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Caustic Precipitation of Plutonium and Uranium with Gadolinium as a Neutron Poison

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ABSTRACT

The caustic precipitation of plutonium (Pu) and uranium (U) from Pu and U-containing waste solutions has been investigated to determine whether gadolinium (Gd) could be used as a neutron poison for precipitation with greater than a fissile mass containing both Pu and enriched U. Precipitation experiments were performed using both actual samples and simulant solutions with a range of 2.6-5.16 g/L U and 0-4.3:1 U:Pu. Analyses were performed on solutions at intermediate pH to determine the partitioning of elements for accident scenarios. When both Pu and U were present in the solution, precipitation began at pH 4.5 and by pH 7, 99% of Pu and U had precipitated. When complete neutralization was achieved at pH > 14 with 1.2 M excess OH^-, greater than 99% of Pu, U, and Gd had precipitated. At pH > 14, the particles sizes were larger and the distribution was a single mode. The ratio of hydrogen:fissile atoms in the precipitate was determined after both settling and centrifuging and indicates that sufficient water was associated with the precipitates to provide the needed neutron moderation for Gd to prevent a criticality in solutions containing up to 4.3:1 U:Pu and up to 5.16 g/L U.

I. INTRODUCTION

Plutonium (Pu) was once produced at the Savannah River Site (SRS) to support nuclear weapons programs and to supply fuel sources for space exploration missions. Now, excess Pu-containing materials will be converted to a mixed oxide (MOX) fuel or discarded to the site's high level waste (HLW) system and vitrified in the Defense Waste Processing Facility. Pu that meets isotopic requirements will be converted into plutonium oxide (PuO_2) for MOX fuel fabrication and used to generate nuclear power. Some of the Pu materials that do not meet MOX requirements will be dissolved and the resulting solutions will be discarded to the SRS HLW system for vitrification and disposal in glass logs at the geologic repository.

In recent years, solutions containing a total of 140 kg of Pu which did not meet MOX specifications were identified and disposed of using Gd as a neutron poison. Prior to vitrification, the acidic Pu waste solutions must be treated in a process in which a 50 wt% NaOH solution is added to the waste solution until a 1.2 M excess of OH^- is obtained. At SRS, this treatment process is referred to as neutralization. The neutralized waste is then transferred into an on-site tank for interim storage. To minimize the number of batches required for neutralization, the Pu-containing solutions were processed with greater than a minimum critical mass (> 450 g) of ^{239}Pu in each batch.

During the neutralization process, most metal ions precipitate as the pH of the waste solutions changes from pH < 1 to pH > 14 when neutralization is complete. Between pH 1 - 1.5, Pu(IV) begins to hydrolyze and forms Pu hydroxides which then undergo polymerization through the formation of hydroxyl bridges.[1] By pH 3, most of the Pu will have precipitated. In aqueous solutions, the uranyl cation (UO_2^{2+}) begins to precipitate at pH 4.5.[2] Pu(IV) polymerization can be reduced by the addition of UO_2^{2+} to the solution[3], effectively terminating Pu polymer chain propagation by attaching to the hydroxyl groups on Pu(IV).

Neutralization of solutions containing greater than a minimum critical mass of material requires the addition of a neutron poison that will precipitate with the fissile (^{239}Pu and ^{235}U) material to prevent a criticality. Depleted U, iron (Fe), and manganese (Mn) have been previously used to poison SRS process solutions. However, processing the Pu solutions with greater than a minimum critical mass per batch requires fissile:depleted U ratios and fissile:Fe ratios of 1:198 and 1:160 by mass, respectively, in the precipitate. The additional precipitate mass due to one of the conventional neutron poisons would significantly increase the volume of solids sent to vitrification and the number of glass logs produced. The use of large amounts of Mn (32:1 Mn:Pu) and Fe would also cause processing problems due to the production of gelatinous Mn hydroxides and complex Fe hydroxides before pH 14.

When a large amount of Pu is neutralized, Gd is the preferred neutron poison because it has a high thermal neutron capture cross section (48,800 barns)[4] and only a 1:1 ^{239}Pu:Gd mass ratio is necessary.[5] In nitrate solutions, Gd begins to precipitate at pH 6.8 in the absence of the actinide elements.[6] A sufficient amount of water must be present to provide hydrogen (H) atoms to thermalize the neutrons, as Gd is only an effective absorber of thermal neutrons. A Nuclear Criticality Safety Evaluation[5] determined that the minimum H:Pu ratio in the precipitate could be no less than 30:1 for Gd to be used.

Bronikowski *et al.* reported[5] that the addition of Gd to Pu-containing solutions and subsequent neutralization removed > 99% of both Pu and Gd from the aqueous phase. The goal of the experiments performed and discussed in the following sections was to determine whether Gd remained a viable neutron poison for solutions containing Pu and U up to a 4.3:1 U:Pu ratio, or solutions containing only enriched U. Five solutions (one actual SRS waste solution and four simulant solutions) were poisoned with Gd and subsequently neutralized with NaOH. The waste solution (Solution A, 3.2 g/L U and 1 g/L Pu) was an actual sample of material intended for neutralization and disposal. Four simulant solutions (Solution B, 1 g/L Pu and 2.7 g/L U; Solution C, 3 g/L U; Solution D, 0.7 g/L Pu and 3.06 g/L U; and Solution E, 5.2 g/L U) were also prepared. The partitioning of selected elements between the precipitate and supernate was monitored at pH 4.5 and 7 and upon full neutralization at pH > 14. Systems neutralized to intermediate pH values were investigated since partial neutralization represents potential accident scenarios. The two solutions containing only U were studied to determine how the precipitation behavior of U compared to that of solutions containing both U and Pu and to establish whether ^{235}U could be poisoned with Gd, neutralized, and discarded as waste in the same manner.

II. EXPERIMENTAL

II.A. Solution Preparation

The solutions were prepared from reagent grade uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6\ H_2O$) and a 40 g/L Pu solution previously purified by anion exchange. All other chemicals were of reagent grade or higher. Unless otherwise specified, all experiments were performed at ambient temperature.

II.B. pH Tests

Neutralization experiments were performed using 25 mL of solution from the SRS H-Canyon facility (Solution A), 40 mL of Solution B, 40 mL of Solution C, 50 mL of Solution D, and 50 mL of Solution E. The composition for elements of interest is summarized in Table I.

To ensure a consistent Gd concentration in each experiment with Solution A, a specific volume of 30 wt% $Gd(NO_3)_3$ was added to the entire solution prior to performing experiments. For Solutions B - E, an appropriate mass of the $Gd(NO_3)_3 \cdot 6\ H_2O$ was added during preparation to produce the final ratios: 1.1:2.7:1 Pu:U:Gd (Solution B), 1.6:1 U:Gd (Solution C), 1:4.3:2.4 Pu:U:Gd (Solution D), and 0.9:1 U:Gd (Solution E).

