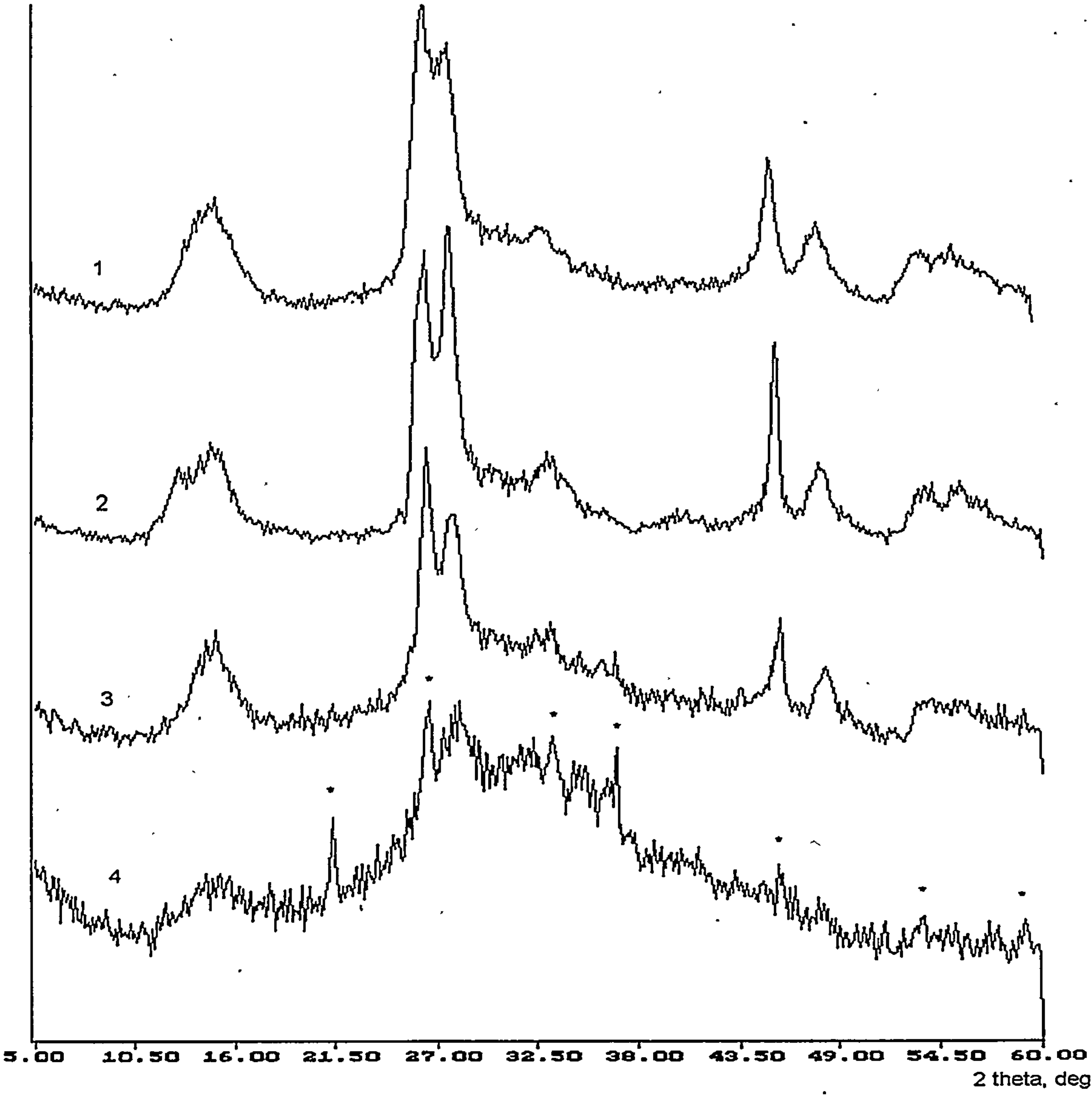

Figure 11. Powder XRD Patterns of Precipitates from Tests 1, 2, 3, and 4 with Plutonium (Table 3)
* - lines of α-FeO(OH)

