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Caustic Precipitation of Plutonium using Gadolinium as the Neutron Poison for Disposition to High Level Waste (U)

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Acronyms and Definitions

2BP	plutonium nitrate product stream from the PUREX process
DOE	U S Department of Energy
DWPF	Defense Waste Processing Facility
Dpm	disintegrations per minute
HLW	High Level Waste
ICP-ES	Inductively Coupled Plasma-Emission Spectrometer
kg	Kilogram
MOX	Mixed OXide reactor fuel
NCSE	Nuclear Criticality Safety Evaluation
NMMD	Nuclear Materials Management Division
PUREX	Plutonium and Uranium Extraction process
SEM	Scanning Electron Microscope
SRAT	Sludge Receipt and Adjustment Tank
SRTC	Savannah River Technology Center
TGA	ThermalGravimetric Analyzer
TSR	Technical Safety Requirements
WSMS	Westinghouse Safety Management Solutions
WSRC	Westinghouse Savannah River Company
XRD	X-Ray Diffraction

Executive Summary

Nuclear Materials Management Division (NMMD) has proposed that up to 100 kg of the plutonium (Pu) solutions stored in H-Canyon be precipitated with a nuclear poison and dispositioned to H-Area Tank Farm. The use of gadolinium (Gd) as the poison would greatly reduce the number of additional glass logs resulting from this disposition.

This report summarizes the characteristics of the precipitation process and addresses criticality concerns in the Nuclear Criticality Safety Evaluation. No problems were found with the nature of the precipitate or the neutralization process.

Two criticality scenarios are of concern. The first is a concern that an inadequate amount of Gd precipitates with the Pu if the process is interrupted at pH 3 (the point that Pu starts to form an insoluble polymer). Our experiments at this pH have determined that 5% (±1%) of the Gd precipitates with the formation of the first Pu. Determination of the water associated with this precipitate in the aqueous tank showed adequate hydrogen to Pu ratios, which makes the precipitate safe at the 0.05:1 ratio of Gd:Pu. The second scenario assumes that the precipitate slurry dries out in the Tank Farm transfer pump tank. Since there is no heat available, and the Gd/Pu is hygroscopic, we have determined that adequate water is retained to thermalize neutrons and maintain the adequacy of Gd as a neutron poison.

Summary

NMMD has proposed that some of the Pu solutions stored in H-Canyon could be precipitated with a nuclear poison and dispositioned to H-Area Tank Farm. The scope of the proposal is up to 100 kg of Pu. To minimize the number of glass logs resulting from this process, NMMD plans to use gadolinium (Gd) as the neutron poison. The Gd poisoned Pu solutions will also be neutralized at more than a critical mass unit to minimize the number of transfers to High Level Waste (HLW). The purpose of the Savannah River Technology Center (SRTC) test program was to produce experimental evidence to ensure the Pu would be homogeneously mixed with Gd in the precipitate to allow safe processing.

Because Gd is extremely effective in capturing thermal neutrons, but less effective in capturing fast neutrons, it is important that the Pu always have enough hydrogen present (in the form of water) for Gd to remain effective as a neutron poison. Results from centrifuged precipitates showed that the water present was more than adequate to maintain adequate poison at equal parts of Gd/Pu by weight. This 1:1 ratio of Gd to Pu was chosen as the baseline flowsheet for the neutralization and precipitation.

Addition of Gd to samples from Pu storage tanks 12.1 and 18.3 was made without any immediate effect on the Pu solution. A sample of Tank 18.3 at 2:1 Gd:Pu ratio was stable for one month. Precipitation of Gd/Pu from the 18.3 sample with NaOH was performed at bounding conditions of 0.5:1, 1:1 and 1.5:1, Gd:Pu and 12.1 was precipitated at 2:1 Gd:Pu without any problems. The precipitation step resulted in fine, easily dispersible particles. No high viscosity gel like material was noted as with the other poisons evaluated. SEM analyses showed an amorphous precipitate with both Gd and Pu present in all particles. Aged samples showed some crystals, which contained Gd/Pu, but an exact composition was not identified. Particle size of the material was measured under two conditions. The first was non-agitated, allowing agglomeration, and the second was agitated to break up agglomerents. The particle size distribution of both mixtures would be considered fine (small size) with agglomerated material between one and 210 microns (76% below 60 microns) and the agitated material from <1 to 22 microns.

Additional study resulted from the partial neutralization of the Gd/Pu solution. At pH 3, most of the Pu precipitates as a polymer (at a slower rate vs. the precipitation at pH above 7), but only 5 wt% of the Gd is present in the precipitate. This partial precipitation of the Gd has been incorporated in the worst case scenario for the criticality safety analyses. This scenario is an operational concern, because by pH 7 all the Gd precipitates with the Pu (NMMD should ensure that the addition does not stop at pH 3). The time to transition from pH 3 to pH 6.8 will be less than a minute at the addition rate planned (less than 20 lb. of 50% wt or 19 molar NaOH). Even in the unlikely event of agitator failure and neutralization stoppage at pH 3, the ratio of H:Pu:Gd is adequate for neutron poison in the precipitate. The H:Pu was found to be greater than 1900:1, which is in the safe zone for Gd:Pu precipitate at pH 3. If agitation is maintained, the Pu solids would be suspended and would behave like a solution and the soluble poison will protect the suspension from criticality.

After the precipitate is transferred to the HLW Tank Farm, it will be mixed with sludge and washed with dilute caustic. The behavior of Gd/Pu with the sludge and waste processing will be addressed in future reports.

Background

Historical Disposition of Pu to Waste

In the past, Pu has been dispositioned to the waste tanks in sub-critical mass units. The neutron poison used was either iron (Fe) or depleted uranium (U) that was already present in the waste streams (either in the waste tanks or from the process activity that generated the Pu waste). Another poison that has been used is manganese (Mn). Depleted U was used for disposition of the Pu/carbonate solutions generated in the solvent washer. Manganese has been used recently by H-Canyon to discard scrap Pu/U and LAP (Low Assay Pu) material but only at lower than a fissile mass unit with borated solutions.[1,2]

These three neutron poisons have a major disadvantage, because they generate a larger quantity of waste that ends up in DWPF glass. According to the Waste Acceptance Criteria[3], to use U as the poison, 198 grams ^{238}U per gram of fissile equivalent Pu must be used. For Fe, 160 gms per gram of equivalent ^{239}Pu must be used and for Mn, 32 grams per gram of equivalent ^{239}Pu must be used. An additional drawback stems from the large quantities of metal hydroxides produced upon neutralization. The hydroxide morphology limits the ability to precipitate and pump the desired amount of Pu in each batch. In the case of the U, the physical mass of the Pu/U slurry precludes large batches. In the case of Fe, similar problems are encountered, compounded by the gelatinous nature of $Fe(OH)_3$. Manganese looked desirable, because much less is required, but it was found that under certain conditions, the precipitate formed a gel in addition to being very viscous. This gel seemed to be reversible, but if it formed in the transfer line or jet, it would be a serious problem. In addition, the $Mn(OH)_2$ produced air-oxidizes to form Mn_2O_3, which may be a potential mechanism for separation of the neutron poison from the Pu.

Planned Disposal of Current Excess Plutonium

The team (consisting of experts from High Level Waste Division (HLWD), Defense Waste Processing Facility (DWPF), Nuclear Material Management Division (NMMD), Westinghouse Safety Management Solutions (WSMS) and SRTC) proposed that Gd be evaluated as the primary poison for excess Pu disposal, with Mn as a back-up. Since Gd has a very large cross section for thermal neutrons, a much smaller amount for poisoning is required in aqueous systems. However, the neutron absorption cross section falls off rapidly with unmoderated neutrons, and hydrogen (in the form of water) must be present for moderation in order for Gd to be much more effective than the poisons used in the past. This neutron moderation must be maintained under all conditions, at least through the precipitation and transport to the waste tank. Since there is no credible means of drying out the precipitate, the team agreed that a centrifuged sample would represent a conservative "worst case" for moisture content in the precipitate. The worst case premise was based on the fact that air evaporation is very ineffective in drying gadolinium hydroxide, because it is very hygroscopic, and that there is no mechanism before the tank farm to force further drying. The precipitate could air dry in the pump transfer tank in the waste Tank Farm if transfer were interrupted for a long period.

Experimental Results and Discussion

Introduction

There are approximately 100 kgs. of excess Pu solution in H-Canyon that are outside the specifications for the planned MOX disposition path. The preferred option for this material is to transfer the Pu to HLW Tank 51, which will be used to make up the next sludge batch for DWPF. The result will be a slight increase in the Pu in the next sludge batch (from ~0.005 to ~0.02 wt%). In order to accomplish this disposition, the Pu must be precipitated with a suitable neutron poison to prevent any possible criticality. In the past, poisons such as depleted U, Fe and Mn have been used. Scoping studies with Mn showed several potential problems (See Appendix 3). Iron and depleted U would create many extra glass logs increasing HLW costs.

Gadolinium can be used in much smaller ratios to Pu in an aqueous system and its use will result in an increase in volume of glass equivalent to less than one glass log. The experiments described in this report were designed to show that Gd/Pu precipitate together to maintain an acceptable Gd:Pu ratio and ensure that criticality is incredible.

Test Plan

A series of tests were planned to build on the findings from earlier scoping tests. The goal was to determine whether neutralization of a solution of $Gd(NO_3)_3$ and $Pu(NO_3)_4$ (with boron present) resulted in an intimate mixture of Gd and Pu species that cannot be separated by mechanical means or incidental chemical phenomena during further operations and transfers.

The effectiveness of Gd as a neutron poison is very dependent upon the energy of the neutrons. To be sure the Pu is protected with adequate neutron poison (Gd) during the transfer to the Tank Farm, the precipitate was centrifuged and the water present was measured using a Thermal Gravimetric Analyzer (TGA). The scoping tests (results 1/18/02) showed that there were ~30 molecules of water (60 atoms of hydrogen) associated with a Pu, gadolinium atom pair when precipitated in a 1:1 wt ratio after being centrifuged. The assumption for the initial criticality calculations was >30 hydrogen atoms per Pu atom[9]. This resulted in the proposed flow sheet that consists of a 1:1 ratio (by weight) of Gd to Pu, which is over twice the amount of Gd needed for 30 hydrogen atoms per Pu atom. Later Calculations showed the atom .ratio for this precipitate to be 1:1.52:152 Pu:Gd:H[8]

Scoping Tests

Scoping tests were run with Mn/Pu and Gd/Pu, to determine if the predicted neutralization solubility and operability were acceptable at the ratios required for criticality control. Since Mn was not selected, results are summarized in Appendix 3.