Solution A was transferred to 100 mL beakers using a graduated cylinder; a 5 mL pipette was used for the surrogate solutions (Solutions B - E) to improve volume control. Separate aliquots were used for each experiment, e.g. one 25 mL aliquot of Solution A was used for the experiments to reach pH 4.5. A second 25 mL aliquot was used for the pH 7 experiments. One of the remaining two 25 mL aliquots was used for neutralization to pH > 14 with 1.2 M excess NaOH and the other to pH > 14 with 3.6 M excess NaOH. Each sample was neutralized to the desired endpoint by the drop-wise addition of 50 wt% NaOH from a volumetric burette while being stirred. The NaOH additions were made such that the temperature of the solutions did not exceed 50^{o}C, a processing constraint. Once the formation of solids was observed and/or the appropriate pH attained (as measured by pH paper, ± 0.5 pH unit), the beakers were covered with Parafilm M™ and the solutions were stirred for an additional two to three hours prior to sampling.

While stirring, four 1.5 mL aliquots of the precipitate slurry were removed from each beaker and transferred into four 1.5 mL conical centrifuge tubes and centrifuged (5000 *g*) for five minutes. The centrifuged solutions were analyzed for ^{238}Pu and $^{239/240}$Pu by thenolyltrifluoroacetone (TTA) extraction and alpha pulse height analysis (APHA). These analyses were performed on the supernate and on the solids after dissolution in HNO_3. The concentrations of U, boron (B), and Gd were obtained by inductively coupled plasma emission spectroscopy (ICP-ES).

After the initial sampling, the beakers were covered with Parafilm M™ and allowed to stand for one week (without stirring), resuspended, and analyzed as described above.

II.C. Density

Densities were determined by measuring the mass of a 1 mL aliquot of supernate only and, after resuspending the solids, a 1 mL aliquot of the slurry.

II.D. Settling Experiments

The settling times for the solids precipitated during selected neutralizations were measured using a 25 mL graduated cylinder. Prior to the measurements, the slurry in each beaker was stirred and approximately 16 mL of each slurry were transferred to a 25 mL graduated cylinder. The solids were allowed to settle and the supernate-solids interface volume from the graduated cylinder was recorded as a function of time.

II.E. Viscosity

A calibration curve for viscosity experiments was established using 15 mL of a series of NaOH solutions (0.5 - 10M) of known viscosity [7] and deionized water. The solutions were passed through a standard glass condenser coil (inner tube diameter was 0.6 cm) and the corresponding elapsed time was recorded. The time recorded was the interval from the moment the solution began to flow until the first drop left the opening at the bottom of the coil. Viscosity measurements were made to ensure the precipitate slurry would flow by gravity following neutralization, thus allowing unobstructed transfer of the slurry to the waste tank used for interim storage.

The apparent viscosity of the solutions neutralized beyond pH 14 was determined by mixing the supernate and the solids and transferring approximately 15 mL of the solution to the coil. The corresponding viscosity was obtained from the calibration curve. Each measurement was performed in triplicate and the coil was rinsed with deionized water before initial use and after each set of measurements.

II.F. Particle Size Analysis

The particle size distribution of the solids from selected systems was measured using a Leeds and Northrup Microtrac II particle size analyzer. Prior to analysis of the actual samples, 300 mL of diluent solution prepared to closely match the ionic strength of the precipitation supernate were analyzed to establish a baseline. The diluent was prepared by adding NaOH to a solution containing 6.8 M HNO_3 and sufficient HNO_3 to account for the metal nitrate in each solution. Sufficient NaOH was added to the diluent to produce solutions at pH 4.5 and pH > 14 with 1.2 M excess OH^-. Analyses were performed by adding the precipitate slurry to the diluent until the concentration of particles was sufficient to perform the measurement. The solids were mixed vigorously prior to analysis.

II.G. Water Content of Solids

The ratio of hydrogen:fissile material in the precipitated solids was determined two different ways: after the solids had settled and in a sample of centrifuged solids. Once the water content of the solids was determined, the H ratios were calculated using the U and Pu analysis for the solids with the assumed solid compounds produced ($Na_2U_2O_7$, $Gd(OH)_3$, and $Pu(OH)_4$).

The water content of the settled solids was determined by mass difference. A 25 mL aliquot was transferred into a 25 mL graduated cylinder. The solids were allowed to settle for at least 24 hours at which time the volume of supernate above the solids was measured. The majority of the supernate was then transferred into a 100 mL beaker, leaving 1-2 mL of supernate above the solids to ensure no solids were transferred. Then, the mass of the supernate in the beaker and the mass of the supernate material remaining in the graduated cylinder were measured. After the mass of the graduated cylinder and its contents was measured, the remaining supernate and solids were poured into another beaker and allowed to dry at ambient temperature, at which time the final mass of the beaker and its solids was obtained. The water associated with the settled solids was then calculated by difference using the mass and volume measurements.

The water content of centrifuged solids was measured by thermogravimetric analysis (TGA). Samples were prepared by transferring 1.5 mL of the well-mixed slurry into a 1.5 mL conical centrifuge vial and centrifuging for five minutes at 5000 *g*. For solids obtained from the 4.3:1 Pu:U and 5.2 g/L U solutions, after the supernate was removed, an additional 1.5 mL of slurry was added and the centrifuging was repeated. After the centrifuging was complete and the supernate was removed, the solids were transferred to the TGA for analysis. A platinum sample pan and a heating rate of 10 °C/minute were used. To check the weight calibration of the TGA, a 30 mg standard was used. Each sample run was 5-25 mg. Calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) was run as a standard to show that the waters of hydration were lost between 150 - 200 °C. The amount of water associated with the centrifuged solids was calculated as the mass difference of the sample at 250 °C as only waters of hydration were lost. The H:U, H:Pu, and H:fissile ratios were calculated using the water content of the solids and the U, Pu, and Gd analyses.

III. RESULTS

III.A. pH Tests

In this series of neutralization experiments, the most significant difference in the precipitation behavior of Pu-Gd, Pu-U-Gd, and U-Gd was the pH at which precipitation began in each solution. Previous neutralization experiments showed that the Pu-Gd precipitate began to form at pH 3.[5] Solutions containing Pu, U, and Gd or U and Gd began to precipitate at pH 4.5,[8-10] consistent with the behavior of U solutions.[2] Although surprising, this observation can be explained by the termination of the Pu polymer chain by UO_2^{2+} which keeps more Pu in solution at pH 3 and, at these U:Pu ratios, prevents precipitation until pH 4.5 when both U and Pu precipitate. Table II shows the percent of each element of interest precipitated at selected pH values. At pH 4.5, only 3-6% of the

Gd precipitated which was expected for Gd in these slightly acidic conditions.[6] A similarly small amount of Gd had precipitated at pH 3 in previous studies.[5] Aluminum hydroxide ($Al(OH)_3$) precipitates at pH 4.5, but at pH >14 the aluminate anion ($Al(OH)_4^-$) is soluble.