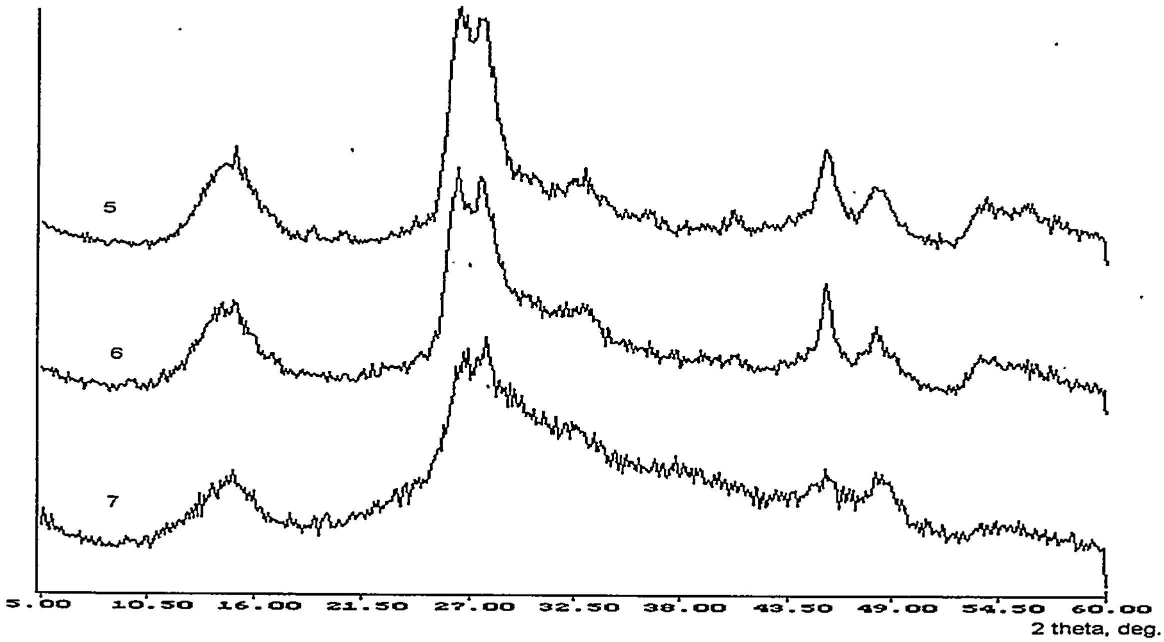

Figure 12. Powder XRD Patterns of Precipitates from Tests 5, 6, and 7 with Plutonium (Table 3)

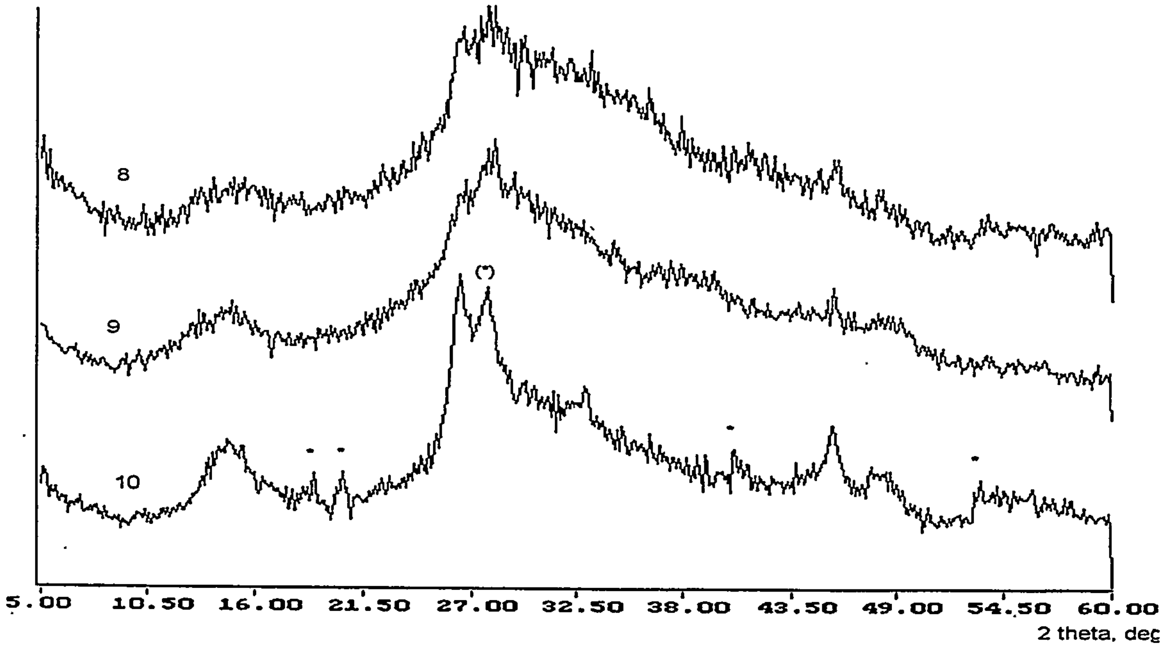

Figure 13. Powder XRD Patterns of Precipitates from Tests 8, 9, and 10 with Plutonium (Table 3)
* - lines of α-Al(OH)$_3$ (bayerite)

From the data in Table 4, it is seen that the completeness of uranium leaching by 1 M Na_2CO_3 + 5 M $NaNO_3$ strongly depends on the precipitate composition. The degree of uranium dissolution increases with decreasing uranium mole fraction in the precipitates. This result corresponds with the XRD data on the crystallinity of sodium diuranate in the solid phases (Figures 11 through 13). It also confirms the conclusion made in the parametric testing that the degree of uranium leaching by carbonate solution is determined by kinetics.