Scoping tests were run with a real F-Canyon PUREX solution (2BP solution) and a simulated H-Canyon Pu solution. Further testing was done with actual samples of the H-Canyon Pu solutions, now stored in tanks 18.3, 16.3, and 12.1 (Table 1). To be certain that there was nothing unusual about the $Gd(NO_3)_3{\bullet}6H_2O$ in storage, samples of that material were used for all the testing after the initial scoping tests.

Table 1 Properties of Solutions in Plutonium Storage Tanks (3-20-02)

Tank no.	Net, lbs	Sp Grav	Acid, N	Pu, gpl	Pu, kg	Boron gpl	~Vol, L
12.1	31,871	1.13	3.99	2.72	34.8	3.46	12,800
18.3	69,554	1.16	5.19	2.0	54.4	2.92	27,200
16.3	41,339	1.239	6.9	1.935	45.0	NA	23,253

Since pH was found to be important for neutralizing with Mn, a series of tests was planned with pH near 3, 7 and 14 to characterize the Gd precipitate ratios. It was expected that the Pu and Gd would precipitate together, because lanthanide and actinide chemistries are very similar, and both produce nearly insoluble hydroxides. Analyses of the Gd/Pu in the solids and solute were to be performed.

Physical characterization of the precipitate was done with the Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD). Pu mass balance between supernate and solids was done by radiochemical methods. Gd concentrations were determined with ICP-ES. Particle size analyses were done by Laser Scattering. Settling rates were determined visually and by weight.

Radioactive Neutralization Tests

Neutralization tests were run with flowsheets provided by F-Canyon engineers, with a ratio of 1:1 Gd to Pu substituted for the Mn (Appendix, Table 10). The standard F & H-Canyon neutralization procedure was followed. The Pu solution to be neutralized was added to a beaker along with the requisite amount of neutron poison from an acidic $Gd(NO_3)_3{\bullet}6H_2O$ solution. By using this acidic solution, no change in the Pu state in the samples was detected. 50 wt.% NaOH was added with agitation so that the temperature was kept below 50°C and the final free hydroxide concentration was > 1.2M. Deionized (DI) water was then added and the solution was left to react for two hours prior to sampling.

Partial neutralization tests were run in the same manner as full neutralization tests except that initially only part of the 50 wt% NaOH was added. The solutions were allowed to react for two hours and sampled. After sampling, the rest of the

NaOH was added to get to a concentration of >1.2M followed by the addition of DI water (See Table 2).

Sampling of each neutralization test after the two-hour reaction period was done as follows. An aliquot of the mixed solution was pulled and centrifuged. The liquid phase was split into two parts. One part was to be analyzed by ICP-ES for elements Gd, U, and B. The other part was analyzed for its Pu concentration using radscreen and corrected for the Am activity using gamma scan results. The solids were washed with a NaOH solution of the same pH and NO_3^- concentration as the test solution and centrifuged. The solids were analyzed by XRD to determine compounds produced and SEM to determine the Pu and Gd distribution.

Further sampling took place 3-4 days, a week, and several weeks after the reactions were completed. A liquid supernate sample was taken after 3-4 days and analyzed by ICPES, Radscreen, and Gamma Scan. After a week, the solution was mixed and a sample was taken to obtain solids. The sample was centrifuged, washed, and analyzed by XRD and SEM. A final long-term supernate sample was taken after several weeks to determine the final Pu and Gd supernate concentrations (Results are shown in Table 4).

Table 2 H-Canyon Simulant Runs

Gd:Pu Ratio (pH)	H-Canyon simulant (3g/L Pu, 5M HNO_3, 4 g/L B, $3x10^{-2}$ g/L U)	5.5 g/L Gd in 1.22M HNO_3	50wt% NaOH	DI water	pH	Total volume
1:1 (pH 14)	30 ml	16.2 ml	9.75 ml + 6.25 ml	80 ml	3	56.0 ml *132 ml
1:1 (pH 7)	30 ml	16.2 ml	9.50 ml + 6.50 ml	80 ml	7	55.7 ml *132 ml
1:1 (pH 3)	30ml	16.2 ml	16 ml	80 ml	14	142 ml

*10.5 ml sampled prior to final neutralization and water addition

Gadolinium Precipitate

The neutralized Gd/Pu solutions produced a light green/brown, easily suspended precipitate. Physically, the precipitate behaved as reported in the literature for a coprecipitation of hydroxide compounds (i.e. $Pu(OH)_4$ and $Gd(OH)_3$). The literature indicates Pu is coprecipitated with a carrier compound in a purification process. Hydroxides coprecipitate with Pu(III) and Pu(IV) nearly quantitatively under the proper conditions. In our case, the conditions would be >pH 7.[4] The precipitate settled slowly when agitation was stopped. The precipitates re-suspended when agitation was resumed (provided by a standard magnetic laboratory stirring-bar in the beaker of precipitate and solute).

SEM analyses showed that all of the material produced in both the simulated runs and the 2BP run had both Pu and Gd present. This result is unlike the Mn case where Pu was found without Mn at pH 3, and a large fraction of Mn was present as $Mn(OH)_2$ and did not contain Pu (Appendix 3).

X-ray Results

The X-ray diffraction showed an amorphous structure with possible fits to PuO_2 and Gd_2O_3. The Pu and Gd were so intimately mixed that the x-ray patterns could not be resolved. The amorphous structure can be explained by the hydroxides being produced, which are not crystalline (See Figure 1). The crystal pattern, which came closest to the observed peaks, belonged to a mixed Pu,Gd oxide structure (See Figure 2). When the PuO_2 structure is assumed, a particle size of 20 microns or less was estimated. Resolution of these peaks could be attempted with heating of the solids to crystallize more of the material (Figure 3). If the Gd and Pu were mixed in uniform structure, a peak between the two expected peaks for an intermediate structure would possibly appear. Resolution of the structure would necessitate determining and comparing lattice dimensions.[5]

