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INVESTIGATION OF PLUTONIUM AND URANIUM PRECIPITATION BEHAVIOR WITH GADOLINIUM AS A NEUTRON POISON

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ABSTRACT

The caustic precipitation of plutonium (Pu)-containing solutions has been investigated to determine whether the presence of 3:1 uranium (U):Pu in solutions stored in the H-Canyon Facility at the U.S. Department of Energy's (DOE) Savannah River Site (SRS) would adversely impact the use of gadolinium nitrate ($Gd(NO_3)_3$) as a neutron poison. In the past, this disposition strategy has been successfully used to discard solutions containing approximately 100 kg of Pu to the SRS high level waste (HLW) system. In the current experiments, gadolinium (as $Gd(NO_3)_3$) was added to samples of a 3:1 U:Pu solution, a surrogate 3 g/L U solution, and a surrogate 3 g/L U with 1 g/L Pu solution. A series of experiments was then performed to observe and characterize the precipitate at selected pH values. Solids formed at pH 4.5 and were found to contain at least 50% of the U and 94% of the Pu, but only 6% of the Gd. As the pH of the solution increased (e.g., pH > 14 with 1.2 or 3.6 M sodium hydroxide (NaOH) excess), the precipitate contained greater than 99% of the Pu, U, and Gd. After the pH > 14 systems were undisturbed for one week, no significant changes were found in the composition of the solid or supernate for each sample. The solids were characterized by X-ray diffraction (XRD) which found sodium diuranate ($Na_2U_2O_7$) and gadolinium hydroxide ($Gd(OH)_3$) at pH 14. Thermal gravimetric analysis (TGA) indicated sufficient water molecules were present in the solids to thermalize the neutrons, a requirement for the use of Gd as a neutron poison. Scanning electron microscopy (SEM) was also performed and the accompanying back-scattering electron analysis

(BSE) found Pu, U, and Gd compounds in all pH > 14 precipitate samples. The rheological properties of the slurries at pH > 14 were also investigated by performing precipitate settling rate studies and measuring the viscosity and density of the materials. Based on the results of these experiments, poisoning the Pu-U solutions with Gd and subsequent neutralization is a viable process for discarding the Pu to the SRS HLW system.

INTRODUCTION

Current missions at SRS involve the dissolution of materials containing quantities of Pu which are in excess of the DOE needs. For solutions containing Pu with isotopic concentrations which meet specifications for mixed oxide (MOX) fuel, the Pu is dispositioned by conversion to plutonium oxide and stored for subsequent fuel fabrication. In recent campaigns, Pu-containing solutions which did not meet fuel specifications were poisoned with Gd under caustic conditions and relegated to the SRS HLW system for subsequent vitrification in the Defense Waste Processing Facility [1]. Approximately 35 kg of Pu which do not meet fuel criteria are currently stored in solution in the SRS H-Canyon Facility. These solutions contain 1 g/L Pu (88% ^{239}Pu and 12% ^{240}Pu) and 3 g/L U (0.8% ^{235}U) in 5M nitric acid (HNO_3). Poisoning these solutions through the addition of $Gd(NO_3)_3$, addition of NaOH to pH >14 and 1.2M excess hydroxide (OH^-), and transfer to the HLW system was proposed as the disposition path for these solutions.

Treatment of solutions containing significant quantities of fissile material and subsequent transfer to the SRS HLW system is accomplished with the addition of a neutron poison to ensure nuclear safety. Depleted U, iron (Fe), and manganese (Mn) have been used to poison SRS process solutions prior to discarding to the HLW system. To process the Pu at greater than a fissile mass and minimize the amount of glass logs produced, the required ratio of U:^{239}Pu and Fe:^{239}Pu in the precipitate is 198:1 and 160:1 by mass, respectively. Large amounts of Mn and Fe can also cause processing problems (i.e., production of metal hydroxides that are difficult to transfer) during the manufacturing of the glass. Gadolinium is the preferred poison for use when a large amount of Pu is being discarded because Gd is very effective in capturing thermal neutrons and, thus, only a small amount of the poison is necessary. The minimum hydrogen (H):Pu ratio was established by a Nuclear Criticality Safety Evaluation. The presence of a sufficient number of water molecules (i.e., H atoms) associated with the Pu-Gd co-precipitate is crucial because Gd is an effective absorber of thermal neutrons, but is less effective as an absorber of fast neutrons. The H atoms act to thermalize the fast neutrons. By adding only a small amount of Gd to the solution, transfer of the slurry is facilitated, and the formation of large amounts of hydroxides is minimized. In addition, the use of Gd allows an increase in the Pu concentration in the HLW glass without increasing the amount of glass produced.