Both U and Pu begin to precipitate in acidic conditions and some boron (B) was also present in the solids from Solution A. Boron is present in the solutions as a nuclear poison when dissolving some Pu materials or in Pu solution storage. The presence of B is beneficial from a poisoning aspect when neutralizing, although its presence is not required for successful use of Gd. At pH 7, a minimum of 95% of the Gd, U, and Pu were removed from solution. Upon complete neutralization (pH > 14), greater than 99% of these elements were found in the precipitated solids. Analysis of the solutions after one week (without stirring) revealed essentially no change in the composition of the solids. Since there was little change in the mass ratios, short-term storage of the precipitate slurry is possible while maintaining the integrity of the solids.

The U:Gd, Pu:Gd, and fissile:Gd ratios obtained from the neutralization experiments are shown as mass ratios in Table III. The U:Gd and Pu:Gd ratios for the solids produced at pH 4.5 were significantly greater than one since much of the Gd remained in solution while the majority of the U and Pu precipitated at pH 4.5. In the previous studies where the Pu:Gd ratios were designed to be 1:1 upon full neutralization,[5] the precipitate contained 20:1 Pu:Gd at pH 3 and, with water present, the Pu:Gd ratio was sufficient to prevent a criticality. At pH 4.5 in Solutions A and D, the Pu:Gd ratio decreases to 6.1:1 and 6.9:1, respectively. The excess of U in Solutions A and D directly impacts the Pu:Gd ratios found in the precipitate. As previously described, U causes Pu to remain in solution until precipitation begins at a higher pH (e.g., pH 4.5 vs. pH 3). As a result, pH 4.5 is closer to the pH at which Gd begins to precipitate.[6] For a given amount of Pu in the precipitate, at pH 4.5, more Gd will be present than at pH 3 thus decreasing the Pu:Gd ratio.

The fissile:Gd ratios in Table III were calculated assuming 33% of the U in the waste solutions is ^{235}U with Pu constituting the rest of the fissile material. The mass ratios reflect the fact that all of the U, Pu, and Gd are expected to precipitate after the solutions are neutralized to pH > 14.

III.B. Density

The density (Table IV) of each solution was measured to characterize the slurry and the supernate. Solutions A - E are within the range of 4 - 6 M $NaNO_3$ (1.2256 - 1.3175 g/mL) diluted with 1.2 M NaOH (1.0538 g/mL),[7] typical of SRS waste.

Only small differences were observed between the supernate and slurry densities which would likely facilitate mixing and suggest that the solids do not immediately settle out of solution and could be easily resuspended.

III.C. Settling Experiments

The settling curves for selected precipitate slurries are shown in Figure 1. The settling rate of solids was measured to determine how the solution would behave if, during processing or transfer, agitation of the slurry was stopped for a period of time.

The density data in Table IV combined with the results in Figure 1 indicate that the density differences between the supernate and the slurry have little effect on the settling time for solids formed from Solutions A - E at pH > 14. The settling rate appears inversely proportional to the concentrations of U + Pu + Gd; although the initial setting rate of the solids from Solution A (6 g/L) was faster than the rate for the solids from Solution D (5.4 g/L). All solids at pH > 14 settle at a rapid rate reaching their approximate final volume at nominally 150 minutes.

At pH 4.5, the settling rates are much slower than at pH > 14. Table II shows that Al remains in the supernate but could act as a flocculent which would slow the settling rate. Aluminum is present in Solution E and in combination with the higher U concentration (5.16 g/L vs. 3.06 g/L for Solution D), produces the slowest initial settling rate at pH 4.5. Solution D also exhibits a relatively slow initial settling rate, although not as slow as that for Solution E. The slower rate for Solution D could be due to a combination of Al speciation and both the rate of polymeric Pu formation and precipitation. The rate of Pu polymer formation is complicated and depends on the method of preparation, temperature, and concentration of Pu in solution.[1] The rate of Pu polymer precipitation is influenced by the pH of the system where, for example, a shift in pH from 3.8 to 5 can quantitatively precipitate polymer that would have remained suspended for as long as six days.[11]

III.D. Viscosity

The viscosity (Table V) for each pH > 14 slurry was determined using a calibration curve developed for a series of NaOH solutions of known concentrations. Each slurry contained a significant amount of solids, yet the flow of the slurry through the coil was not obstructed. The increase in salt concentration from 1.2M OH^- to 3.6M OH^- resulted in an expected increase in the viscosity, although the effect was small. For comparison, the viscosities of Solutions A - C are similar to that of 4 - 6M NaOH.[7]

III.E. Solids Characterization

Samples of the precipitate were qualitatively characterized by scanning electron microscopy (SEM) and particle size analysis. Quadropole backscattered electron (QBSE) spectra combined with energy dispersive spectroscopy (EDS) and X-ray diffraction were used to determine the elemental composition of the solids and identify the precipitated solids.

At pH 4.5, the precipitate obtained from Solution A was amorphous with crystalline solids on top. The crystalline material on top was identified as a Na-bearing compound (most likely $NaNO_3$) by EDS and small amounts of nickel and iron were also detected. EDS analysis of the solids underneath the crystalline material detected U, Pu, and Gd.

At pH 7, SEM analysis of the solids obtained from Solution A show amorphous morphology down to 500X (10µm) magnification. EDS characterization of selected portions of the solids detected Pu, U, and Gd.

At pH > 14, Solution A solids have broad areas of Pu-U-Gd and U-Gd, but no specific Pu or U particles. EDS spectra for solids obtained from Solution D showed no Pu due to its relatively low concentration and spectral interference from U. However, TTA/APHA analysis confirmed the presence of Pu in Solution D solids. EDS detected both U and Gd in solids from Solution E and the solids appeared more crystalline. SEM micrographs for Solutions D and E are shown in Figures 2 and 3, respectively, and associated QBSE/EDS characterization of selected areas are shown in Figures 4 and 5.

Precipitates from Solutions D and E have a distinct difference. In Figures 2 and 3, the most readily observable difference is the presence of 10-20 µm "boulders" in the precipitate from Solution E at pH > 14. The boulders appear more crystalline than the surrounding solids and EDS analysis confirms the boulders contain U and Gd. As noted previously, the presence of some U during the neutralization of Pu-containing waste solution is advantageous since it reduces the formation of Pu polymers by chain termination; however, large amounts of U promotes crystallization and larger particle sizes. If the U concentration is too great, the particle size may grow to more than 100 µm size where neutron shielding may become a problem for using Gd as a poison. Thus, a U concentration limit may exist when using Gd as a neutron poison for neutralizing greater than a fissile mass of equivalent Pu.