The degree of plutonium leaching also depends significantly on the precipitate composition. If the precipitate consists only of sodium diuranate or sodium diuranate with aluminum hydroxide, the degrees of plutonium and uranium leaching are similar. However, the degree of plutonium leaching into the carbonate solution decreases markedly in proportion to the amount of Fe(III) hydroxide present in the solid phase. This confirms the previously stated assertion that plutonium is primarily associated with Fe(III) hydroxide in the precipitates.

Likewise, the degree of americium leaching depends on precipitate composition. In Test 1, which only contains sodium diuranate precipitate, the degrees of americium and uranium leaching are similar. The degree of americium leaching decreases sharply in the presence of Fe(III) hydroxide, indicating that americium associates with Fe(III) hydroxide preferentially over sodium diuranate. The extent of americium leaching is intermediate in precipitates containing uranium and aluminum but without iron. Americium thus preferentially associates with aluminum hydroxide over sodium diuranate.

Table 4. Uranium and Plutonium Concentrations in Carbonate and EDTA Leach Solutions in the Dissolver Composition Tests

Test	Concentration in Dissolver Solution					Carbonate Leaching(a)			EDTA Leaching		
	U, g/L	Fe, g/L	Al, g/L	Pu, 10^{-6} M	Am, 10^{-9} M	[U], 10^{-3} M	[Pu], 10^{-6} M	[Am], 10^{-9} M	[U], 10^{-6} M	[Pu], 10^{-9} M	[Am], 10^{-9} M
1	37.5	0	0	190		11.0 (28)	6.7 (15)		18	3	
					7880	15.0 (39)		550 (29)	14.4		6.8
2	33.7	3.8	0	190		10.2 (27)	4.2 (8.4)		8.4	5	
					7090	14.0 (51)		9.6 (0.7)	17.0		7.4
3	18.8	18.8	0	190		7.4 (69)	1.8 (7.2)		7.2	8	
					3940	8.3 (79)		4.2 (0.8)	10.9		0.87
4	3.8	33.7	0	190		1.6 (89)	3.2 (16)		10	21	
					788	1.5 (89)		1.0 (1.2)	10.1		0.28
5	30.0	0	7.5	190		9.4 (38)	13.0 (34)		12	19	
					6300	11.0 (36)		230 (15)	13.6		17.0
6	18.8	0	18.8	190		5.4 (48)	11.0 (43)		6.6	14	
					3940	3.0 (27)		25 (4.5)	10.2		120
7	7.5	0	30.0	190		2.1 (76)	9.0 (57)		7.7	16	
					1580	1.1 (42)		5.7 (4.3)	10.1		40
8	3.8	30.0	3.8	190		1.5 (86)	2.1 (11)		7.7	24	
					788	0.86 (62)		0.62 (0.9)	11.4		0.96
9	3.8	3.8	30.0	190		1.1 (79)	4.0 (27)		11	19	
					788	0.43 (32)		1.3 (2)	14.0		1.6
10	12.5	12.5	12.5	190		3.8 (51)	3.0 (12)		8.1	18	
					2630	3.9 (52)		1.7 (0.5)	14.9		1.4

(a) Percent uranium, plutonium, and americium leached are presented within the parentheses.
Note: TRU level is 5.5×10^{-6} M Pu or 1.2×10^{-7} M Am.

Uranium and plutonium concentrations in alkaline EDTA leaching solutions are similar to the concentrations observed for the mother solutions obtained by NaOH treatment of the simulated dissolver solutions. The concentrations show no regular dependence on the precipitate compositions. Americium leaching, however, is lower for those precipitates containing iron. The high americium leaching observed for precipitates containing only sodium diuranate and aluminum hydroxide confirms that americium preferentially associates with aluminum hydroxide. This is because the EDTA leaching solution also contains 1 M NaOH. The NaOH dissolves aluminum hydroxide but not sodium diuranate.

4.3 Particle Size Distributions

The particle volume distributions of the precipitates as functions of $2R_g$, $f(2R_g)$, are presented in Figures 14 through 18, where $2R_g$ is an effective particle diameter. The curves were normalized to achieve maximum function value $f_{max}(2R_g)$ of unity. Figure 19 shows the particle volume distributions of the pure sodium diuranate and Fe(III) hydroxide systems.