In a caustic environment, Pu will precipitate and form polymeric materials or hydroxides [2,3] and uranyl (UO_2^{2+}) precipitates as a complex solid (e.g., $Na_2U_2O_7$) [2]. When Gd is present in solution prior to Pu precipitation, the co-precipitate will contain an intimate mixture of Gd and Pu, both likely present as hydroxides [1]. However, there remains a minimal amount of information regarding characterization and precipitation behavior of Pu-U-Gd in caustic media.

In the past, when Pu-containing solutions were poisoned with Gd, the pH adjusted to > 14, and discarded to the HLW system, the solutions contained very little U [1]. It was hypothesized that, despite the presence of 3 g/L U in solution with Pu, caustic precipitation of Pu with Gd as a neutron poison would remain a viable process for the treatment of this material. There are literature reports of precipitation in U-Gd systems and the poisoning behavior of Gd in solution with Pu. The U-Gd precipitates from the nitrate [4,5] and carbonate [6] salts were not examined and, instead, were heated to form the oxides. Poisoning of Pu with Gd [7] was performed in the presence of 4.1 M HNO_3 with no precipitation observed, despite maximum concentrations of 363 g/L Pu and 20 g/L Gd.

The goal of the experiments performed and discussed in the following sections was to determine if the presence of a 3:1 ratio of U to Pu in these solutions would have a detrimental effect (e.g., Gd would no longer precipitate homogeneously with Pu) on caustic precipitation and if Gd could be used as a poison in this system.

EXPERIMENTAL

Precipitation and Sampling

Caustic precipitation experiments were performed using 25 mL aliquots from a sample of the 3:1 H-Canyon solution. The solution composition for elements of interest is summarized in Table 1. Neutralization experiments were also performed using 40 mL of surrogate solutions containing 3 g/L U or 3 g/L U with 1 g/L Pu. 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. Unless otherwise specified, all experiments were performed at ambient temperature.

To ensure a consistent Gd^{3+} concentration in each experiment, a specific volume of 30 wt% $Gd(NO_3)_3$ solution was added to the 100 mL bottle containing the 1:3 Pu:U H-Canyon solution. A 1:1 Pu:Gd mass ratio was targeted although the final ratio was 1:1.5. An appropriate volume of the 30 wt% $Gd(NO_3)_3$ solution was also added to the 3 g/L U surrogate and the 3 g/L U with 1 g/L Pu surrogate solution targeting 3:1 U:Gd and 1:3:1 Pu:U:Gd ratios. The actual ratios for the surrogate solutions were approximately 1.6:1 U:Gd (U surrogate) and 1:2.74:1.05 Pu:U:Gd (Pu-U surrogate).

The H-Canyon solution was transferred to 100 mL beakers using a graduated cylinder; a 5 mL pipette was used for the surrogate solutions to improve volume control. Each sample was neutralized to the desired endpoint (Table 2) by the drop-wise addition of 50 wt% NaOH using a volumetric burette in aliquots such that the temperature of the solutions did not exceed 50^oC. The solutions were stirred using a magnetic stirring bar. 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 2-3 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 5 minutes. Using two of the centrifuge tubes, aliquots of sufficient volume were removed from the supernate for ^{238}Pu and $^{239/240}Pu$ analysis (by thenolyltrifluoroacetone (TTA) extraction). Americium-241 (^{241}Am) and ^{241}Pu were analyzed by gamma pulse height analysis (PHA). The concentrations of U, boron (B), and Gd were obtained by inductively coupled plasma emission spectroscopy (ICP-ES). For each ICP-ES analysis, a 1 mL aliquot of the supernate or dissolved solids was diluted (1:9) with deionized water. The remaining supernate was then removed from the centrifuge tubes and the precipitate dissolved in 1 mL of 8M HNO_3. The aqueous phase was subsequently removed from the two remaining centrifuge tubes and a small amount of the precipitate was analyzed by XRD and SEM.

After the initial sampling, the beakers were covered with Parafilm M™ and allowed to stand for one week (without stirring). After resuspending the solids to form the slurry, the sampling routine was repeated and a set of samples was analyzed as described above.