X-ray diffraction results were obtained for the solids precipitated during each of the neutralization tests. At pH > 14, U was present in the solids from Solution A as sodium diuranate ($Na_2U_2O_7$). After one week, uranium dioxide (UO_2) and clarkeite ($Na[(UO_2)O](OH)\cdot H_2O$) were also found in the solids. Solids obtained from Solution C at pH > 14 contained clarkeite, $NaNO_3$, sodium carbonate (Na_2CO_3), and gadolinium hydroxide ($Gd(OH)_3$). At pH 4.5, the predominant spectral lines associated with the solids obtained from Solutions D and E were attributed to $NaNO_3$ and an alkaline earth aluminum hydroxide (likely Ca^{2+}). Solids from Solution D contained Na_3UO_4 and clarkeite. After full neutralization, X-ray diffraction analysis revealed Na_2CO_3, sodium uranate (Na_2UO_4), Na_3UO_4, and $Na_2U_{2.5}O_{8.5}$ in addition to $NaNO_3$ present in the Solution E solids. No crystalline compounds containing Pu, U, and Gd or U and Gd were detected by X-ray diffraction in any precipitate obtained from Solutions A - E. Thus, the X-ray diffraction results support the amorphous nature of the Pu-U-Gd and U-Gd solids or indicate any crystals present were less than 10 µm in size.

In the previous Pu-Gd caustic precipitation studies,[5] amorphous material was produced at pH > 14, likely due to the formation of Pu and Gd hydroxides. The X-ray diffraction pattern from the amorphous material after it was heated fit between those for plutonium oxide (PuO_2) and gadolinium oxide (Gd_2O_3) and showed homogeneous mixing, a requirement for the process. Pu was not seen by X-ray diffraction because it was either < 10 µm or intimately mixed. Furthermore, Figures 4 and 5 show the presence of homogeneous mixtures of U and Gd. The presence of Pu was determined by other analyses.

Coprecipitation of lanthanides and actinides in the same crystal structure is not without precedence. Leyva *et al.* analyzed the crystal structure of solids containing UO_2 and 0-8% weight percent Gd.[12] Diffraction patterns obtained from inhomogeneous $(U,Gd)O_2$ solids and pure UO_2 show the duplication of the diffraction peaks corresponding to the two coexistent phases observed in the heterogeneous $(U,Gd)O_2$ sample. The peak positions of the inhomogeneous solid and UO_2 were coincident. Riella *et al.*[13] indicated that X-ray powder diffraction patterns from coprecipitated UO_2-Gd_2O_3 powders show no gadolinium oxide peaks, indicating the gadolinium is incorporated into the UO_2 lattice in the early stages of precipitation.

Particle size distributions for the solids were examined at pH 4.5 and pH > 14 for Solution D (Figure 6) and pH > 14 for Solution E (Figure 7). The solids obtained from Solution D are shown in Figure 6 as the fraction of solids present with increasing particle size. At pH 4.5, the particle size distribution is bimodal with maxima at 1 and 10 µm. Examination of SEM micrographs for particle sizes and energy dispersive spectra for compositional information indicates it is likely that the smaller particle sizes are due to amorphous Al compounds and/or Pu-U-Gd solids while the larger particles are Pu-U-Gd solids that contain Na.

At pH > 14, solids obtained from Solutions D and E had a single size distribution with maxima at 6 and 18 µm, respectively. The change from bimodal to single distribution was due to the dissolution of Al compounds under alkaline conditions. The larger particle sizes formed at pH > 14 were due to the complete precipitation of Pu, U, and Gd or U and Gd onto the nucleation sites already present at pH 4.5 or through agglomeration.

The particle size characterizations were within the range of those reported by Hobbs.[14] Hobbs reported that SEM analysis of the precipitates showed some irregular particle morphologies and particle sizes between 1 - 80 µm, encompassing the particle sizes observed in this work. The particle sizes of all precipitated solids from Solutions A - E are less than 100 µm and, with the homogeneous nature of the solids, self-shielding of Gd is avoided.[1]

III.F. H:Fissile Material Ratios

A potential processing concern involved loss of agitation in the neutralization tank followed by a period in which the solids begin to settle out of solution. A relationship between the minimum safe Gd:Pu and H:Pu ratios was calculated[5] and, based on the Gd:Pu ratio present in each precipitate, the minimum H:Pu ratio can be determined. In previous Pu-Gd neutralization experiments,[5] the solution contained a 1:1 Pu:Gd ratio and the precipitate had a Pu:Gd ratio of 20:1 at pH 3. At pH 3, the H:Pu ratio in settled solids was 1900:1, well into the safe poison region (> 1500:1 H:Pu) required to ensure nuclear safety. For Solutions D and E, the H:X (X = Pu, U, or fissile) ratios after settling are summarized in Table VI.

The H:Pu analyses in Table VI were used to evaluate a second accident scenario. The water content of centrifuged solids was selected to determine the amount of water remaining in the solids following failure of an agitator and evaporation of water in a tank used during transfer of the slurry to the HLW system. This scenario would not include the addition of heat since there is no heating mechanism to dry the solids in the transfer line or tank. Thus, the centrifuged solids were not dried prior to TGA analysis.

In the absence of Nuclear Criticality Safety Evaluations for the varying compositions of Solutions A-E, the 30:1 H:X ratio, obtained from previous studies,[5] will be used as the minimum H:X ratio for a 1:1 Gd:Pu mass ratio. For solutions containing ^{235}U instead of ^{239}Pu, it is expected that the required H:^{235}U will be lower than that for H:^{239}Pu due to the lower mass deficit and lower neutron energies for ^{235}U.

In the initial Pu-Gd precipitation experiments,[5] centrifuged solids obtained at pH > 14 contained a H:Pu ratio of 150:1. Precipitate obtained from Solution A at pH > 14 with either 1.2 M or 3.6 M excess OH^- had H:Pu ratios of 338:1 and 243:1, respectively.[8,9] Table VII shows the H:Pu, H:U, and H:Fissile ratios for centrifuged solids under selected conditions.

The ratios in Table VII were determined by assuming the solids were $Gd(OH)_3$, $Pu(OH)_4$, and $Na_2U_2O_7$ and represent a conservative value since H atoms in the hydroxides were not included in the calculations. Any boron that might be present in the solution prior to processing was not included in the calculations. The 31:1 H:U ratio at pH 4.5 is essentially at the minimum value; although, the H:Fissile ratio (94:1) is a factor of 3 higher. From a processing perspective, this indicates that 5.16 g/L is nearing the maximum U concentration that can be safely processed with Gd as a neutron poison if there was an agitator failure and drying of the solids in a tank.

IV. CONCLUSIONS

Precipitation experiments were performed on four waste simulant solutions and one actual SRS waste solution to both characterize the systems and determine the precipitation behavior of Pu, U, and Gd. The presence of U and Pu in solution caused Pu to begin precipitation at pH 4.5 instead of pH 3, commensurate with the precipitation behavior of U. The addition of Gd at a 1:1 Gd:Fissile mass ratio was found to be a viable neutron poison for neutralizing solutions containing U:Pu mass ratios up to 4.3:1.