To analyze the data from these experiments, it must first be recognized that most of the product solids are multiphase and that each separate phase, to a first approximation, scatters independently. In such cases, the measured distribution function, $f(2R_g)$, is the sum of the scattering of individual components according to their electron densities; that is, $f(2R_g) = \sum \alpha_i f_i(2R_g)$, where α_i is a coefficient determining the contribution of component i to $f_i(2R_g)$. In general, separating the combined particle volume distribution into components is complex and cannot be performed reliably. Only in the simplest case of two-component systems having well-separated distribution curves is it possible to estimate the contributions of the individual components.

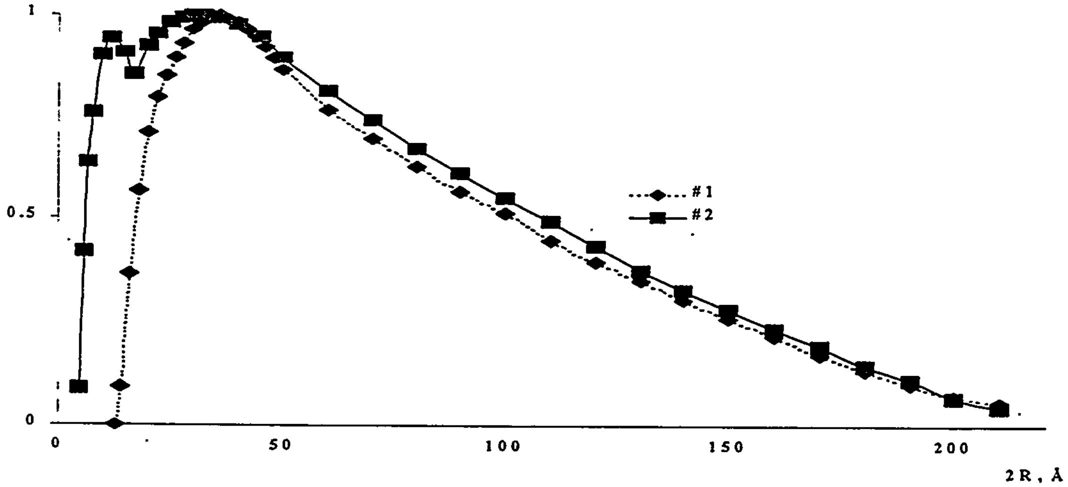

Figure 14. Particle Volume Distributions for the Precipitates in Tests 1 and 2

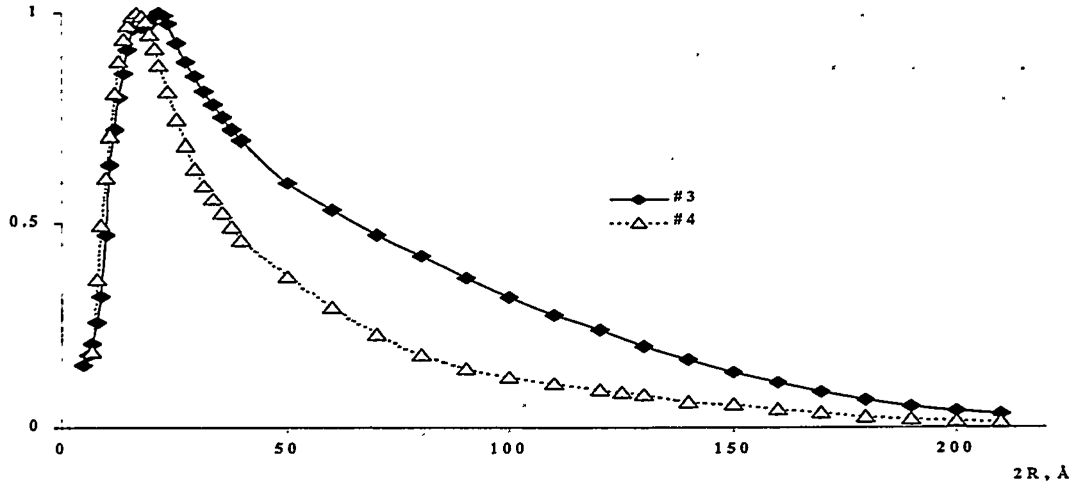

Figure 15. Particle Volume Distributions for the Precipitates in Tests 3 and 4

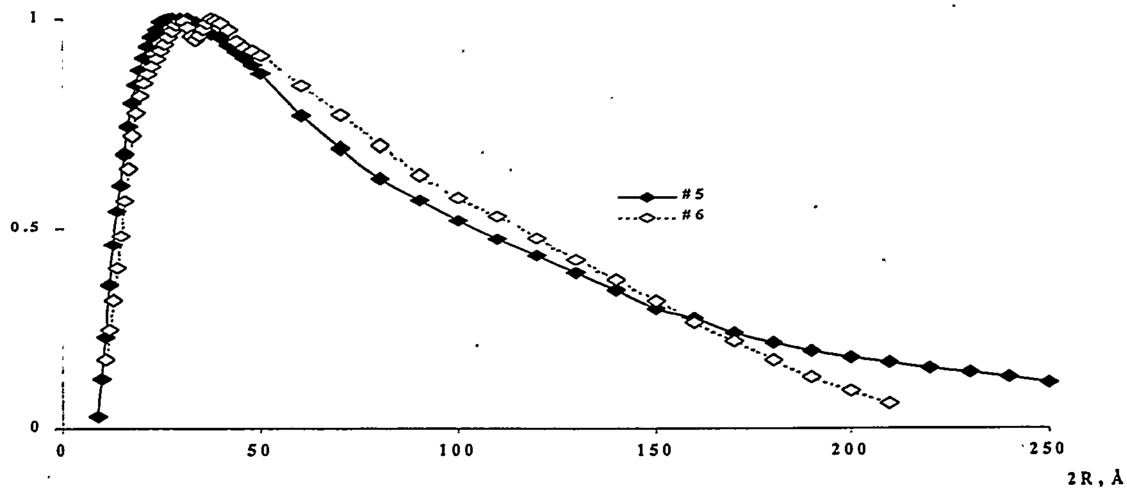

Figure 16. Particle Volume Distributions for the Precipitates in Tests 5 and 6