Figure 1 SEM of pH 7 Gd/Pu

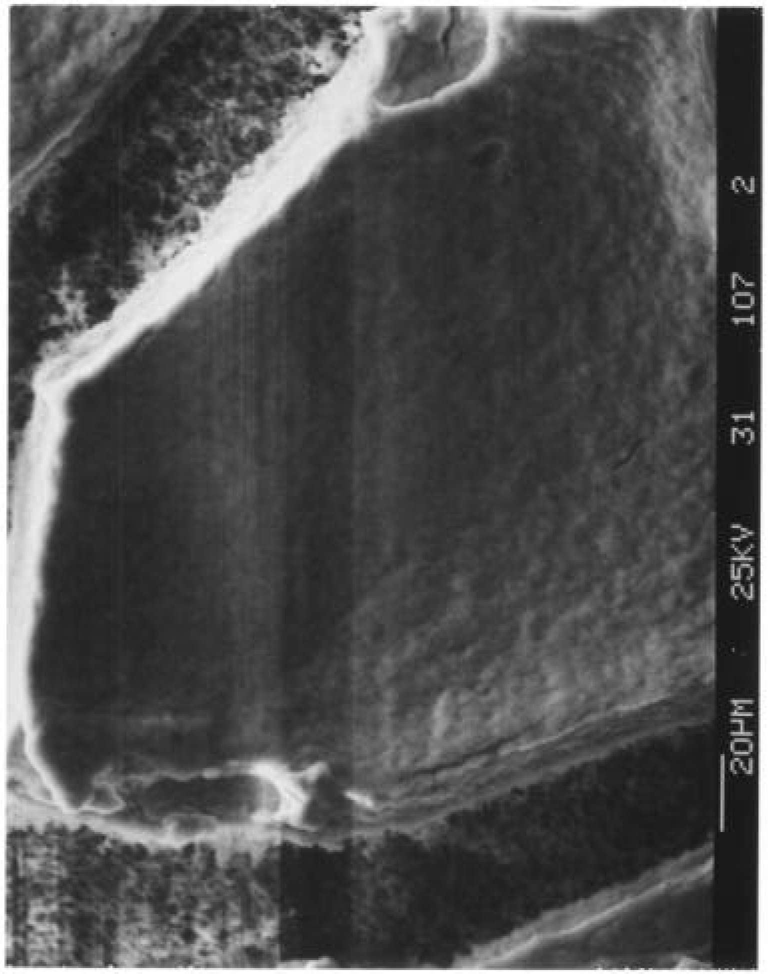

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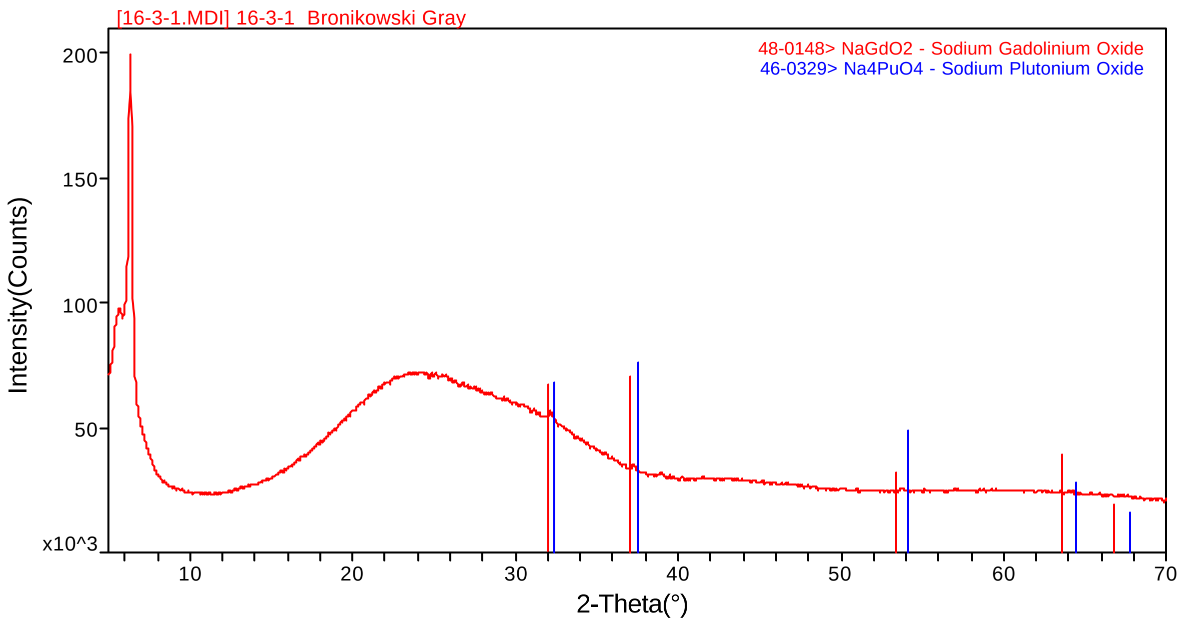
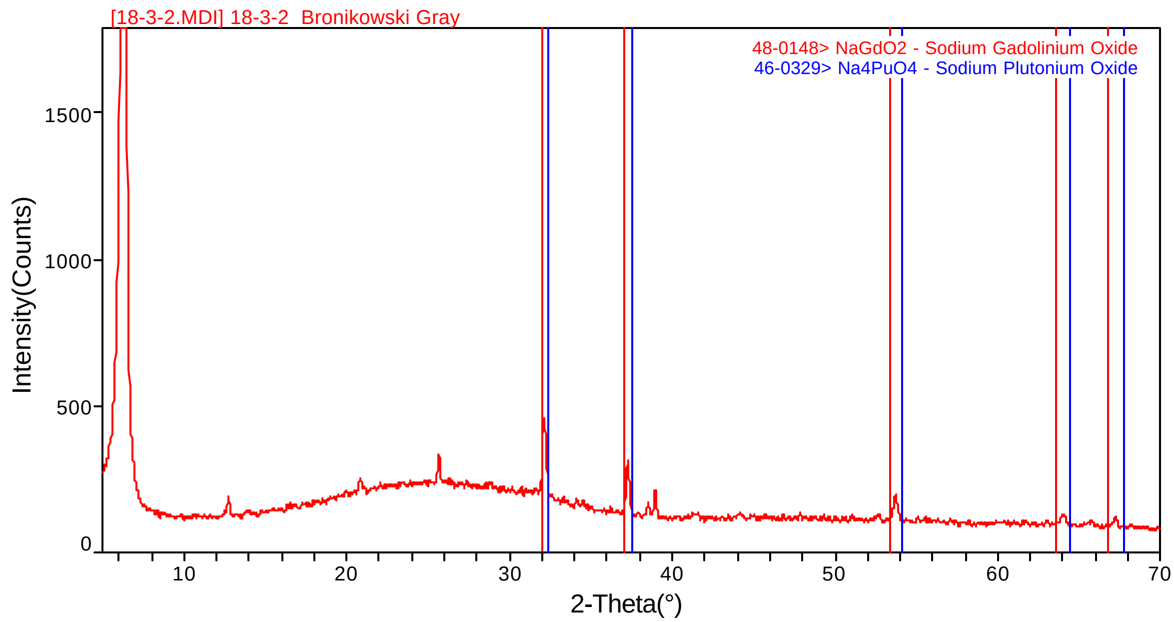
Figure 2 X-ray Spectra of Precipitate from Tank 16.3 and 18.3

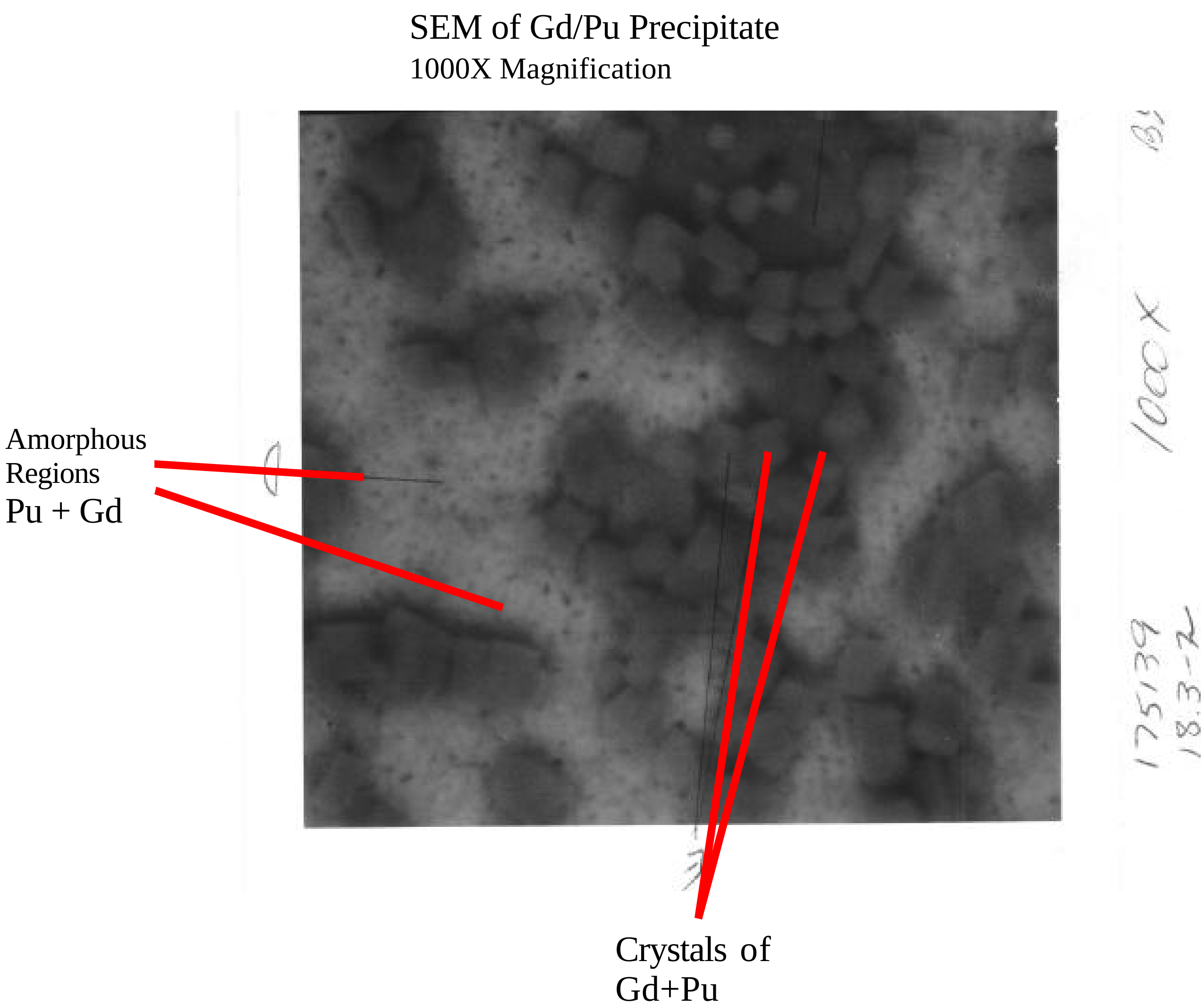




A sample of the precipitate was centrifuged and moisture was determined using a TGA. From the percentage water given off, the hydrogen to Pu ratio was determined to be about 130:1.

Since no negatives were identified, NMMD started to develop a baseline flowsheet and supporting safety documentation. From this baseline, a test plan was developed for precipitation studies of Gd/Pu at a nominal ratio of 1:1.

Figure 3 SEM of Gd/Pu Precipitate



Baseline Process Experiments

Neutralization Experiments:

Five bulk neutralization experiments were run. Three experiments were run with 18.3 solution, one with 16.3 solution, and one with 12.1 solution. A change in plans resulted in the addition of 12.1 solution as one of the primary candidates for disposition. NMMD now plans to stop processing 12.1 through H-B Line and process 16.3 instead. Tank 16.3 will not be discarded at this point. The Gd solution was made up from a $Gd(NO_3)_3 \bullet 6H_2O$ sample from the lot that will be used when neutralizing in H-Canyon. The actual precipitation process was carried out using the proposed H-Canyon flow sheet supplied by NMMD Engineering (see Appendix 1) with only a small amount of additional water and NaOH to get to a 1g/L final Pu concentration. A range of final Gd to Pu ratios run in these experiments was chosen to encompass possible operating conditions below k_{eff} = 0.95 as listed in Table 3. The test plan is shown in Appendix 4.

Table 3 Final Weight Ratio of Neutralization Experiments

Experiment	Gd:Pu ratio (wt)
18.3 solution	0.5:1.0
18.3 solution	1.0:1.0
18.3 solution	1.5:1.0
16.3 solution	1.0:1.0
12.1 solution	2.0:1.0

A small amount of solution at 1.5:1.0 Gd:Pu was made up and left to sit for the duration of the experiment to check stability (solubility) of the mixed solution. Previous criticality work suggests that solubility will not be a problem with simple Pu, Gd, and HNO_3 solutions[6]. The Gd/Pu case is unlike the 2BP solution case where the tested Pu^{3+} in solution oxidized to Pu^{4+} after a few weeks. However, the test was run, as the real 18.3 solution contains both B and U. Additionally, the 18.3 and 12.1 solutions were analyzed for Pu, B, Fe, Mn, and acid concentration.

The fundamental experiment was run by adding the needed amount of a 30 wt% $Gd(NO_3)_3 \bullet 6H_2O$ solution to a beaker containing 30 ml of the tank solution to obtain the Pu:Gd ratio needed when neutralized. 50% wt NaOH was then added until the concentration reached >1.2M in OH^-. The temperature was kept under 50°C during addition to approximate the plant neutralization process. Process water was added as needed to allow the solution to be pumped or to meet the waste acceptance criteria. The solution was mixed for at least two hours prior to sampling.

The solution was mixed, an aliquot taken, and centrifuged. The solids were rinsed and dissolved in concentrated HNO_3. The rinse solution was matched in concentration to the

NO_3^- and NaOH concentration of the final neutralized solution. Then both the dissolved solids solution and supernate were sent for radscreen (Pu conc.), gamma scan (Am correction), and ICPES (B, Gd, and U conc.) analyses

The solutions were allowed to sit for a week, and then the supernate from each solution was sampled. The supernate and mixed densities were determined by specific weights. This measurement allowed an estimate of the sludge density. The solution was mixed, and again an aliquot was removed and centrifuged, and the solids were submitted for analyses. The analyses consisted of radscreens, gamma scans, and ICPES for the supernate and dissolved solids. Additionally, some solids were submitted for XRD and SEM analyses.

Three 18.3 and one 16.3 solutions were mixed. This solution was analyzed for particle size distribution using laser scattering. For dilution to the solution volume needed for the test, 150 ml of a 1.2M NaOH solution with the expected [NO_3^-] was used.