Density

The approximate densities of the supernate and precipitate slurry from the solutions neutralized beyond pH 14 were determined gravimetrically. A 1 mL pipet was used to transfer an aliquot of the unmixed supernate to a pre-weighed 1 dram vial and the mass measured. Then, while the solution was being stirred and the solids were resuspended, 1 mL of the slurry mixture was removed and transferred to a pre-weighed 1 dram vial to determine the density of the mixture.

Settling Experiments

Each solution neutralized beyond pH 14 was subjected to settling experiments where the solutions in each beaker were stirred and approximately 16 mL of each solution were transferred to a 25 mL graduated cylinder. The solids were allowed to settle as time progressed and the volume corresponding to the top of the solids in the graduated cylinder was recorded.

Viscosity

A calibration curve for the viscosity experiments was established using 15 mL of a series of NaOH solutions (0.5 – 10M) of known viscosity [9] and deionized water. The solutions were passed through a standard glass condenser coil (the condenser coil or "racetrack" 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. 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 racetrack. 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.

TGA

The amount of water present in the precipitate was determined by TGA. Samples (5 – 25 mg) for analysis were removed from each solution neutralized beyond pH 14 after thorough mixing, transferred to a centrifuge tube, capped, and allowed to settle for several days. The samples were then centrifuged (5000 *g* for five minutes) and the supernate removed. The solids were removed from the sealed tubes just prior to analysis. A 10 ^{o}C/min linear heating rate was used for the duration of each run. A platinum sample pan was used and nitrogen was the flow gas.

Previous results with calcium oxalate (a TGA standard used to determine H_2O and CO_2) revealed that waters of hydration are typically removed between 150 – 200 ^{o}C [1]. Using the difference in the weight of the initial sample compared to the weight of the sample at 250^{o}C allowed the calculation of H:Pu ratios [1].

RESULTS AND DISCUSSION

Visual Observations

Prior to any treatment, the initial H-Canyon solution was light yellow-brown in color and transparent with no observable particulate matter. As NaOH was added, the solution became more orange-brown and solids were briefly observed in solution from pH 3.5 – 4.5. At pH 4.5, the solids did not redissolve and, after the mixed solution was sampled and centrifuged for five minutes, the supernate was light yellow and the precipitate was yellow-orange. The solids were approximately 10% (by volume) in each beaker. When additional NaOH was added to the H-Canyon solution to reach pH 7, the amount of solids in the bottom of the centrifuge vials appeared to be greater than at pH 4.5. At pH > 14 with either 1.2 or 3.6 M excess OH^-, there was no observable color in the supernate and the precipitate was an orange-brown color.

After the solution was allowed to stand for one week and the stirring was resumed, the solids were easily dispersed into solution in a manner similar to the previous studies [1].

pH Tests

In the neutralization experiments, the most significant difference in the precipitate behavior from the Pu-Gd experiments [1] was the onset of precipitation at pH 4.5 instead of pH 3. The precipitation of solids at the higher pH is consistent with the behavior of U solutions [2]. The termination of the Pu polymer chain by UO_2^{2+} would reduce the amount of precipitate at lower pHs, allowing Pu to remain in solution until U began to precipitate. Figure 1 shows the precipitated solutions at the specified pH values. Table 3 shows the behavior of U-Gd and Pu-Gd in these experiments as mass ratios. As expected at pH 4.5, much of the Gd remained in solution while the majority of the U and Pu precipitated, the ratios for U/Gd and Pu/Gd for the solids were significantly greater than one. If, during processing, a mechanical failure were to stop the addition of NaOH before pH 7 were attained, the presence of water (H is also a neutron poison) would be necessary to prevent a criticality event. Although only a fraction of the Gd is present in the precipitate at pH 4.5, the H:Pu ratio is sufficient (at least 30:1 H:Pu) to avoid a criticality incident [1]. In the previous studies where the Gd:Pu ratios were designed to be 1:1, the precipitate contained 1:20 (Gd:Pu) at pH 3 [1]. Here, the presence of U in solution increases the ratio to 1:6.1 (Gd:Pu) at pH 4.5.