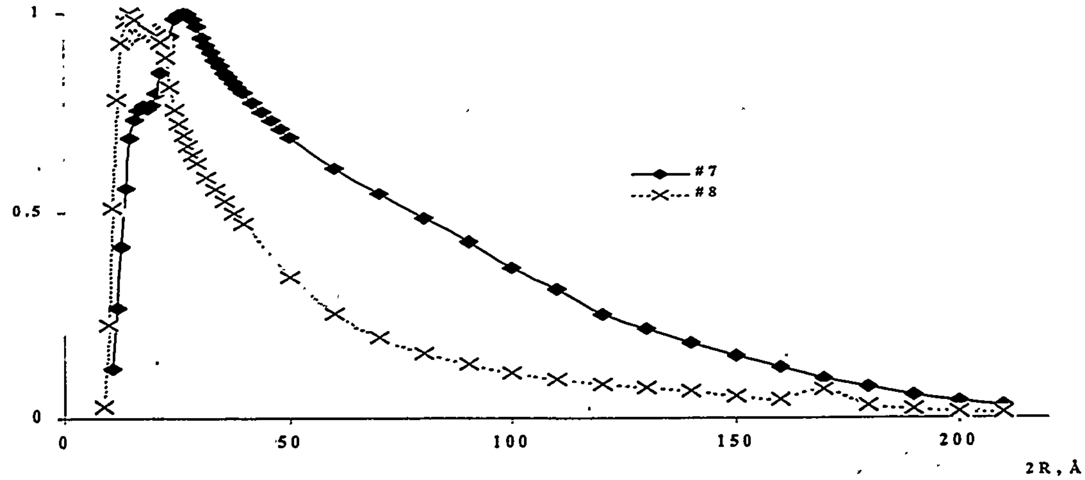

Figure 17. Particle Volume Distributions for the Precipitates in Tests 7 and 8

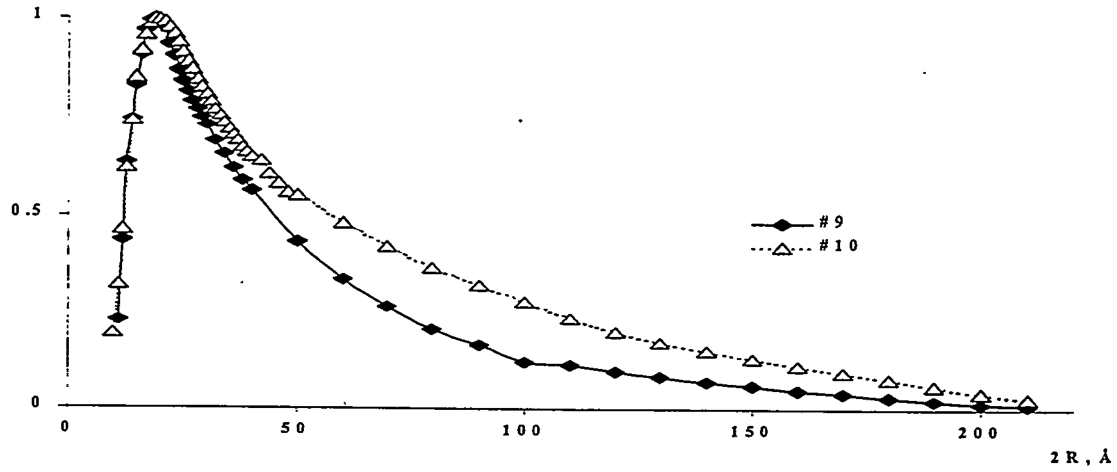

Figure 18. Particle Volume Distributions for the Precipitates in Tests 9 and 10

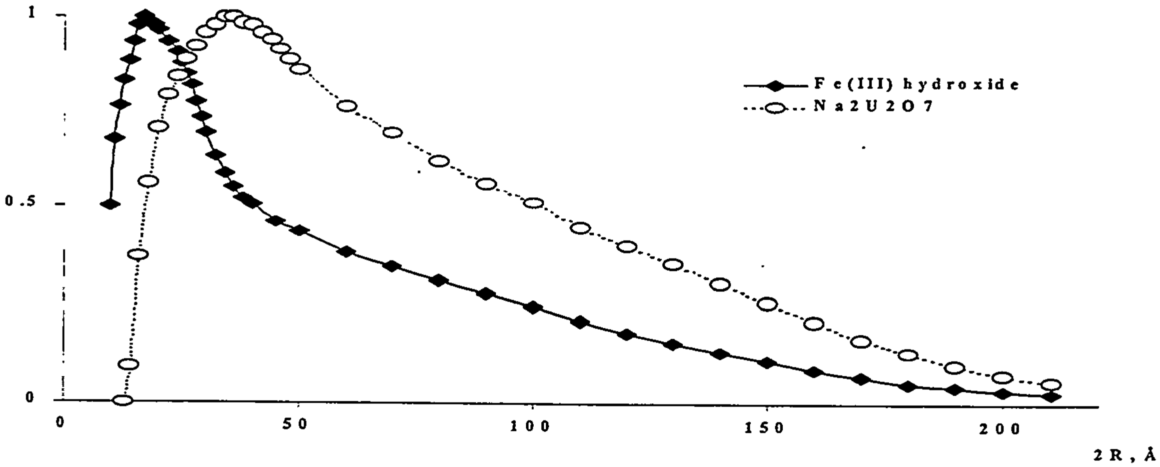

Figure 19. Particle Volume Distributions for Pure Fe(III) Hydroxide and Sodium Diuranate Precipitates

As seen in Figure 19, the particle size distributions for the monophase sodium diuranate and Fe(III) hydroxide systems overlap with the Fe(III) hydroxide having the smaller particle size distribution. The maximum position of the diuranate $2R_g$ distribution curve exceeds that of Fe(III) hydroxide more than two-fold (Table 5). This phenomenon is observed for the $Na_2U_2O_7$-$Fe(OH)_3$ two-phase systems in Tests 2 and 3 in which the distribution curves have two maxima (Figures 14 and 15). The maximum at higher particle size may be attributed to diuranate particles. With increasing Fe(III) concentration, the maximum shifts to lower $2R_g$ values, specifically, from 3.4-3.6 nm to 2.2 nm (Table 5). With very high Fe(III) content in the simulated dissolver solution (Test 4), the diuranate maximum disappears, and only the maximum of Fe(III) hydroxide, at 1.7 nm diameter ($2R_g$), remains on the distribution curve.