The H:X ratios for two potential accident scenarios were determined. The first scenario involved the loss of agitation and subsequent settling of the solids in a tank. In the event of agitation failure, the H:X ratio in settled solids at pH > 14 was at least 3000:1. If the agitator failure were to occur at pH 4.5, the H:X ratios was at least 5100:1. The second scenario included a tank agitator failure with the solids drying out. The water content of centrifuged solids was used to determine H:Pu:U, H:U, and H:Fissile values. The minimum H:Pu:U, H:U, and H:Fissile ratios for centrifuged solids are 219:1:4.7, 31:1, and 85:1, respectively.

Solutions containing enriched ^{235}U may have a concentration limit where Gd may not be a viable poison when added at a 1:1 mass ratio. Solution E contained 5.16 g/L U and the centrifuged solids contained 31:1 H:U, essentially the same as the minimum 30:1 H:X ratio required for nuclear safety.

The potential cost savings and waste volume reduction associated with disposal of excess fissile material to the SRS HLW system merit further investigation into the behavior of Pu-U-Gd systems upon neutralization. Before solutions containing greater than 4.3:1 U:Pu are poisoned with Gd, neutralized, and vitrified, several questions should be addressed. First, determine whether there is an optimum Pu:U ratio that would keep the solids amorphous and homogeneous. Second, determine the concentration limits for processing U-containing solutions with Gd as a neutron poison. Third, assess the impact that other waste stream components (B and Fe) have on the precipitation, rheology, and settling profile for solutions containing greater than 3:1 U:Pu.

REFERENCES

1. M. G. BRONIKOWSKI, M. L. CROWDER, and M. C. THOMPSON, "Technical Basis for Safe Operations with Pu-239 Polymer in NMS&S Operating Facilities (F & H Areas)," WSRC-TR-99-00008, Savannah River Technology Center, January 1999.

2. C. F. BAES and R. E. MESMER, "The Hydrolysis of Cations," Wiley & Sons: New York, 1976, 176-180.

3. L. M. TOTH, A. FRIEDMAN, and M. M. OSBORNE, "Polymerization of Pu(IV) in Aqueous Nitric Acid Solutions," *J. Inorg. Nucl. Chem.* **43**, 1981, 2929-2935

4. *Handbook of Chemistry and Physics*, 69th Edition, CRC Press: Boca Raton, 1988, B-341.

5. M. G. BRONIKOWSKI, J. H. GRAY, B. C. HILL, F. R. GRAHAM, and D. G. KARRAKER, "Caustic Precipitation of Plutonium Using Gadolinium as the Neutron Poison for Disposition to High Level Waste," WSRC-TR-2002-00198, Savannah River Technology Center, May 2002.

6. T. MOELLER and H. E. KREMERS, "Observations on the Rare Earths: an Electrometric Study of the Precipitation of Trivalent Hydrous Rare Earth Oxides or Hydroxides," *J. Phys. Chem.* **48**, 1944, 395-406.

7. *Handbook of Chemistry and Physics*, 69th Edition, CRC Press: Boca Raton, 1988, D-257.

8. A. E. VISSER, T. S. RUDISILL, and M. G. BRONIKOWSKI, "Investigation of Plutonium and Uranium Precipitation Behavior with Gadolinium as a Neutron Poison," WSRC-TR-2003-00602, Savannah River Technology Center, May 2003.

9. A. E. VISSER, T. S. RUDISILL, and M. G. BRONIKOWSKI, "Investigation of Plutonium and Uranium Precipitation Behavior with Gadolinium as a Neutron Poison," *Sep. Sci. Technol.*, **40**, 2004, In press.

10. M. G. BRONIKOWSKI and T. S. RUDISILL "Neutralization of Plutonium and Enriched Uranium Solutions Containing Gadolinium as a Neutron Poison," WSRC-TR-2004-00053, Savannah River Technology Center, February 2004.

11. D. RAI and J. L. SWANSON, "Properties of Plutonium (IV) Polymer of Environmental Importance," *Nucl. Technol.* **54**, 1981, 107-114.

12. A. G. LEYVA, D. VEGA, V. TRIMACOR, and D. MAR, "Homogeneity Characterization of Sintered $(U,Gd)O_2$ Pellets by X-ray Diffraction," *J. Nucl. Mater.* **303**, 2002, 29-33.

13. H. G. RIELLA, M. DURAZZO, M. HIRATA, R. A. NOGUIERA, "UO_2-Gd_2O_3 Solid Solution Formation From Wet and Dry Processes," *J. Nucl. Mater.* **178**, 1991, 204-211.

14. D. T. HOBBS, "Precipitation of Uranium and Plutonium from Alkaline Salt Solutions," *Nucl. Technol.*, **128**, 1999, 103-112.

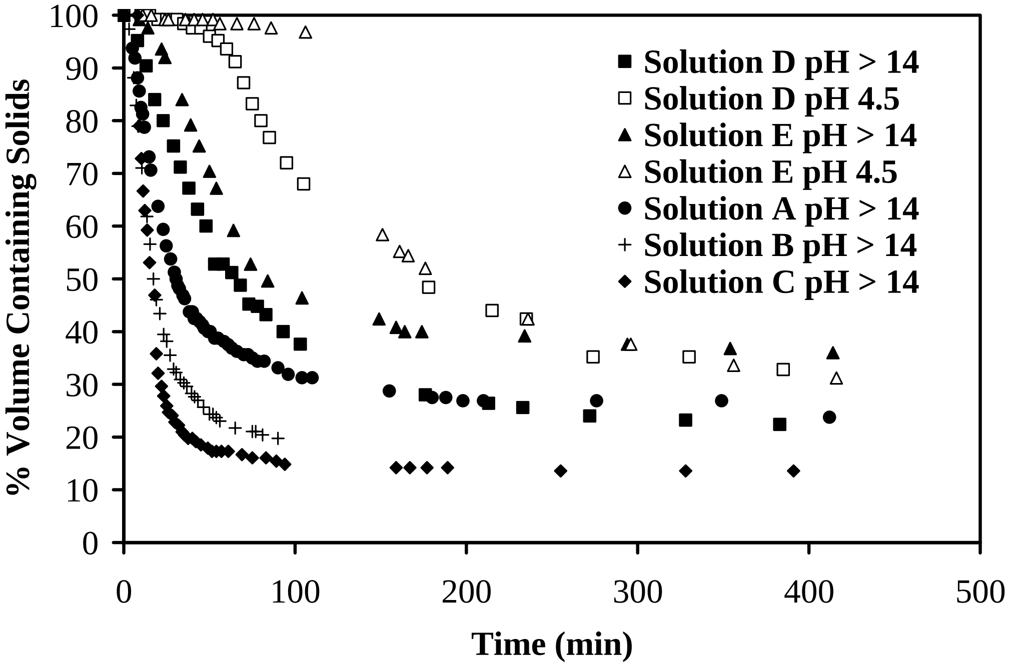
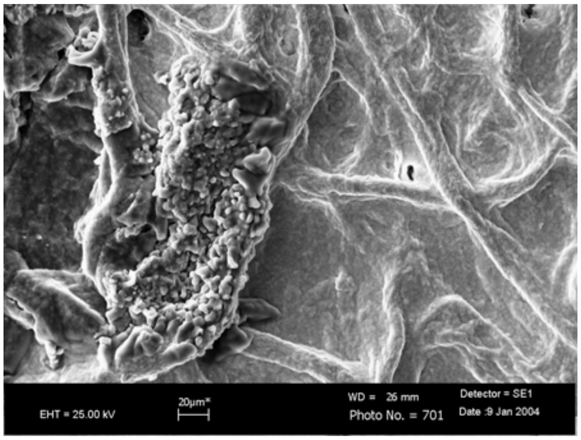
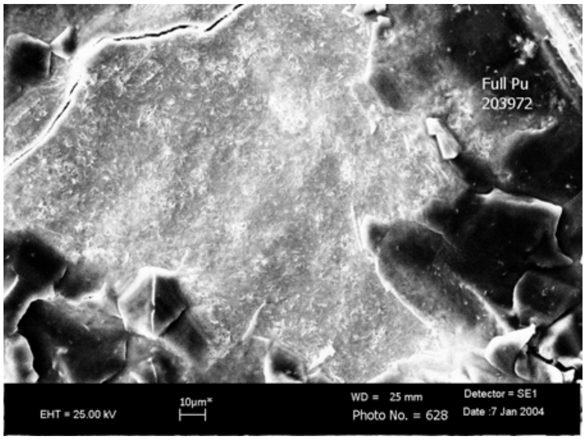