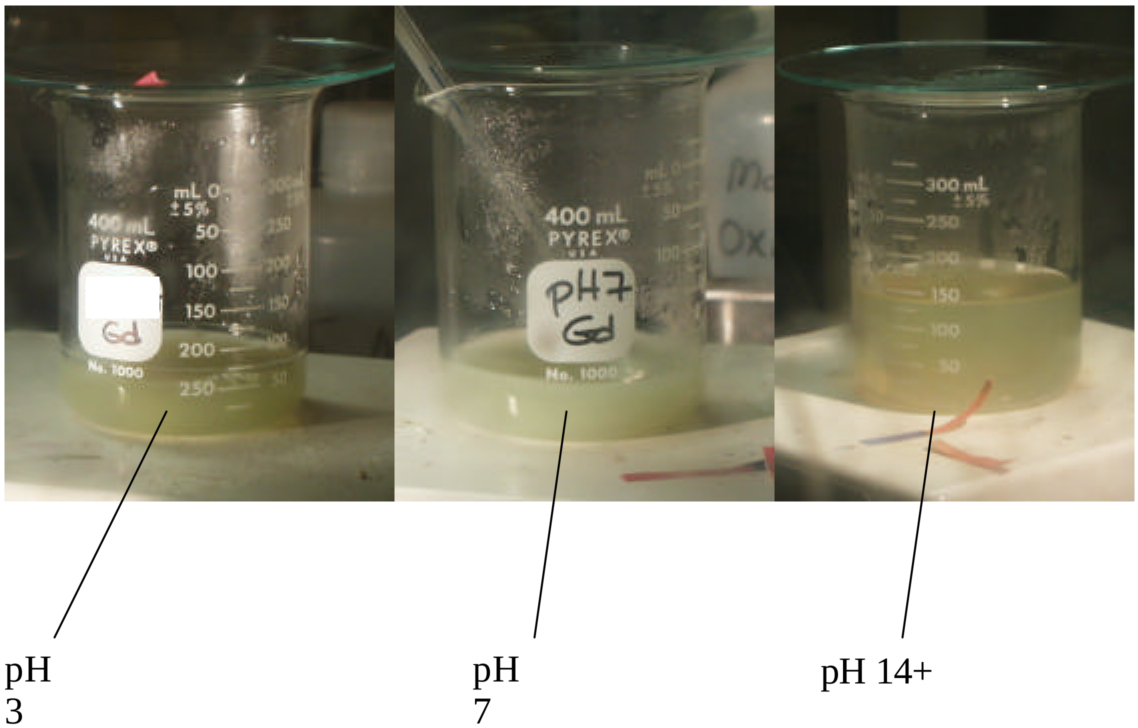
The TGA was run on the Gd/Pu solids and the Gd/Pu solids in the simulated waste to determine the weight of water that is contained in the dry sludge. The weight percent of water is needed by WSMS for criticality calculations. As done previously in the scoping tests, the solids were centrifuged and the supernate liquid was decanted prior to running the TGA.

pH Tests

The first pH series of tests used a simulated H-Canyon Pu solution. The composition of the simulated H-Canyon solution was five moles HNO_3 containing 0.03 grams U/L, 3.0 grams Pu/L and 4.0 grams B/L. Sufficient Gd was added to the 30 ml batches of the simulated solutions to produce a 1:1 Gd:Pu ratio in each solution.

To evaluate the behavior of Gd and Pu during the neutralization studies, each of the three solutions was adjusted to a different pH by slowly adding a 50% NaOH solution. Slow addition of the 50% solution was required maintain solution temperatures below 50 °C (the H-Canyon standard). The adjusted pH values of the three solutions were 3, 7, and >14. After the solution and precipitate samples were taken from the three different pH solutions, additional caustic solution was added to increase the final pH in all solutions to >14. Figure 5 shows the calculated solubility of Gd:Pu vs. pH..

Figure 4 Precipitate Appearance vs. pH



The solutions were analyzed to determine the solubility of Gd and Pu at the intermediate pH and after extended storage at >pH 14. Solubility results from analyses of the supernate are shown in Table 4.

Table 4 Solubility of Pu and Gd vs. pH

Sample	Gd Soluble (%)	Pu Soluble (%)
End of Titration (pH 3)	~95	5.1
After 7 Days (pH>14)	<0.5	<0.1
After 25 Days (pH>14)	<0.05	<0.001
End of Titration (pH 7)	1.5	1.1
After 7 Days (pH>14)	<0.3	<1.0
After 25 Days (pH>14)	<0.03	<0.1
End of Titration (pH>14)	<1.0	<0.1
After 7 Days (pH>14)	<0.2	<0.05
After 25 Days (pH>14)	<0.1	<0.005

Solid samples were taken from each of the different pH solutions when the initial caustic addition was completed. Analyses of the solids by SEM confirmed that all Pu was intimately mixed with gadolinium and indicated there were no Pu particles that did not contain Gd. In addition, no free Gd was detected. Due to the amorphous nature of the solids, XRD scans of the solids could not identify any specific Gd-Pu compounds.

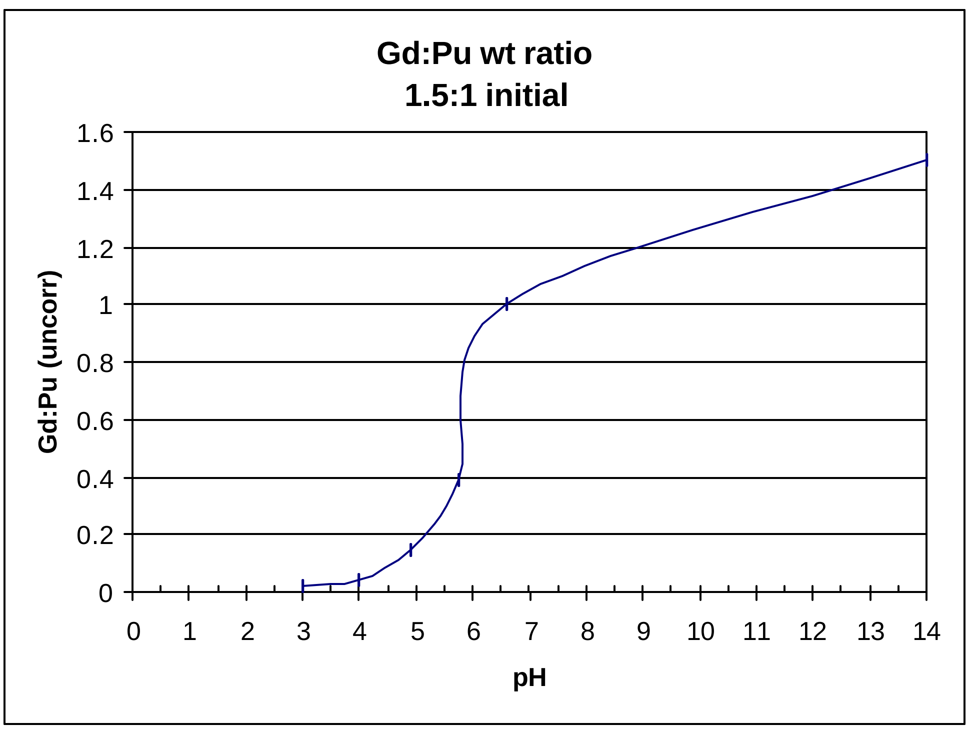
Some of the remaining solids were dissolved to determine the Gd:Pu ratio in the precipitate. These Gd:Pu solids are shown in Table 5 as a function of solution pH. Each of the experiments was designed at Gd:Pu ratios of 1:1. The data in Table 8 confirms that only at pH 3 most of the Gd remains in solution. Another series was run at a Gd:Pu ratio of 1.5:1. The ratio of the Pu:Gd in the precipitate is shown in Figure 5.

Table 5 Gd:Pu Ratios in Precipitates vs. pH

Sample	Gd Conc (ppm)	Pu Conc, (dpm/ml)	Gd:Pu
pH 3	17.4	4.1×10^{7}	1:20
pH 7	318	5.3×10^{7}	1:1
pH >14	365	6.5×10^{7}	1:1
pH >14 2BP from F-Canyon	617	9.1×10^{7}	1:1

The second series of Gd-Pu precipitation studies was conducted with actual Pu solutions taken from H-Canyon tanks 18.3 and 16.3. In this series, the 18.3 solution was used with Gd:Pu ratios from 0.5:1 to 1.5:1. Sufficient Gd was added to the 16.3 solution to attain Gd:Pu ratios of 1:1. All four solutions were adjusted with 50% NaOH to have pH >14.

Figure 5 Gd:Pu Ratio in the Precipitate



At the end of the NaOH addition, both solution and solid samples were taken. The solutions were analyzed for Gd and Pu to determine remaining concentrations of Gd and Pu left in solution after the caustic addition. The solids were analyzed by SEM and XRD to determine particle size characteristics and elemental structure of the precipitate. TGA was run to determine moisture content in the precipitate. All results from the SEM reconfirmed that Pu and Gd remain well mixed in the precipitate. The XRD showed little crystal structure.

The amount of Pu and Gd found in solution at the end of the run, and after a six day storage period, are shown in Table 6.

Table 6 Pu and Gd Solubilities in pH >14 Solutions

Sample	Gd Solubility (wt.%)	Pu Solubility (wt.%)
Tank 18.3 0.5:1 Gd:Pu	—	—
End of Titration	0.13	0.17
After 6 Days	0.20	0.50
Tank 18.3 1:1 Gd:Pu	—	—
End of Titration	0.18	0.11
After 6 Days	0.35	0.74
Tank 18.3 1.5:1 Gd:Pu	—	—
End of Titration	0.63	0.8
After 6 Days	0.32	0.38
Tank 16.3 1:1 Gd:Pu	—	—
End of Titration	0.83	0.15
After 6 Days	0.18	0.35

Some of the solids sampled after six days were re-dissolved in HNO_3 to determine the Gd:Pu ratio in the precipitates from Tanks 18.3 and 16.3. These solid samples dissolved almost instantaneously in the HNO_3 solution. The ability to dissolve some of the Gd-Pu solids in acid solution was shown in subsequent SRAT (DWPF processing –Sludge Receiving and Adjustment Tank) tests, reported in a subsequent report[7]. The results from dissolution of the Gd-Pu are shown in Table 7. These data confirm good correlation between the calculated ratios and the ratios determined by re-dissolving in HNO_3 and measuring the resultant solution.