Table 4 summarizes the behavior of the elements of interest as a function of pH. At pH 4.5, only 6% of the Gd precipitated, however, this value is essentially the same as the 5% measured at pH

3 in the previous studies [1]. Both U and Pu begin to precipitate under these slightly acidic conditions and some boron (B) is also present in the non-crystalline precipitates. Boron is a nuclear poison and is also used at SRS to poison some dissolver and Pu solutions. In these experiments, its presence is beneficial from a poisoning aspect; however, its presence is not required. At pH 7, at least 95% of the Gd, U, and Pu are removed from solution. At pH > 14, greater than 99% of Pu, U, and Gd were found in the precipitated solids. Based on these results and as long as the solids are homogeneous, poisoning the Pu-U solutions with Gd and subsequent neutralization is a viable means for discarding the Pu to the HLW system.

After one week, analysis of the solids revealed no significant changes in their mass ratios. Thus, short-term storage of the precipitate slurry is possible and the integrity of the solids would be maintained even if left in contact with the aqueous phase.

Density and Settling

The density (Table 5) of each solution neutralized to greater than pH 14 was measured to characterize the supernate and the supernate/solids mixture. The settling rate of the solids (Figure 2) was also measured to determine how the solution would behave if, during processing or transfer, agitation of the solution was stopped for a period of time. The densities of the phases in each system are close to that of 1 M NaOH. The slight differences in the density of the supernate and the solid-supernate mixture suggest that the solids would not immediately settle out of solution and the mixtures could be easily re-suspended and transferred. In both the U surrogate and the H-Canyon surrogate solutions, the absence of B and other salts decreases the density of both the supernate and the mixed phases.

The density data combined with the results in Figure 2 indicate that the difference in density between the supernate and the solid-supernate mixture had little effect on the settling time for solids formed from the H-Canyon solutions at pH > 14 with excess OH^-. Despite the small difference in density for the U surrogate solution phases, the solids settled out of that solution at a relatively rapid rate. It took ~250 minutes for the solids in both H-Canyon solutions to settle to one-quarter of the initial volume. However, it took only 25 minutes for the solids in the U surrogate solution to settle to one-quarter of the initial volume. As expected, the final volume of the settled solids depends on the amount of total metal ions in solution [9], although certain metal ions (e.g., B) may be especially important. The H-Canyon solutions contained B and settled more slowly and resulted in a larger settled solids volume in comparison to both surrogate solutions. Hobbs reported settling times of > 12 days for caustic HLW simulant solutions containing U and Pu with a total metal ion concentration between 11 - 49 g/L [9].

Viscosity

The apparent viscosity for each pH > 14 mixture containing supernate and solids was determined using the calibration curve developed from the viscosity of NaOH solutions using the "racetrack" apparatus. The racetrack is the spiral glass tubing removed from the inside of a standard laboratory condenser and is used at SRS to check solution transport properties. The solution is poured into the top of the coil and the elapsed time before the solution exits the bottom of the 28 cm long coil is related to the viscosity. The results are summarized in Table 6.

In each case, the presence of a significant amount of solids in the solution did not obstruct the flow of the mixture through the 0.6 cm inner diameter coil. (After each run, some solution was retained along the bottom of each turn throughout the length of the condenser, but this residual amount did not build up during triplicate runs.) The increase in the salt concentration from 1.2 M OH^- to 3.6 M OH^- resulted in an expected increase in the viscosity, although the effect was small. For comparison, the viscosities of both H-Canyon solutions and both surrogate solutions are similar to that of 4 – 6 M NaOH solutions [8].

SEM and XRD

Figure 3 shows SEM, BSE, and an energy dispersive spectrum (EDS) for a selected spot for solids from each sample. XRD analyses of the solids obtained from these precipitation experiments reveal a variety of solids. At pH 4.5, the solids were amorphous with crystalline sodium nitrate ($NaNO_3$) on top.

The EDS have broad areas of Pu-U-Gd and U-Gd, but no specific Pu particles. This analysis agrees with the results from the XRD analysis for the initial samples where few crystal structures were found, which would occur in samples containing amorphous solids or < 10 μm crystals. At pH 4.5, the solids contained an abundance of Pu and U with small amounts of iron (Fe). Although only 6% of Gd precipitated at pH 4.5, no Gd is detected in the EDS for this spot of the sample. At pH 7 and pH > 14 (for both 1.2 and 3.6 M excess OH^-), Pu, U, Fe, and Gd were all detected in the solids.