Figure 1: Settling of Solids at pH 4.5 and pH > 14 as a Function of Time

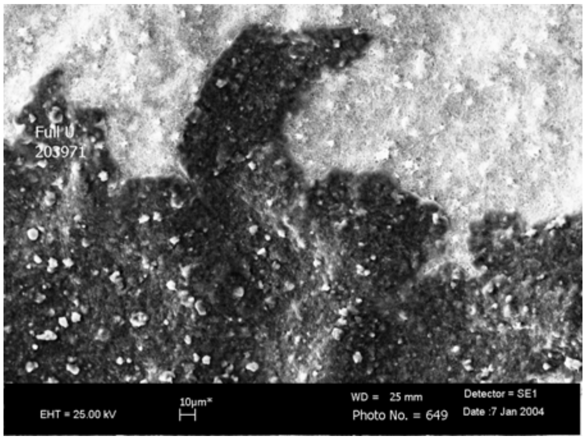


300X at pH 4.5

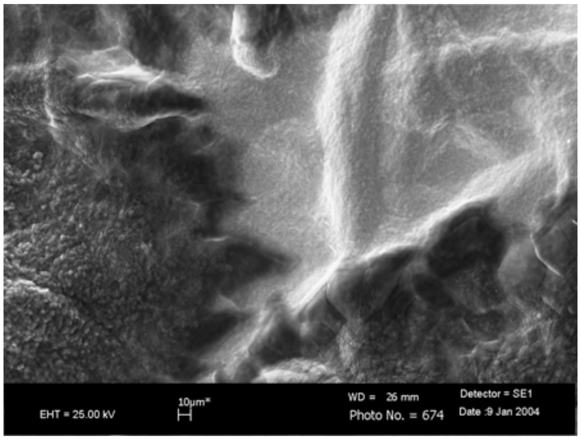


500X at pH > 14

Figure 2: SEM for Solids From Solution D



250X at pH 4.5



300X at pH > 14

Figure 3: SEM for Solids from Solution E

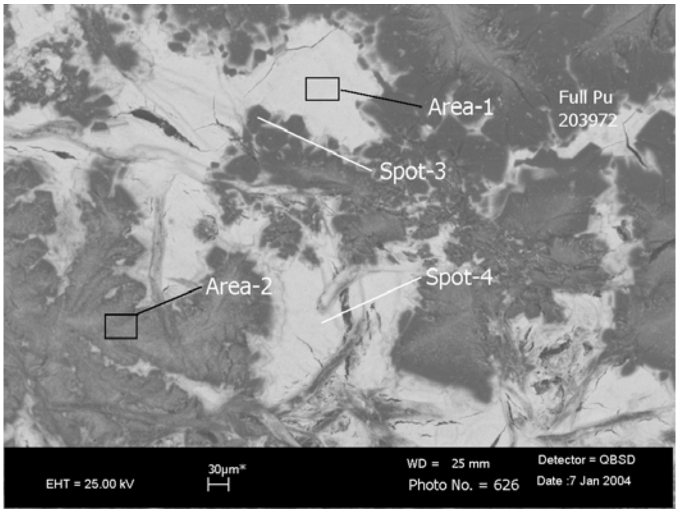


Figure 4: QBSE Spectrum of Solids from Solution D at pH > 14

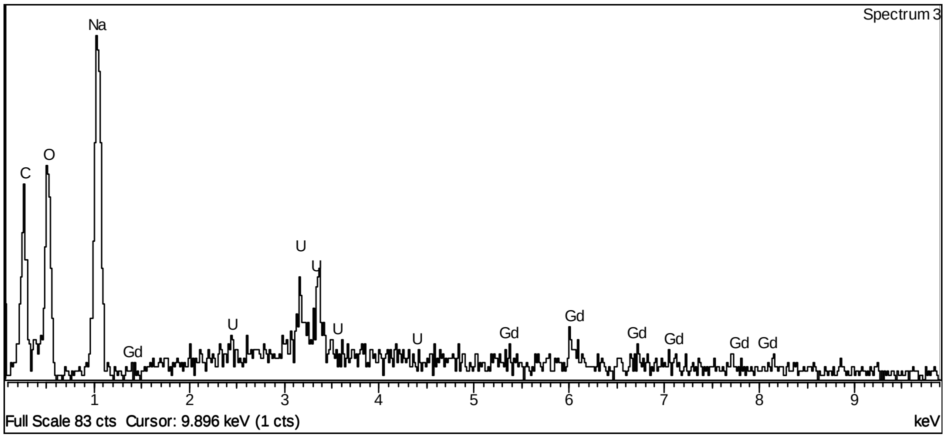


Figure 4a: EDS Analysis of Spot 3 in Figure 4