Table 7 Gadolinium to Plutonium Ratios in Re-dissolved Solids

Sample @Gd:Pu	Gd conc. (mg)	Pu conc. (mg)	Gd:Pu Ratio
Tank 18.3-1 @ 0.5:1	0.7	1.13	0.62
Tank 18.3-2 @ 1.:1	1.145	1.13	1.01
Tank 18.3-3 @ 1.5:1	2.775	1.91	1.45
Tank 16.3 @ 1:1	0.342	0.35	0.97

Moisture Measurements

To ensure the Pu is protected with adequate neutron poison (i.e., Gd) in the transfer to the tank farm, a panel of experts from HLWD, DWPF, NMMD, WSMS, and SRTC determined that a “worst case” would be a centrifuged sample. This condition was selected because there is no heat to drive off water in the transfer line or pump tank in HLW, and air drying is extremely slow (10 plus days to lose 25% of volume at ~50°C). Samples of the precipitate slurry were centrifuged for five minutes in a Clay-Adams compact centrifuge that generates ~1000 G’s. Approximately 25 mg of the centrifuged precipitate was then run on the TGA to determine the amount of residual moisture present after centrifuging. The material from the centrifuge tube was sticky, much like paste. The temperature was ramped up to 500°C and the differential weight was calculated as water (Appendix 7). Results showed that the sample was ~80% water, which translated into the following atom ratio: for each Pu atom, 1.5 gadolinium atoms and 75.6 H atoms.[8] Since the NCSE[9] assumed 30 H atoms were present, this result shows the NCSE is conservative.

<u>Precipitate Moisture in H-Canyon Tank</u>

Because only part of the Gd precipitates when the Pu precipitates at pH 3, an experiment was added to determine the amount of water associated with the Pu precipitate. NMMD requested an additional test to measure the settling rate of the Gd/Pu precipitate at pH 3. Samples of 18.3 with 1:1 and 1.5:1 Gd:Pu ratios were neutralized to pH 4 and 4.5 and allowed to settle in a graduated cylinder for several days. The settling curve is shown in Figure 6. The thickness of the settled layer was measured and the apparent density was then calculated. The resultant precipitate was then force dried by heating (below 90°C) and blowing air over the sample. The amount of water and the H:Pu ratio were calculated.

The H:Pu ratios are shown on a plot of the effect of H on the safe Gd:Pu ratio in Figure 7. From table 5 the washed precipitate at pH 3 had a solid Gd:Pu ratio of 0.05. This condition is represented by the upper line through the curve in Figure 7. Washing the precipitate with distilled water as in the 1.5:1 Gd:Pu titration case shown in Figure 5 resulted in the lower line in Figure 7. This results in a very conservative number, because no mechanism for washing the precipitate could be postulated. The H:Pu ratio (atom ratio) was then calculated and found to be >1900 for 1:1 Gd:Pu and >2500 for 1.5:1 Gd:Pu. These ratios are represented by the vertical lines through the curve in Figure 7. The intersected area bounds the area of the Pu precipitation at the lower pH.

Figure 6 Settling Time vs. Volume

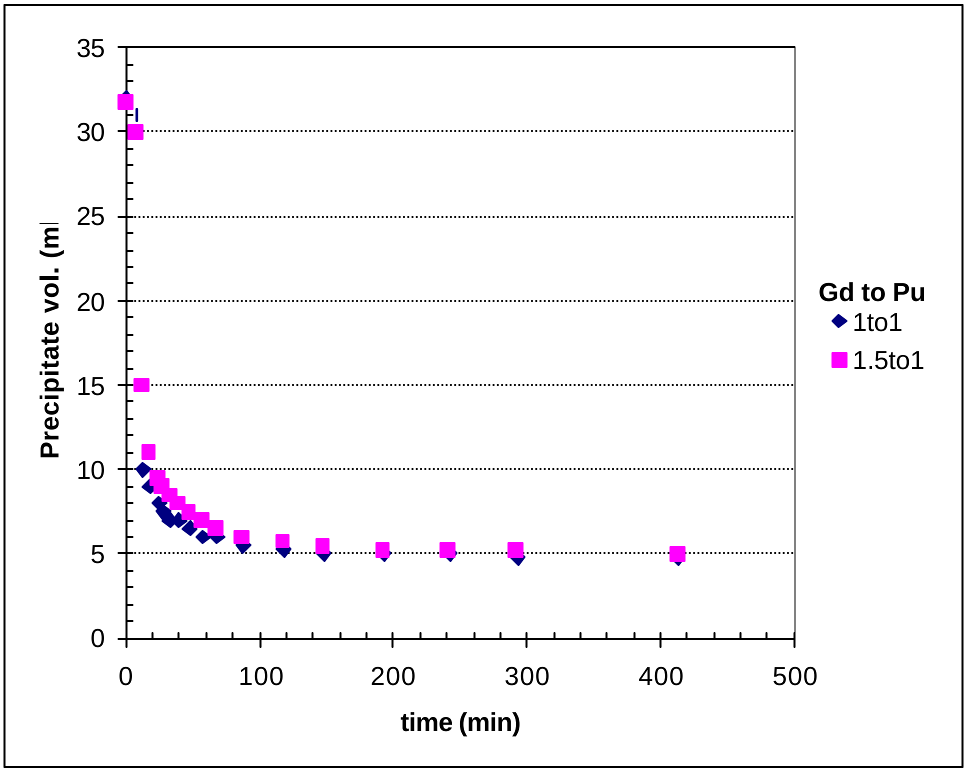
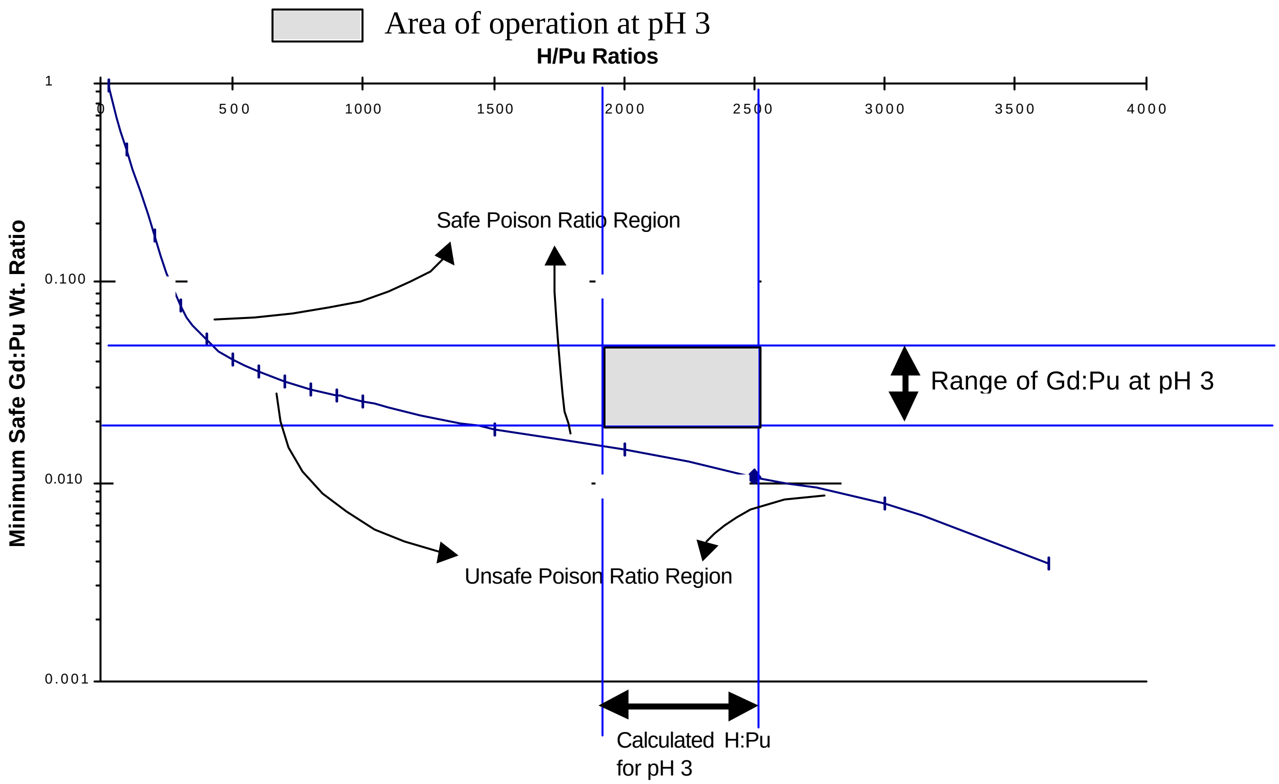


Table 8 Apparent Densities

Canyon Tank No.	Supernate Sp. G.	Mixed Sp. G.	Sludge density Vol. est.
18.3-1	1.195	1.241	1.423
18.3-2	1.190	1.253	1.505
18.3-3	1.225	1.279	1.405
16.3-1	1.231	1.287	1.332

Figure 7 Effect of Hydrogen on Safe Gd:Pu[9]



Particle size Measurement

The precipitates from Tanks 16.3 and 18.3 were combined and submitted for particle size distribution by laser scattering. The sample that was submitted was allowed to settle for 3 days and significant agglomeration occurred (Figure 8). The sample was then mixed to re-suspend the particles, and a second measurement was made (Figure 9). The particles in the settled material had a bimodal distribution. Re-suspending the material resulted in a single particle size distribution, skewed toward very small particles.