Analysis of the XRD results revealed that at 3.6 M excess OH^-, U was present in the solids in the form of $Na_2U_2O_7$. After one week, uranium dioxide (UO_2) and clarkeite ($Na[(UO_2)O](OH)\cdot H_2O$) were also found in the solids. Clarkeite was present at pH 4.5. In addition to clarkeite, $NaNO_3$, sodium carbonate (Na_2CO_3), and $Gd(OH)_3$ were detected in the solids obtained from the U surrogate solution. No crystalline compounds containing Pu or Gd were detected by XRD in any precipitate obtained from H-Canyon solutions. In the previous studies [1], an amorphous material was produced, likely due to the formation of hydroxides. The x-ray diffraction pattern from the amorphous material after it was heated could be fit to plutonium oxide (PuO_2) and gadolinium oxide (Gd_2O_3), although the Pu and Gd were so closely associated that the x-ray patterns could not be uniquely assigned.

TGA

The solutions neutralized to pH > 14 were analyzed by TGA to determine the number of water molecules associated with the solids and, ultimately, the ratio of H atoms to Pu atoms. Bronikowski et al., performed similar analyses on Pu-Gd precipitates and the resulting H:Pu ratio was 150:1 [1]. The minimum H:Pu ratio for use of Gd as a neutron poison at a 1:1 Pu:Gd weight ratio was 30:1 H:Pu.

The H-Canyon samples neutralized to 1.2 or 3.6 M excess OH^- had H:Pu ratios of 483:1 and 343:1, respectively. Thus, the H:Pu ratios here are at least two times greater in comparison to the previous results [1]. The loss of water from precipitated U mineral phases has been observed for different systems and quantitated by TGA up to 450 ^{o}C [10]. The U in the co-precipitate from the H-Canyon solution likely has associated waters of hydration which account for the increased H content in the solids in comparison to the H:Pu precipitate.

CONCLUSIONS

Small-scale precipitation experiments were performed to assess the behavior of Pu-U solutions from H-Canyon after the addition of Gd, pH adjustment with NaOH, and precipitation. These experiments confirmed that Gd co-precipitates with Pu and U and, thus, is a viable poison for dispositioning these solutions to the SRS HLW system. The presence of three times more U than Pu caused a sample of the H-Canyon solution to precipitate at pH 4.5 which is consistent with the behavior of uranium solutions. At this pH, 6% of the Gd was found in the precipitate solids. This value is essentially the same as the 5% measured at pH 3 in previous studies on Pu-Gd solutions. At pH 7, at least 95% of the Gd, U, and Pu were removed from solution. Upon complete neutralization (to 1.2 and 3.6M excess OH^-), greater than 99% of these elements was found in the precipitated solids.

Thermal gravimetric analysis of centrifuged solids indicated the ratio of H (from water) to Pu was 343:1 following neutralization to 3.6 M excess OH^- and 483:1 following neutralization to 1.2 M excess OH^-. These values greatly exceed the minimum H:Pu ratio of 30:1 required for the use of Gd as a neutron poison. Rheological properties of the precipitate slurry were also evaluated following adjustment to pH > 14. After one week without agitation, the precipitate solids were easily re-suspended in the supernate and settled to approximately 25% of the total volume in approximately 250 minutes. The apparent viscosity of the slurry at pH > 14 with 1.2M excess OH^- was equivalent to 4-6M NaOH; therefore, no problems in transferring the precipitate slurry to the waste tanks are anticipated.

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Table 1: Composition of 3:1 U:Pu Solution

Element	Concentration (mg/L)(1)
Al	161
B	3130
Fe	177
Gd(2)	1740
Na	64.5
$^{239/240}$Pu	1140
U	3240

(1) Savannah River Technology Center analysis.
(2) Added as a 30 wt.% $Gd(NO_3)_3$ solution.

Table 2: pH Adjustment of H-Canyon Samples

Sample ID	50% (wt.) NaOH Added (mL)	Volume of Solution Neutralized (mL)
pH 4.5⁽¹⁾	8.2	25
pH 7	8.1	25
pH 14 (1.2 M OH^-)	10.2	25
pH 14 (3.6 M OH^-)	13.9	25
U-surrogate (pH 14 & 1.2 M OH^-)	14.0	40
Tank 12.1 Surrogate (pH 14 & 1.2M OH^-)	14.0	40