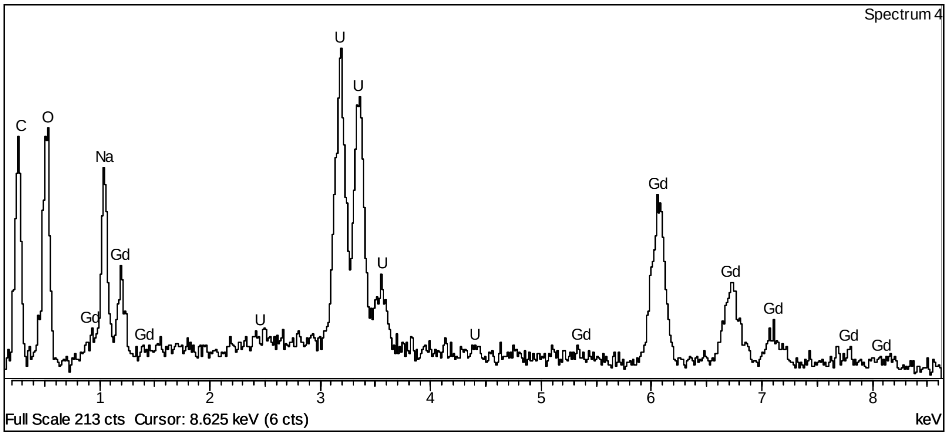


Figure 4b: EDS Analysis of Spot 4 in Figure 4

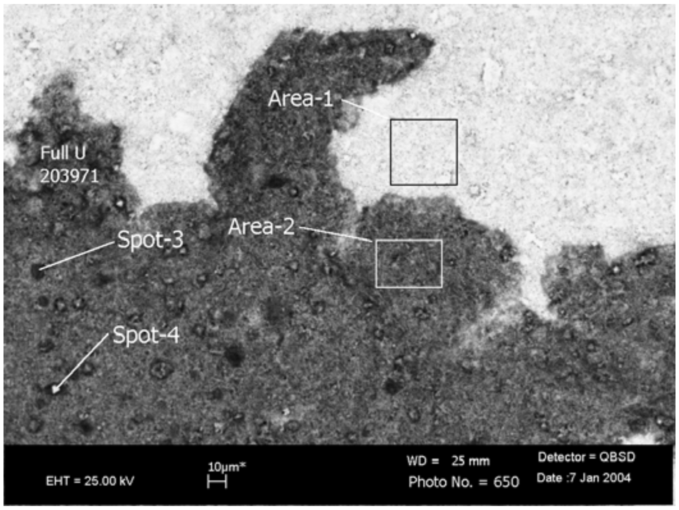


Figure 5: QBSE Spectrum of Solids From Solution E at pH > 14

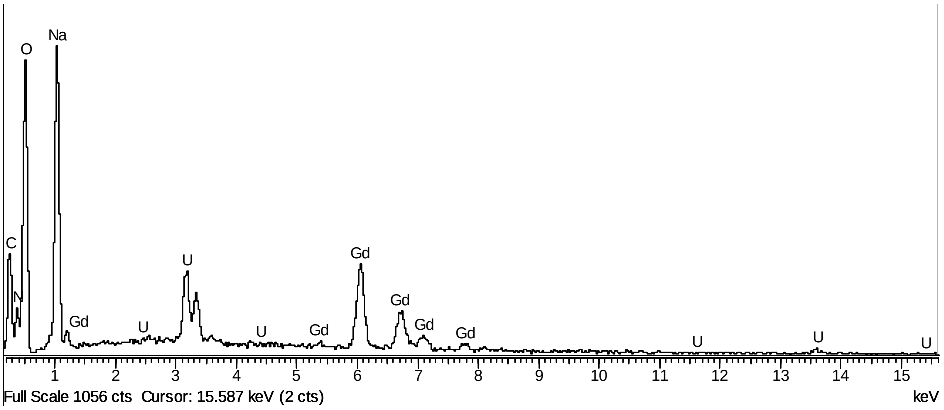


Figure 5a: Analysis of Area 2 in Figure 5

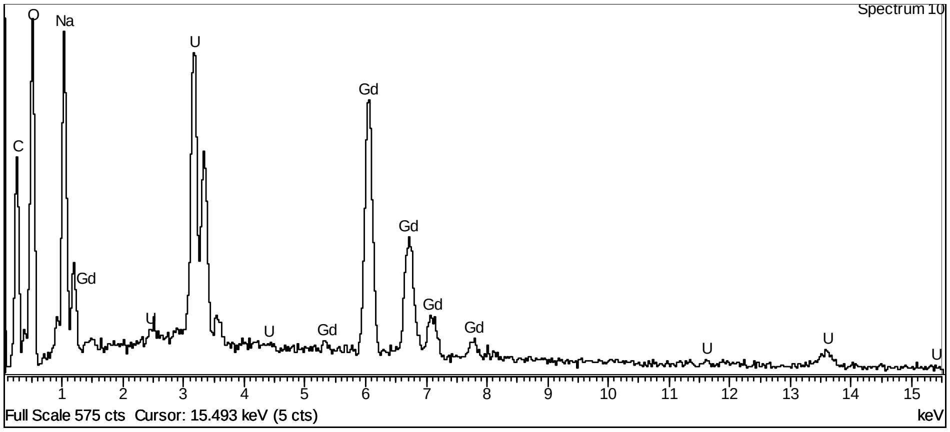


Figure 5b: Analysis of Area 1 in Figure 5

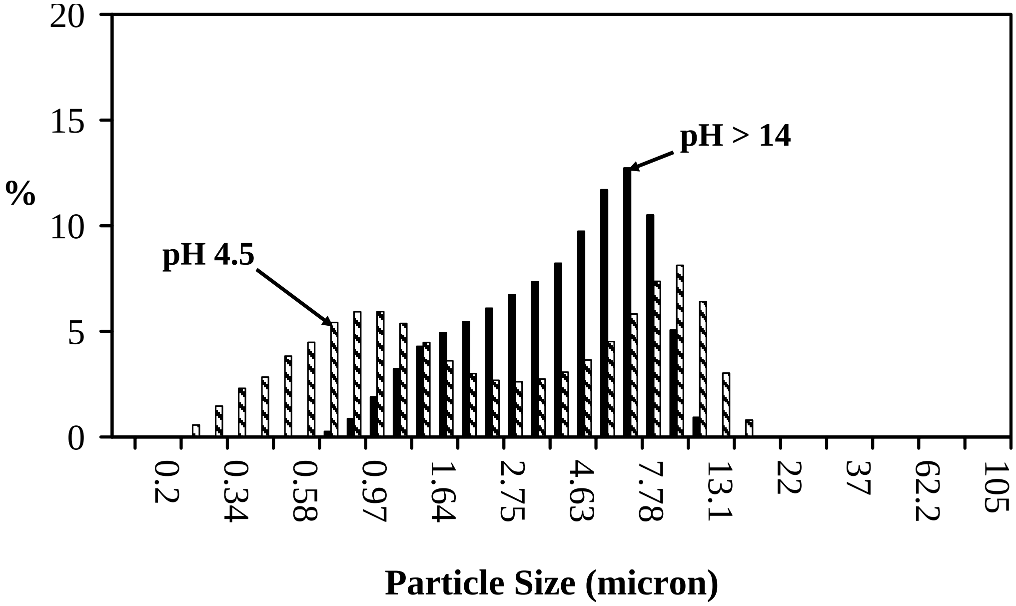


Figure 6: Particle Size Distribution for Solution D, pH 4.5 (hatched boxes) and pH > 14 (black boxes)