Figure 8 Agglomerated Particle Size in Microns

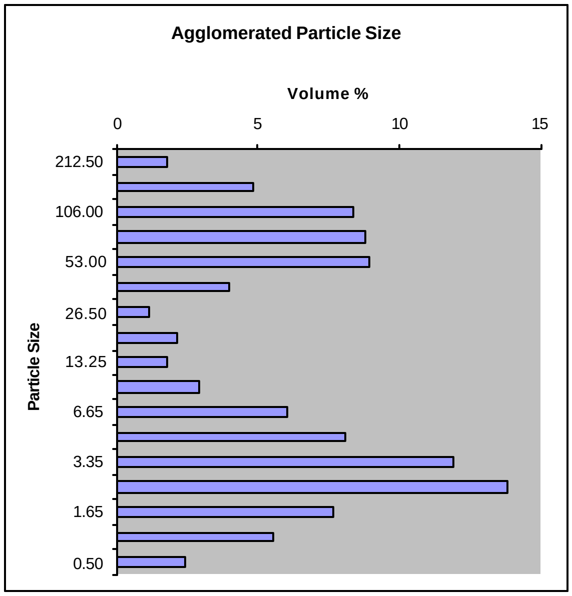
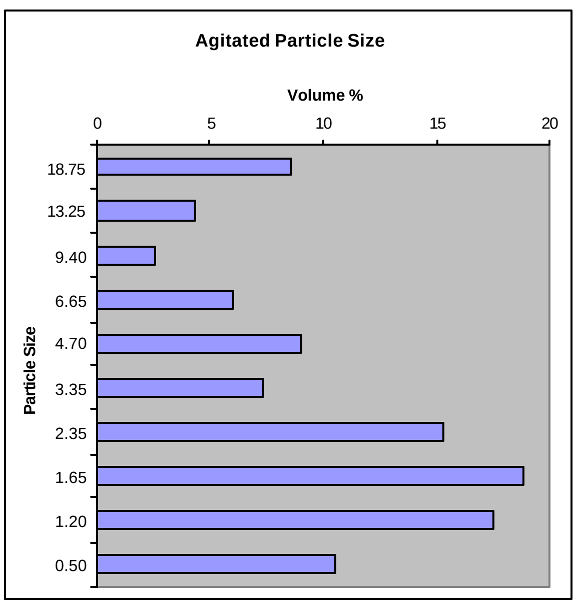


Figure 9 Agitated Particle Size in Microns



The precipitates were dried and prepared for XRD. The results showed an amorphous material, with some crystalline structure. Gd and Pu were present in all samples. The crystals were probably some form of $NaGdPuO_x$, which was not identified. The amorphous material was probably a mixture of $Pu(OH)_4$ and $Gd(OH)_3$, although the XRD was not definitive.

Sludge Washing and SRAT tests:

The new Pu/Gd sludge was made up for the SRAT tests. The Gd:Pu ratio was 1.4:1.0 and 100ml of 18.3 was used. The 100ml sample of 18.3 was the largest amount of Pu solution neutralized. No difference in the precipitation process or precipitate was noted. This new precipitate was added to simulated sludge obtained from the waste immobilization group to produce the final expected concentration of the waste.

As in the real process, inhibited water (0.01M NaOH) was used to wash the sludge. The wash solution was tested for Gd, B, Fe, and Pu concentration. The sludge was then heated to 93°C, acidified to ~pH 5.5 and boiled at 103°C for 12 hours. The sludge was sampled for analysis. The sludge was again run through the SRAT cycle above but at a lower pH of ~3. These results will be discussed in separate report[7].

Conclusions

Precipitation of Pu from a HNO_3 solution with NaOH can be done safely using gadolinium as a neutron absorber (poison). Concerns are centered on the transient during neutralization between pH 3, when Pu starts to precipitate, and pH 7, when gadolinium precipitates. This transient will only last seconds with normal operation. Experimental work has shown that the precipitate at pH 3 has a high water content with enough Gd to remain safe. The precipitate particle size was found to be less than 20 microns when agitated and particles were easily re-suspended with a standard laboratory stirring-bar. The material did not tend to adhere to the walls of glassware, or give any other indications that there would be a problem in transporting the precipitate to the waste tanks. Behavior during processing of the sludge batch for DWPF will be discussed in subsequent reports[7,10].

Appendix

Appendix 1 Flow Sheets for Gd Addition and Neutralization

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POISONING PLUTONIUM WITH GADOLINIUM NITRATE AND NEUTRALIZING WITH 50% NAOH

SOLUTION TO NEUTRALIZE

POUNDS	=	78623	ENTER
NITRIC ACID, M	=	5.00	THESE
PU CONCENTRATION, G/L	=	1.87	AMOUNTS
GRAMS PU TO POISON	=	57400	FIRST
GADOLINIUM TO PU WT RATIO	=	1.0	

DILUTION WATER, LB	=	26000	THEN PLAY WITH THESE
EXCESS 50% NAOH, LBS	=	12200	AMOUNTS TO GIVE TO YOU
			THE FINAL PU CONCENTRATION
			AND EXCESS CAUSTIC, M
			YOU WANT, SEE BELOW

POUNDS OF 30% GD(NO3)3-6H2O ADDED	=	1212	
NEUTRALIZED SOLU PU CONC, G/L	=	0.992	
NEUTRALIZED SOLU EXCESS CAUSTIC, M	=	1.20	(Greater than 1.10)
TOTAL AMOUNT OF 50% NAOH ADDED, LB	=	39636	
PERCENT DISSOLVED SOLIDS	=	25.0	(45.0 MAX)

POISONING FLOWSHEET

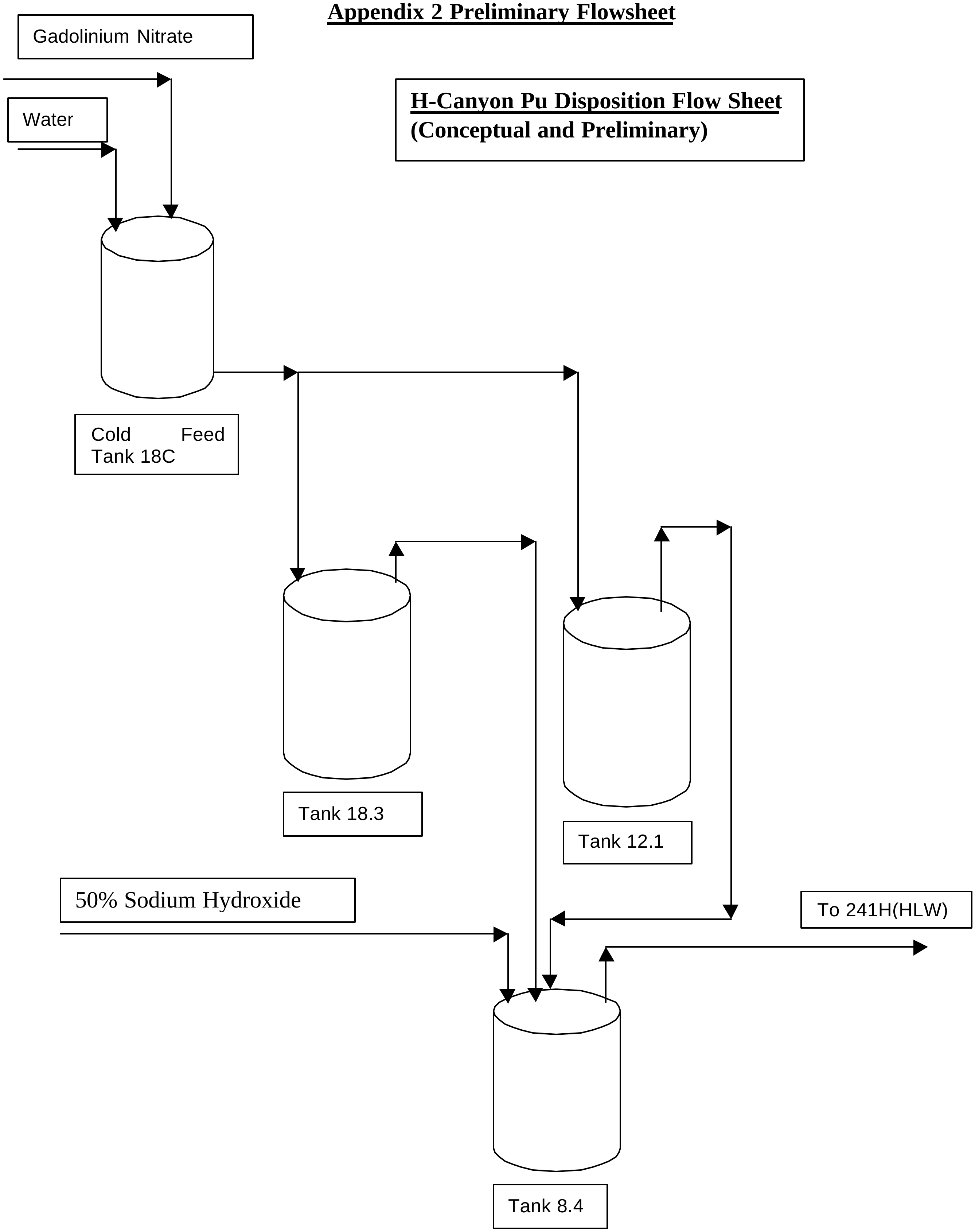
					HNO3			PU		PU(NO3)4			GD	GD(NO3)
MATERIAL	LB	KG	LITERS	DENSITY	MOLAR	MOLES	KG	G/L	GRAMS	MOLAR	MOLES	KG	GRAMS	MOLAR
SOLU TO NEUTRALIZE	78623	35657	30695	1.162	5.00	153476	9669	1.87	57400	0.0078		117.0		
30% GD(NO3)3-6H2O	1212	549.6	448.8	1.225									57400	0.81
DILUTION WATER	26000													
TOTAL	105835	47998	43008	1.116	3.57	153476	9669	1.33	57400	0.0056	240.2	117.0	57400	0.0085

NEUTRALIZING FLOWSHEET

					NANO3		PU		PU(OH)4		GD
MATERIAL	LB	KG	LITERS	DENSITY	MOLES	KG	G/L	GRAMS	MOLES	KG	GRAMS
50% NAOH	27436	12443									
NEUTRALIZED WASTE	133271	60440	54158	1.116	155533	13220			240.2		
50% NAOH EXTRA	12200	5533	3689	1.5							
1.2M NAOH EXCESS	142348	64557	57846	1.116	155533	13220	0.9923	57400	240.2	73.7	57400

||\028E

Appendix 2 Preliminary Flowsheet



Appendix 3 Scoping Studies with Mn as Poison

Neutralization tests were run with the 64:1 and 32:1 Mn to Pu flowsheets provided by F-Canyon engineers. The normal F-Canyon neutralization procedure was followed. The Pu solution to be neutralized was added to a beaker along with the requisite amount of neutron poison from an acidic $Mn(NO_3)_2$. 50 wt.% NaOH was added with agitation so that the temperature was kept below 50°C and the final free hydroxide concentration was > 1.2M. Two temperature ranges were run: 1) between 30-40°C and 2) between 40-50°C. DI water was then added and the solution was left to react for two hours prior to sampling.