(1) Tank 12.1 solution added with a graduated cylinder

Table 3: U/Gd and Pu/Gd Ratios vs. pH of H-Canyon Solution

Sample	Supernate U/Gd (mg/mg)	Solids U/Gd (mg/mg)	Supernate Pu/Gd (mg/mg)	Solids Pu/Gd (mg/mg)
pH 4.5	0.736	13.046	0.024	6.102
pH 7	(9.860)	1.734	(5.304)	0.521
pH 14 (1.2 M OH^-)	(0.974)	1.679	(0.890)	0.539
pH 14 (3.6 M OH^-)	(4.283)	1.723	0.371	0.520
U Surrogate (pH 14 & 1.2M OH^-)	(2.270)	1.847	na	na
Tank 12.1 Surrogate (pH 14 & 1.2 M OH^-)	3.318	2.723	0.030	1.125
After One Week				
pH 4.5	0.674	9.078	0.012	4.612
pH 7	17.549	1.592	3.177	0.544
pH 14 (1.2 M OH^-)	(8.380)	1.727	0.628	0.513
pH 14 (3.6 M OH^-)	3.764	1.695	0.194	0.523
U Surrogate (pH 14 & 1.2M OH^-)	(9.740)	1.509	na	na
Tank 12.1 Surrogate (pH 14 & 1.2M OH^-)	3.318	2.729	0.066	1.435

na = not applicable to sample

Results in parentheses include calculations on data below limit of detection for that element.

Table 4: % (Element in Precipitate/Element in Initial Solution) at each pH

Initial Sample	% Gd	% U	% Pu	% B
pH 4.5	6.0	53.2	94.2	9.8
pH 7	99.7	99.8	95.4	33.7
pH 14 (1.2 M OH^-)	99.9	99.9	99.7	7.2
pH 14 (3.6 M OH^-)	99.5	99.8	99.8	7.0
U Surrogate (pH 14 & 1.2M OH^-)	99.9	99.8	na	na
Tank 12.1 Surrogate (pH 14 & 1.2 M OH^-)	99.9	99.9	99.9	na
After One Week				
pH 4.5	9.8	59.6	97.8	13.9
pH 7	99.2	91.6	99.5	37.7
pH 14 (1.2 M OH^-)	99.9	99.9	99.5	7.3
pH 14 (3.6 M OH^-)	99.7	99.2	99.9	6.3
U Surrogate (pH 14 & 1.2M OH^-)	99.9	99.5	na	na
Tank 12.1 Surrogate (pH 14 & 1.2M OH^-)	99.9	99.9	99.9	na

na = not applicable to this sample

Table 5: Density of pH 14 Solutions

Sample	Density (g/mL) Supernate	Density (g/mL) Supernate and Solids
pH 14 (1.2 M OH^-)	1.299	1.302
pH 14 (3.6 M OH^-)	1.322	1.338
pH 14 U surrogate (1.2 M OH^-)	1.249	1.247
Tank 12.1 Surrogate (pH 14 & 1.2 M OH^-)	1.285	1.289

[*] volume of solids in the cylinder, initial mixture volume between 15.9 – 16.2 mL

Table 6: Viscosity (cP) for pH 14 H-Canyon and Surrogate Solutions

Sample	Calculated Viscosity (cP)
pH 14 (1.2 M OH^-)	3.12
pH 14 (3.6 M OH^-)	4.54
U Surrogate (pH 14 & 1.2 M OH^-)	2.43
Tank 12.1 Surrogate (pH 14 & 1.2 M OH^-)	2.21

pH 4.5

pH 7

pH 14
(1.2 M OH^-)

pH 14
(3.6 M OH^-)