The conclusion that Fe(III) hydroxide particles are smaller sized than diuranate also is confirmed by the data on $f(2R_g)$ values at 4 and 5 nm $2R_g$ (Table 5). These parameters decrease significantly with increase in Fe(III) concentration in the initial simulated dissolver solutions.

Table 5. Positions of Maxima on the Particle Size Distribution and Values of $f(2R_g)$ for the Varied Simulated Dissolver Solution Precipitates

Test	Element Concentration, g/L			Maxima Position, nm		$f(2R_g)$ Value at $2R_g$, nm		
	U	Fe	Al	First	Second	4.0	5.0	10.0
1	37.5	0	0	--	3.4 - 3.6	0.98	0.86	0.51
2	33.7	3.8	0	1.3	3.0 - 3.2	0.98	0.89	0.55
3	18.8	18.8	0	1.7	2.2	0.70	0.60	0.32
4	3.8	33.7	0	1.7	--	0.46	0.37	0.12
5	30.0	0	7.5	--	2.8 - 3.2	0.96	0.94	0.52
6	18.8	0	18.8	3.0 - 3.1	3.7 - 4.0	0.99	0.91	0.58
7	7.5	0	30.0	1.8 - 1.9	2.6 - 2.8	0.81	0.70	0.36
8	3.8	30.0	3.8	1.5	1.9	0.47	0.34	0.11
9	3.8	3.8	30.0	1.9	--	0.56	0.44	0.12
10	12.5	12.5	12.5	1.9	--	0.65	0.55	0.28
Fe	0	37.5	0	1.4	--	0.51	0.43	0.34