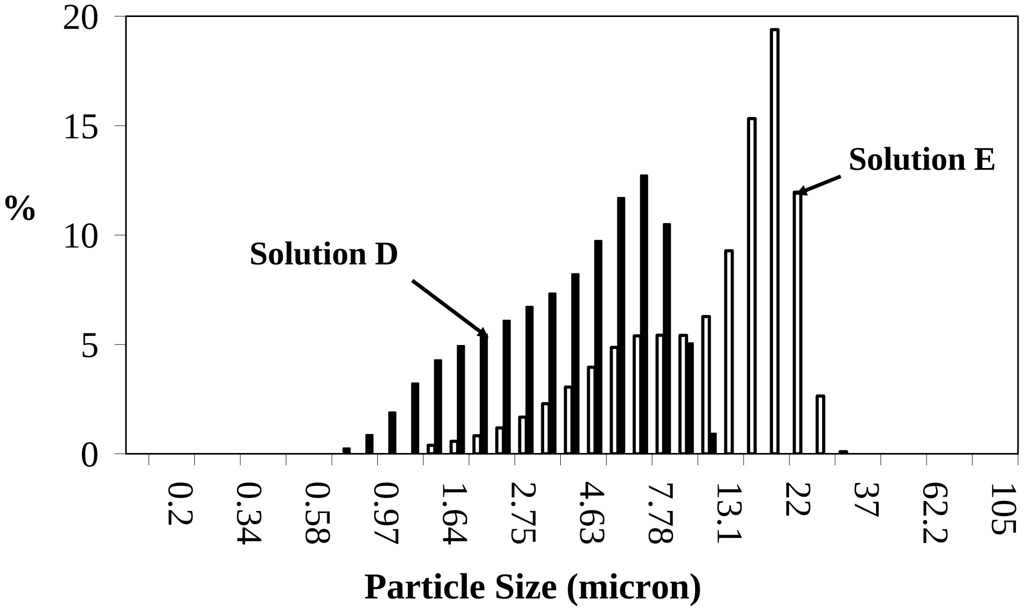


Figure 7: Particle Size Distribution at pH > 14 for Solution D (black boxes) and Solution E (white boxes)

Table I: Composition of H-Canyon and Simulant Solutions

Element	Solution A H-Canyon Solution (g/L)	Solution B 3:1 U:Pu Simulant (g/L)	Solution C 3 g/L U Simulant (g/L)	Solution D 4.3:1 U:Pu Simulant (g/L)	Solution E 5 g/L U Simulant (g/L)
Al	0.161	NA	NA	0.068	NR
B	3.13	2.91	0.007	NA	NA
Gd	1.74	0.968	1.920	1.73	5.71
Pu	1.14	1.02	NA	0.71	NA
U	3.24	2.65	3.01	3.06	5.16

NR = Not resolvable due to Gd interference

NA = Not applicable

Table II: Percent of Each Element Precipitated From Solution

Solution	pH	Pu (%)	U (%)	Gd (%)	B (%)	Al (%)
Solution A	4.5	94.2	53.2	6.0	9.8	1.08
	7	95.4	99.8	99.7	33.7	94.9
	> 14*	99.7	99.9	99.9	7.2	52.0
	> 14+	99.8	99.8	99.5	7.0	1.03
Solution B	> 14*	99.9	99.8	99.9	NA	NA
Solution C	> 14*	NA	99.9	99.9	NA	NA
Solution D	4.5	90.5	92.2	4.4	NA	83.6
	> 14*	99.6	98.9	99.9	NA	0[A]
Solution E	4.5	NA	89.1	3.0	NA	100[A]
	> 14*	NA	99.3	99.8	NA	0[A]

* 1.2M excess NaOH   NA = Not applicable

\+ 3.6M excess NaOH   [A] Not resolvable due to Gd peak interference

Table III: U:Gd and Pu:Gd Ratios vs. pH

Solution	pH	Supernate U:Gd	Solids U:Gd	Supernate Pu:Gd	Solids Pu:Gd	Supernate Fissile[‡]:Gd	Solids Fissile[‡]:Gd
Solution A	4.5	0.736	13.1	0.024	6.10	0.267	10.4
	7	0.970	1.73	5.30	0.521	8.56	0.809
	>14[*]	0.974	1.68	0.890	0.539	4.09	1.01
	>14[+]	4.28	1.72	0.371	0.520	1.77	1.18
Solution B	>14[*]	3.32	2.72	3.02×10^{-2}	1.13	1.18	2.85
Solution C	>14[*]	2.27	1.85	NA	NA	NA	NA
Solution D	4.5	0.127	32.5	3.34×10^{-2}	6.90	7.53×10^{-2}	17.6
	>14[*]	18.5	1.70	1.47	0.349	7.59	0.911
Solution E	4.5	0.986	26.5	NA	NA	3.25×10^{-2}	8.74
	>14[*]	4.32	0.951	NA	NA	1.43	0.314

[*] 1.2 M excess NaOH

[+] 3.6 M excess NaOH

NA = Not applicable

[‡] Assumes 33% ^{235}U and remaining amount is ^{239}Pu

Table IV: Density of pH > 14 Solutions

Solution	pH	Density (g/mL) Supernate	Density (g/mL) Slurry
Solution A	pH > 14[*]	1.299	1.302
	pH > 14[+]	1.322	1.338
Solution B	pH > 14[*]	1.285	1.289
Solution C	pH > 14[*]	1.249	1.247
Solution D	pH > 14[*]	1.158	1.281
Solution E	pH > 14[*]	1.197	1.285

[*] 1.2M excess NaOH

[+] 3.6M excess NaOH

Table V: Viscosity for pH > 14 Slurries

Solution	pH	Viscosity (cP)
Solution A	pH > 14*	3.12
	pH > 14+	4.54
Solution B	pH > 14*	2.21
Solution C	pH > 14*	2.43

[*] 1.2M NaOH excess
[+] 3.6M NaOH excess

Table VI: H:X Ratio in Settled Solids After One Day

Solution	pH	H:Pu	H:U	H:Fissile
D	4.5	12500:1	2800:1	5100:1
	>14	7400:1	1700:1	3000:1
E	> 14	NA	> 1700:1	5800:1

NA = Not applicable

Table VII: H:X Ratios in Centrifuged Solids

Solution	pH	H:Pu	H:U	H:Fissile
D	4.5	219:1	46:1	85:1
	>14	370:1	76:1	141:1
E	4.5	NA	31:1	94:1
	> 14	NA	126:1	382:1

NA = Not Applicable

List of Figure Captions

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