pH 14 U
Surrogate

pH 14
Tank 12.1
Surrogate

Figure 1: 12.1 Solutions at Specific pH

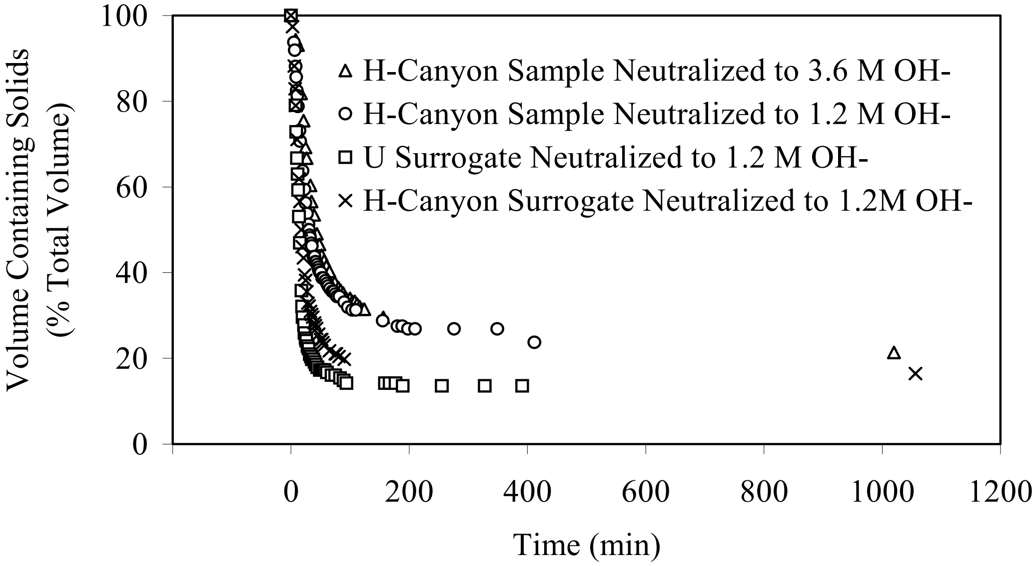
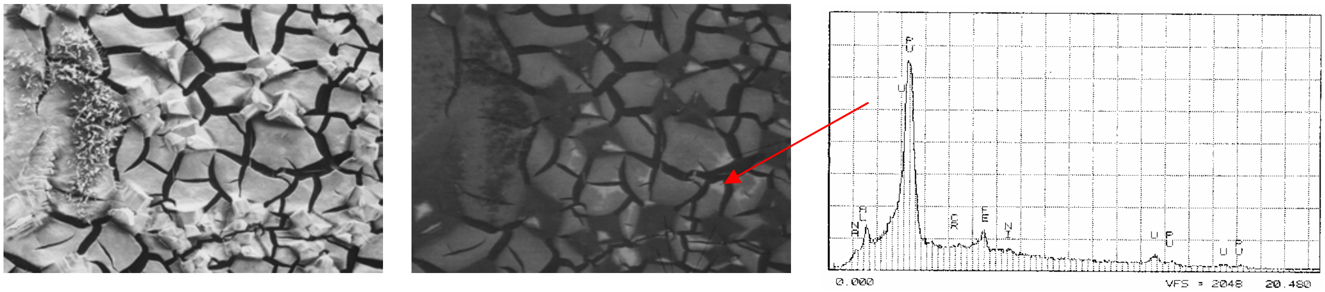
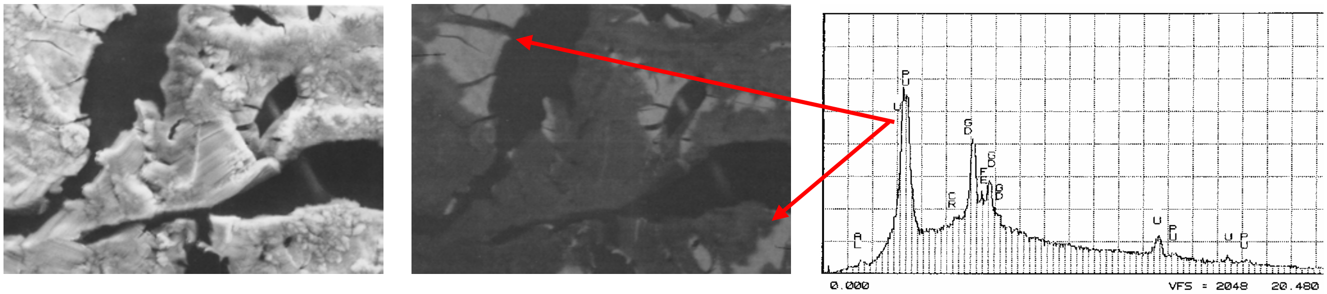