Partial neutralization tests were run in the same manner as full neutralization tests except that initially only part of the 50 wt.% NaOH was used. The solutions were allowed to react for two hours and sampled. After sampling, the rest of the NaOH was added to get to a concentration of >1.2M followed by the addition of DI water.

Sampling of each neutralization test after the two-hour reaction period was done as follows. An aliquot of the mixed solution was pulled and centrifuged. The liquid phase was split into two parts. One part was to be analyzed by ICP-ES for elements Mn, U, and B. The other part was analyzed for its Pu concentration using radscreen and corrected for the Am activity using gamma scan results. The solids were washed with a NaOH solution of the same pH and NO_3^- concentration as the test solution and centrifuged. The solids were analyzed by x-ray diffraction (XRD) to determine compounds produced and scanning electron microscopy to determine the Pu and Mn distribution.

Table 9 30 ml Tests at pH 14 or Full Neutralization

Mn:Pu Ratio (pattern)	2BP Simulant (2g/L Pu, 0.4M HNO_3, 0.1 HAN)	50wt% $Mn(NO_3)_2$	50wt% NaOH	DI water	Temp.	Total volume
64:1 (121)	30 ml	16.2 ml	22.4 ml	159 ml	25-30	228 ml
32:1 (111)	30 ml	8.1 ml	22.4 ml	159 ml	25-30	220 ml
64:1 (122)	30 ml	16.2 ml	22.4 ml	159 ml	40-50	228 ml
32:1 (112)	30 ml	8.1 ml	22.4 ml	159 ml	40-50	220 ml

Several problems were noted with the Mn precipitation that would preclude using Mn as a neutron poison, when neutralizing more than a critical mass of Pu. Mn use for less than a critical mass would still be acceptable[1]. The rheology of the neutralized product and known potential chemical changes during the aging of the product are minor problems. The separation of Pu from Mn seen below a pH of 5 was seen as a major problem. Possible separation mechanisms can be postulated at full neutralization to >1.2M OH^- as seen in the SEM (figure 10) where amorphous $Mn(OH)_2$, and Pu and Mn solids are formed separately.

Table 10 pH 3 Runs

Mn:Pu Ratio (pattern)	2BP Simulant (2g/L Pu, 0.4M HNO_3, 0.1 HAN)	50 wt% $Mn(NO_3)_2$	50wt% NaOH	DI water	Temp.	Total volume
64:1 (221)	30 ml	16.2 ml	1.0 ml + 18 ml	132 ml	25-30	47.2 ml *189 ml
32:1 (211)	30 ml	8.1 ml	1.0 ml + 17 ml	126 ml	25-30	39.1 ml *182 ml
64:1 (222)	30 ml	16.2 ml	1.0 ml + 18 ml	132 ml	40-50	47.2 ml *189 ml
32:1 (212)	30 ml	8.1 ml	1.0 ml + 17 ml	126 ml	40-50	39.1 ml *182 ml

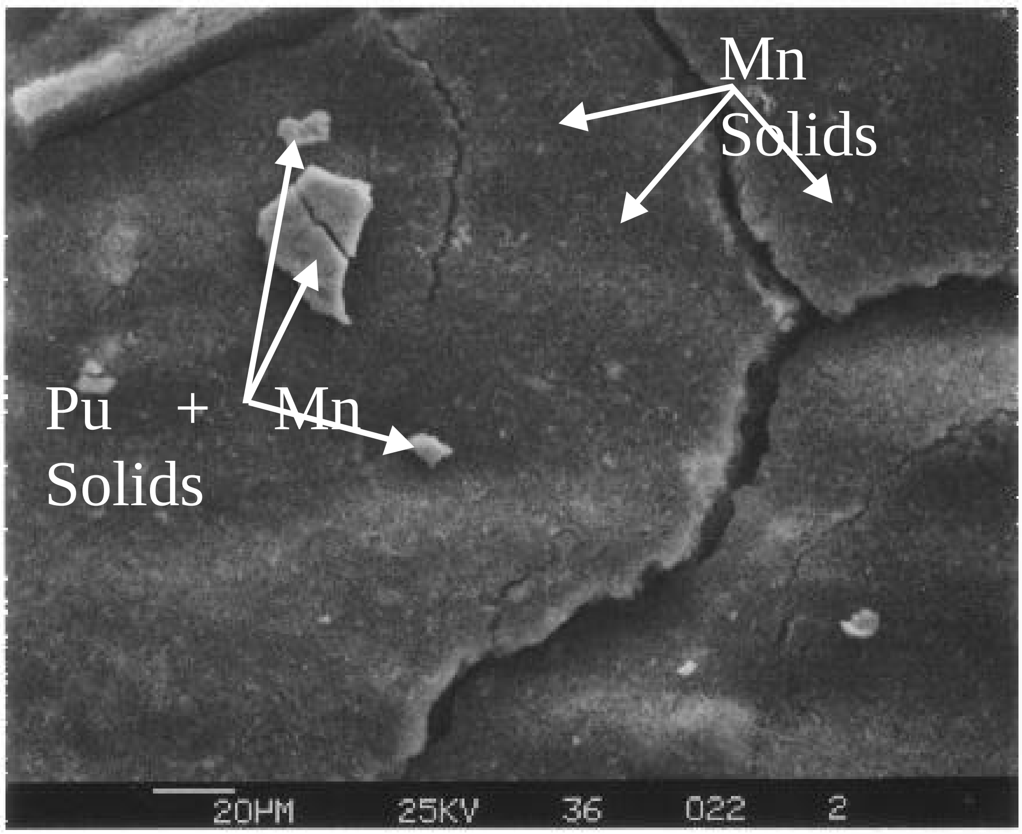
*8.0 ml was sampled prior to final neutralization and water addition

Table 11 Real 2BP Runs

Mn:Pu Ratio (pattern)	2BP	50 wt% $Mn(NO_3)_2$	50wt% NaOH	DI water	Temp.	Total volume
64:1 (R122)	30 ml	16.2 ml	22.4 ml	159 ml	40-50	228 ml
64:1 (R221)	30 ml	16.2 ml	1.0 ml + 18 ml	*132 ml	25-30	47.2 ml *197 ml
Gd:Pu Ratio (pattern)	2BP	3.7 g/L Gd in 1.22M HNO_3	50wt% NaOH	DI water	Temp.	Total volume
1:1 (R122)	30ml	16.2 ml	22.4 ml	159 ml	25-40	228 ml

*sampled after final neutralization and water addition, should have been prior to neutralization

Figure 10 SEM of Pu & Mn Precipitate



Appendix 4 Test Plan for Gd/Pu Neutralization Tests

Gd:Pu Experiment of 1/30/02	Solution	30% $Gd(NO_3)_3 \bullet 6H_20$ (~1.236g/ml)	0.01M HNO_3	50% wt NaOH (1.5g/ml)	Additional Process H_2O
0.5:1.0	30ml 18.3	0.264g	11.7250g	17.5198g	2.4108g
1.0:1.0	30ml 18.3	0.535g	11.5478g	17.5689g	2.4036g
1.5:1.0	30ml 18.3	0.810g	11.3161g	17.6414g	2.4202g
1.0:1.0	30ml 16.3	0.446g	5.9571g	16.5955g	0g

Added 30ml to 125 ml beaker; added grams Gd nitrate solution by rinsing of small vial it was in twice with the 18.3 or 16.3 solution. Added the first step of process water in the same way.

Stirring was set at 276 rpm with ¾"x 5/16" stir bars. NaOH was added slowly with a transfer pipette to attempt to keep the solution temperature below 50°C (highest temperature attained was 53°C). The first 18.3 neutralization took 15 min due to change in stirbars. Subsequent neutralizations took ~8 min. Added rest of process water after neutralization. Let stir for 2 hours. Samples were taken after stirring..

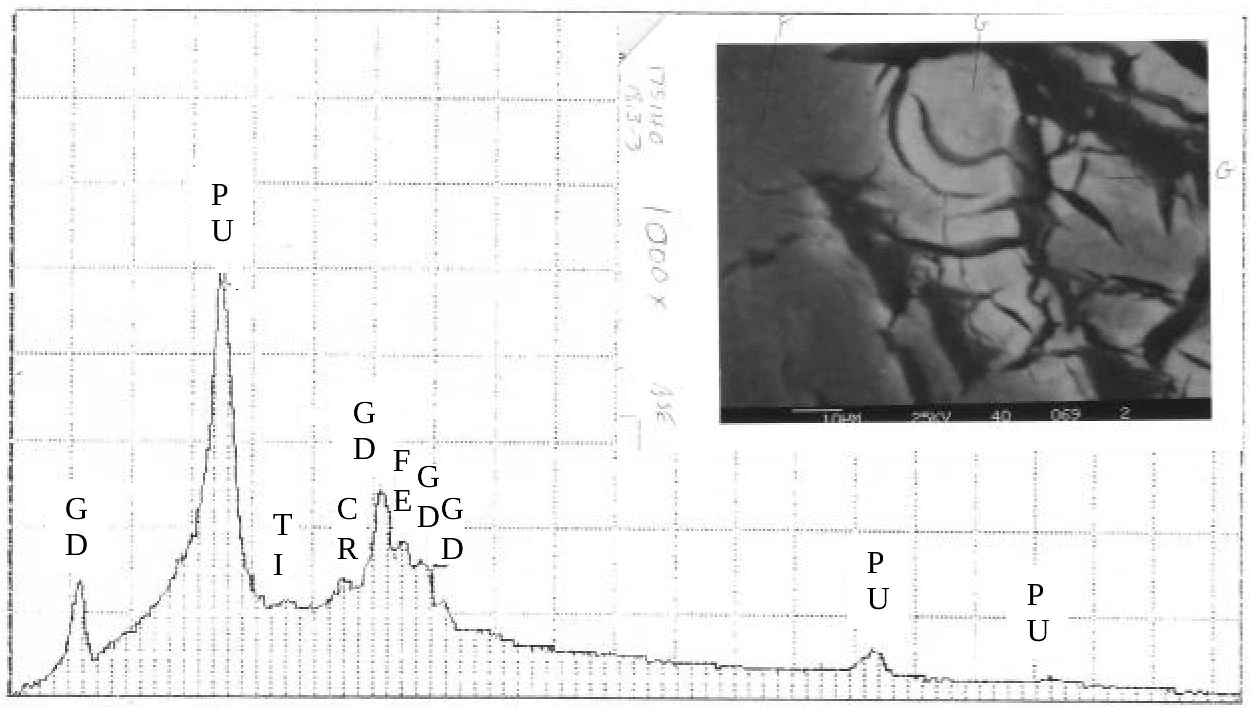
Appendix 5 Experimental Procedure to Determine Gd/Pu Ratio vs. pH

Titration Precipitation

1) Made up the initial solution that would be neutralized.
2) To 20ml of 18.3, 0.5640g of a 30% wt $Gd(NO_3)_3 \cdot 6H_2O$ (~0.434ml using sp.g. = 1.236) added 7.5583g of 0.01M HNO_3.
3) 26.5ml of this solution was found to weigh 30.17g giving a sp.g. of 1.138.
4) Free acid concentration was determined by titration to be 3.2M.