Additional information on the particle sizes of $Na_2U_2O_7$ and $Na_2U_2O_7$-$Fe(OH)_3$ mixtures was obtained by an XRD method. It was observed that the XRD patterns of precipitates in Tests 2, 3, and 4 did not contain any lines of Fe(III) compounds. The absence of lines means that the size of the Fe(III) hydroxide crystallites was less than 3 nm. The diffraction patterns of solids in Tests 1, 2, and 3 produced lines of $Na_2U_2O_7$. The line widths correspond to a pure sodium diuranate crystallite size of about 5 to 8 nm. With increasing Fe(III) hydroxide content, the size of the diuranate crystallites decreased. These data are in good agreement with the results of the particle volume size distribution study obtained by SAXS, taking into account the asymmetry of the size distribution curves and the crystallite size averaging inherent to the XRD method.

The effects of aluminum particle size distributions of precipitates formed in simulated dissolver solutions containing uranium and aluminum are less evident. Aluminum hydroxide appears to hamper the crystallite growth of sodium diuranate. Thus, the $2R_g$ maxima at 2.8 to 3.2 nm and 1.8 to 1.9 nm in the distribution curves of Tests 5 and 6, respectively, arise from diuranate particles. Aluminum in the simulated dissolver solution also broadens the particle size distribution, as shown by the relatively high $f(2R_g)$ values at 5.0 and 10.0 nm in Tests 5, 6, and 7 (Table 5).

The first maximum on the distribution curve in Test 8 (a U/Fe/Al dissolver solution with a large amount of iron) is attributed to Fe(III) hydroxide particles. The second maximum on the curve probably comes from diuranate particles. For solids from Tests 9 and 10, the maximum at 1.9 nm $2R_g$ can be attributed to diuranate. As shown in Table 5, the yield of large-size particles in the triple U/Fe/Al systems is noticeably lower than found in the U/Al systems.

5.0 Conclusions

The purpose of this work was to determine the completeness of uranium, plutonium, and americium precipitation; the rate of sedimentation; and the physico-chemical characteristics of the solids formed by alkali treatment of simulated acidic dissolver solutions arising from the dissolution of K Basin sludge. An additional task was to study the possible redistribution of uranium, plutonium, and americium from the sodium diuranate and iron and aluminum hydroxide precipitates upon contact with carbonate- and EDTA-bearing simulated waste solutions.

During the testing, the sedimentation rate of precipitates formed by alkali treatment of a simulated dissolver solution [1 $\underline{M}$ HNO_3, 0.096 $\underline{M}$ $UO_2(NO_3)_2$, 0.246 $\underline{M}$ $Fe(NO_3)_3$, 0.033 $\underline{M}$ $Al(NO_3)_3$, 0.001 $\underline{M}$ Na_2SiO_3, and 1.9×10^{-4} $\underline{M}$ $Pu(NO_3)_4$] showed only minor dependence on temperature and no regular dependence on the alkali excess or direction of mixing. The sedimentation rate also was not dependent on the dissolver solution composition. The precipitate volumes, after a 24-hour settling, showed only a 5% to 10% decrease with increasing temperature. Solids volume increased as the total molar concentration of the macrocomponents (U, Fe, and Al) in the dissolver solution increased. The sodium diuranate precipitates were denser than the Fe(III) or Al(III) hydroxides by a factor of ~2.

As shown by XRD, the precipitates consisted of crystalline $Na_2U_2O_7$ with Fe(III) and Al(III) hydroxides generally present as amorphous species. However, in some precipitate products, especially after coagulation at 80°C, diffraction lines attributed to α-Fe_2O_3 (hematite) were reliably observed. A small amount of crystalline α-$Al(OH)_3$ (bayerite) also was present in one test. The lines of $Na_2U_2O_7$ were diffuse and broad, indicating the very small crystallite size (5 to 8 nm) of the compound. In contrast to $Na_2U_2O_7$, the α-Fe_2O_3 lines were narrow, which means the α-Fe_2O_3 was well crystallized. However, only part of the amorphous Fe(III) hydroxide ripened into crystalline oxide. Based on Mössbauer effect data, amorphous Fe(III) hydroxide did not interact with sodium diuranate under the experimental conditions.