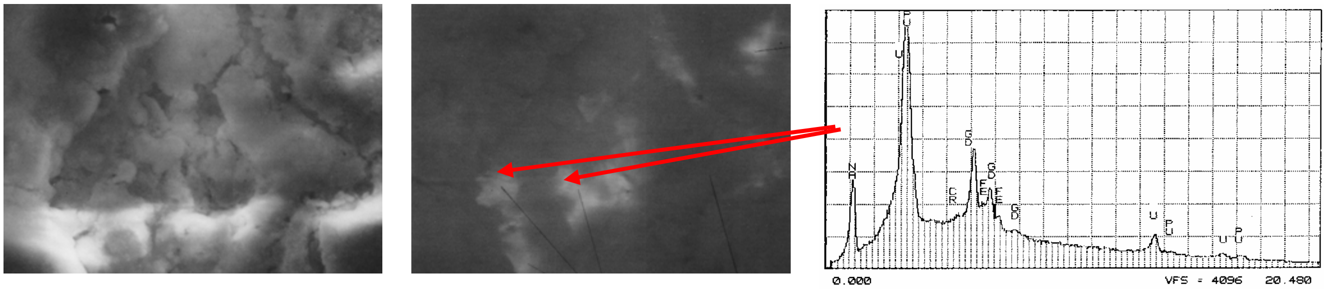
Figure 2: Settling of Solids in pH > 14 H-Canyon Solutions (1.2 M OH^- and 3.6 M OH^-) and pH > 14 Surrogate Solutions as a Function of Time.



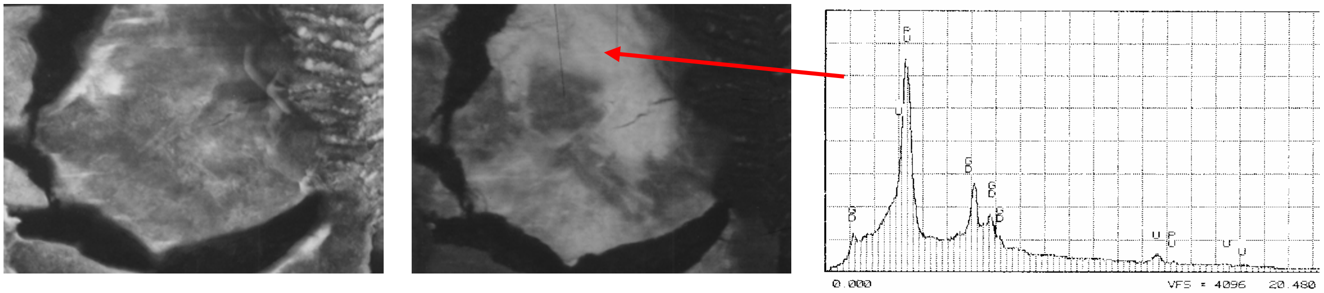
SEM pH 4.5 (500X) BSE pH 4.5 (500X) EDS pH 4.5



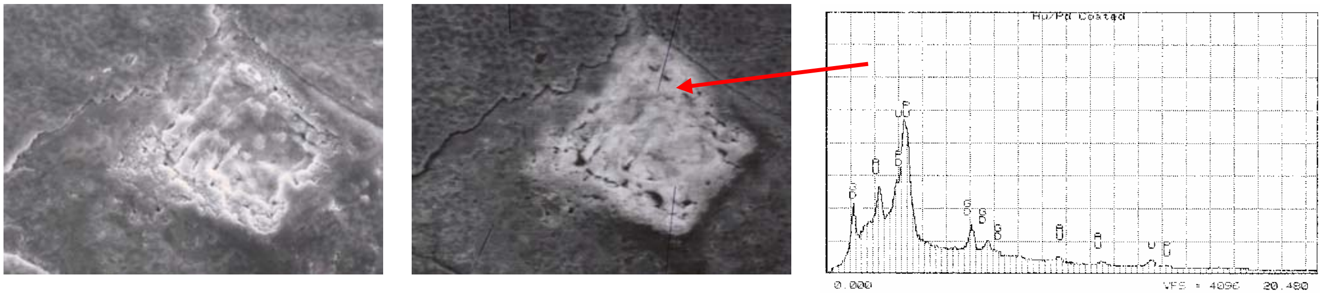
SEM pH 7 (50X) BSE pH 7 (50X) EDS pH 7



SEM pH 14, 3.6 M (1000X) BSE pH 14, 3.6 M (1000X) EDS pH 14, 3.6 M OH$^-$



SEM pH 14, 1.2 M (500X) BSE pH 14, 1.2 M (500X) EDS pH 14, 1.2 M OH$^-$



SEM Tk. 12.1 Surr. (500X) BSE Tk. 12.1 Surr. (500X) EDS Tk. 12.1 Surr.

Figure 3: SEM, BSE, and EDS of precipitates from solutions adjusted to the specified pH