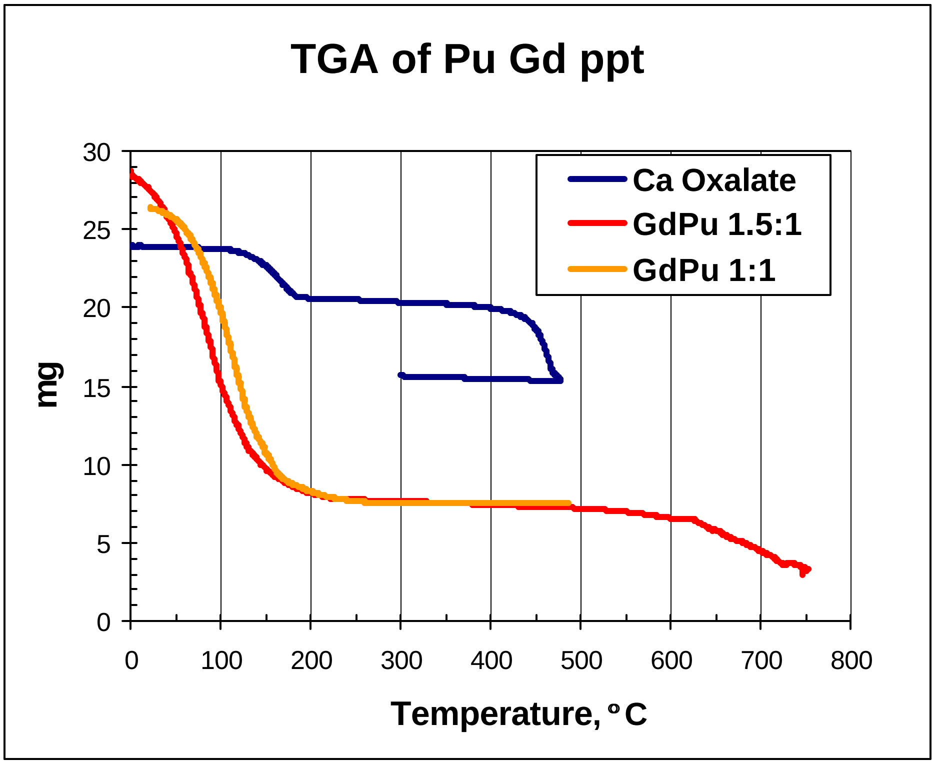
Solution required 8.1g or 5.3 ml. of 50% NaOH to reach a pH of 3 as measured by a pH probe. At pH =3.0 one drop of 50% caustic increases the pH to 6-7. Solution was acidified and a dilute ~0.1 M NaOH solution was used to adjust the pH to pH of 3.0, 4.0, 4.9, 5.75, and 6.6. After adjustment to a pH a 3ml slurried sample was pulled. The samples were left overnight, and centrifuged. The solids were washed with 3ml of distilled water and dissolved in 1ml of 8M HNO_3.

Appendix 6 18.3 Pu/Gd Precipitates Contain Fe



The figure above is an SEM photo and elemental analysis of solids produced by neutralizing 18.3 solution at the 1.5:1 Gd:Pu ratio. These solids precipitated in a 30ml neutralization are the same as those precipitated in the 100ml batch for subsequent use in the simulated batch 3 sludge washing and SRAT testing. Note that the Fe that was in the initial solution precipitates in the solid along with the Pu and Gd. The final Gd to Pu ratio was determined to be 1.4 to 1 since the 100ml 18.3 sample now contained 2.0 g/l Pu and not the 1.87 g/l it had contained in previously. The 1.4 to 1 Gd:Pu ratio is in the range (1.0-1.5) of Gd concentration that will be used in the process.

Appendix 7 TGA Curve To Determine Moisture



These representative TGA curves show that only water is removed upon TGA analyses. Calcium oxalate standard curve shows the expected temperature range for water of hydration loss between 150°C and 200°C. Using the weight loss of the initial solid to that at 250°C allowed calculation of the H to Pu atom ratio given in the text and the Pu:Gd:H atom ratio.[7]

Appendix 8 Water Estimates of H-Canyon Precipitate

For this determination 20ml samples of 18.3 were neutralized to 1:1 and 1.5:1 Gd to Pu ratio and a pH of 3 (actual pH attained was 4.5 and 5.0) and allowed to settle in graduated cylinders. Tank 18.3 samples have varied between 1.87 and 2.0g/l Pu due to evaporation. Using the 2g/l concentration of the sample the Gd to Pu ratio is 0.94:1 and 1.4:1. After settling, the supernate was removed from the graduated cylinders to 1ml and 0.5 ml above the solids in the 1:1 and 1.4:1 case respectively. The solids were dried in the cylinders under low heat and vacuum. A 10 ml sample of each supernate was also dried to determine the water content of these supernates. The weight of the water in the solids was calculated from the difference of the weight of the original precipitate and the dried precipitate minus the weight of the water associated with the 1ml and 0.5ml of supernate. To be conservative for estimating the water we assumed 2g/L Pu in 18.3 and not having the solids completely dry. Still visible water on the cylinder for 1 to 1 case. We can say that H to Pu ratio in the settled (71 hrs or 3days) Gd/Pu precipitates is:

0.94:1.0, pH = 4.5, settled to 12.5%, H:Pu >1900:1
1.4:1.0, pH = 5.0, solids settled to 15.7%, H:Pu >2500:1

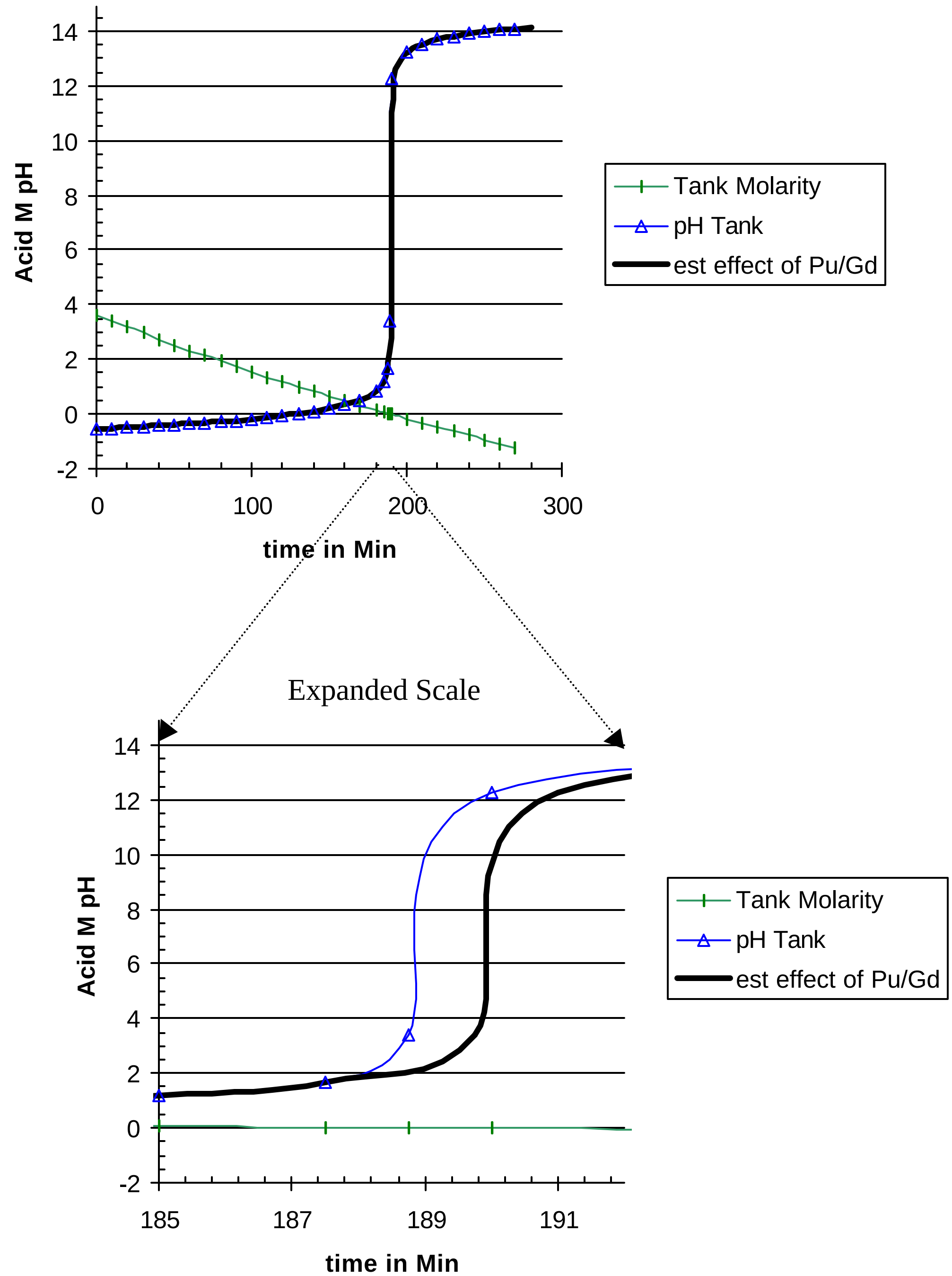
The H:Pu ratio would be higher if 1.87g/L was used.

As of 4/25/02

Gd:Pu	Initial Mass	Supernate	Final Mass	Water Mass	Water in Supernate	H to Pu (Atom)
0.94:1.0	98.2568g	1.0 ml	94.4362	3.8206g	0.8845g	1949:1
1.4:1.0	98.2641	0.5 ml	93.8850	4.3791g	0.4429g	2613:1

Appendix 9 Neutralization Curves

Estimated based on 8kg of Pu neutralized with 50% NaOH at 20 lbs/min 1.5:1 Gd:Pu



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