Particle size distributions were measured by a SAXS technique for precipitates produced by treatment of 10 different simulated dissolver solutions with NaOH solution. The maximum population occurred at crystallite particle sizes of 2 to 3 nm (0.002 to 0.003 microns). The particle size distribution for pure Fe(III) hydroxide was slightly lower than that of sodium diuranate. As a result, size distributions of several of the dissolver product solids were bimodal, with the larger particles associated with the sodium diuranate. Increasing amounts of Fe(III) in the dissolver solution appeared to decrease the resulting sodium diuranate particle size.

Plutonium concentrations in the mother solutions obtained by alkali treatment of the dissolver solutions were scattered and low (~2×10^{-8} $\underline{M}$, versus 5.5×10^{-6} $\underline{M}$ Pu equivalent to the 100 nCi $^{239,240}Pu$/g transuranic, TRU, waste limit). The scatter perhaps was caused by the presence in the mother solutions of very small precipitate particles that were not completely separated by 0.45-µm filtration. Americium concentrations in the mother solutions also were low [$(5\text{-}11)\times10^{-11}$ $\underline{M}$ versus 1.2×10^{-7} $\underline{M}$ Am equivalent to 100 nCi ^{241}Am/g] and not strongly dependent on the precipitate composition. When the NaOH concentration was increased from 0.01 to 1 $\underline{M}$, uranium concentrations in the mother solutions increased from 1.5×10^{-6} to 18×10^{-6} $\underline{M}$. This increase is explained by the change of sodium diuranate solubility caused by hydroxide complexation.

As much as 90% of the uranium dissolved from the precipitates by a 1-week contact at ~30°C with a simulated high carbonate waste solution (1 $\underline{M}$ Na_2CO_3 + 5 $\underline{M}$ $NaNO_3$). The solubility of uranium in this carbonate system was found to be higher than that contributed by the precipitates. Thus, the incomplete dissolution was caused by kinetic factors. Uranium concentrations in the carbonate leach solutions decreased noticeably, under otherwise similar conditions, with increasing precipitate coagulation temperature; that is, with increased $Na_2U_2O_7$ crystallinity. The degree of uranium leaching markedly decreased with the increase of excess NaOH concentration used during the precipitate preparation. This effect likely was caused by the retention of NaOH in the moist $Na_2U_2O_7$ solids. The NaOH inhibited the formation of the more soluble U(VI) carbonate complexes.

Some correlation was found between the concentrations of plutonium and americium versus the uranium dissolved by the carbonate leaching solutions. However, only a fraction of the plutonium, perhaps that associated with sodium diuranate, dissolved in the carbonate solution. In most tests, the degree of plutonium leaching was lower than that of uranium. Plutonium preferentially associates with Fe(III) hydroxide in the precipitates; plutonium concentrations in the carbonate leach exceeded the TRU limit (100 nCi/g or 5.5×10^{-6} $\underline{M}$) only for those solids containing no Fe(III), but approached the TRU limit and were greater than 1×10^{-6} $\underline{M}$ in all cases. No association of plutonium with aluminum hydroxide was found. Similarly, americium dissolution by the carbonate leaching solution was lowest for the solid phases highest in Fe(III) hydroxide and exceeded the TRU limit (1.2×10^{-7} $\underline{M}$) only for two tests having no Fe(III).

Leaching of the precipitates by a simulated alkaline waste solution containing a high concentration of organic complexing agent (0.1 M EDTA + 1 $\underline{M}$ NaOH + 5 $\underline{M}$ $NaNO_3$) was also tested. The uranium concentrations were about three times higher than found in the original alkaline mother solution. The plutonium concentrations in the EDTA leachates (about 2×10^{-8} $\underline{M}$) were similar to those observed in the original alkaline mother solutions and were well below the TRU limit. The precipitation conditions and the precipitate compositions had little effect on the degree of uranium and plutonium dissolution in the EDTA-bearing leachates. In contrast, the americium concentrations in the EDTA leachates approached the TRU limit for solids having no Fe(III).

Based on these studies, the alkali treatment of the acidic dissolver solution is best performed by precipitation and digestion at 40°C with 0.01 $\underline{M}$ NaOH excess (pH 12) using direct strike addition of NaOH solution to the dissolver solution. These conditions yield the lowest uranium concentration in the supernatant, require the least excess NaOH, and provide the highest apparent partitioning of plutonium to the carbonate-resistant Fe(III) hydroxide solid phase. However, other conditions (reverse strike, 80°C) have little effect on precipitate properties. The resulting supernatant solutions from any of the treatment conditions tested are non-TRU for both plutonium and americium. Contacting product precipitates having no Fe(III) in the solid phase with carbonate-bearing solutions can produce TRU-level plutonium and americium concentrations in solution. Alkaline solutions containing EDTA also can leach americium to near-TRU levels from iron-free solids.

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