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Evaluation of the Magnesium Hydroxide Treatment Process for Stabilizing PFP Plutonium/Nitric Acid Solutions

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September 2000

Prepared for the U.S. Department of Energy
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Summary

This document summarizes an evaluation of the magnesium hydroxide [$Mg(OH)_2$] process to be used at the Hanford Plutonium Finishing Plant (PFP) for stabilizing plutonium/nitric acid solutions. The evaluation, conducted by Pacific Northwest National Laboratory (PNNL), included a literature review and laboratory- and bench-scale testing. Applying the results from this analysis will improve process throughput and efficacy, thereby minimizing the amount of material that must be reprocessed and lowering the associated costs.

The process evaluated here is being employed under the Plutonium Solutions Processing Program at PFP to meet the goal of stabilizing the plutonium in an oxide form suitable for storage under the U.S. Department of Energy (DOE) standard DOE-STD-3013-99, and treating the remaining solutions for disposition to the Hanford double shell tanks (DSTs). During the treatment process, nitric acid solutions bearing plutonium nitrate will be neutralized with $Mg(OH)_2$ in an air sparge reactor. The resulting slurry, containing plutonium hydroxide, will be filtered and calcined.

The equipment and operating strategy are based on a process built and operated at the Rocky Flats Environmental Technology Site (RFETS) to stabilize similar nitric acid solutions containing plutonium and contaminants. However, the processing objectives and feed streams are different. At RFETS, the key processing goal was to produce a filtrate containing less than 4 mg/L plutonium, which at times required adding a great excess of $Mg(OH)_2$. Also, due to criticality constraints, all solutions processed at RFETS contained less than 25 g/L plutonium. At PFP, the key processing objectives are focused on the final oxide product: meeting vault storage constraints by reducing the calcined filtercake volume; meeting the DOE-STD-3013-99 stabilization acceptance criterion moisture limit (or weight loss if using the loss-on-ignition, LOI, method) of <0.5% for oxide packaged in sealed containers; obtaining a minimum 30% PuO_2 concentration in the calcined product to meet the requirements of the DOE Nuclear Materials Stabilization Program; and providing an acceptable means for dispositioning the process filtrate. Another goal at PFP is to process feed streams containing as much as 50 g/L plutonium.

PNNL developed a disciplined testing strategy focused on optimizing the process and understanding and mitigating potential issues identified from the literature review and from previous testing by PFP. Based on the recommendations in the strategy report and recommendations from PFP staff, laboratory testing was initiated in March 2000 under the PFP Stabilization Project, which is managed by Fluor Hanford, Inc. The testing was conducted using cerium as a surrogate for plutonium to identify and quantify the effects of key processing variables on processing time (primarily neutralization and filtration time) and calcined product properties. Cerium solutions were also used by RFETS and the Los Alamos National Laboratory in the development of the process.

The evaluation and testing of the $Mg(OH)_2$ process has resulted in a better understanding of the process chemistry and operating behavior. From this understanding, strategies and recommendations have been developed for mitigating some previously and newly identified processing challenges. If unresolved, these issues have the potential to greatly diminish the effectiveness and efficiency of the process. Table S.1 summarizes technical issues and resolution strategies. Because each operating parameter in the process (e.g., initial acid and plutonium concentration, excess reagent addition, mixing rate, etc.) affects multiple process outcomes and issues (e.g., calcined product volume and LOI), the issues and resolution strategies are interdependent; that is, adjusting a single parameter will have an effect on multiple issues.

An overview of the specific issues and challenges potentially affecting operability and product quality is given below to provide further background for Table S.1.

Key Process Operability and Product Quality Issues/Technical Challenges

Filter Breakthrough: Laboratory testing with the planned filter material showed that under likely processing conditions, a large fraction of the solids formed in the precipitator reactor can pass through the filter media. It is not known whether these fine solids (which will contain plutonium hydroxide) would be captured in the downstream polishing filter. In a limited study, several types of alternative filter media were tested, but except for the laboratory paper filters, none performed satisfactorily. A process supervisor at RFETS recommended modifying the process to include a settling/particle-ripening period (about 20 min) before filtration.

This near-term issue must be addressed before process startup. A more detailed investigation of other filter media is needed, along with testing of flocculating agents and evaluating the effects of a settling/ripening period before filtration.

Weight Gain/Loss-on-Ignition: Weight gain/LOI measures how much moisture the calcined filtercake contains or adsorbs before packaging. During long-term storage, residual moisture will undergo radiolytic decomposition to produce hydrogen and oxygen gas. In turn, the gas can pressurize and deform or breach the storage container. Results from LOI testing at RFETS and laboratory testing at PNNL show that at certain feed conditions [Pu, HNO_3, and excess $Mg(OH)_2$ concentrations], the DOE-STD-3013-99 LOI criterion is unlikely to be met using currently planned operating procedures. If frequent failures occur, the process throughput will decrease because material will need to be reprocessed.

Potential LOI failure is a near-term issue that will impact the success of the process startup. Nearly every parameter in the process has been found to affect weight gain/LOI. Strategies to improve the LOI include calcining at temperatures 50°C to 100°C higher than the baseline temperature (950°C); basing the amount of excess $Mg(OH)_2$ used in the process on a molar quantity as opposed to a percent of stoichiometry [i.e., minimize $Mg(OH)_2$ to optimize process]; performing minimal rinsing of the wet filtercake; and appropriate blending/diluting of solutions to be processed.

Calcined Filtercake Volume: The available vault storage space for calcined filtercake is limited. If the average calcined filtercake density is less than 2 g/cm^3, then vault storage space will not be adequate. Previous testing with actual solutions at PFP and testing at RFETS resulted in densities of calcined product well below 2 g/cm^3. Additionally, PNNL testing with surrogates revealed operating conditions that can result in a low-density calcined product.

Strategies to reduce the volume of the calcined filtercake or increase the bulk density include increasing the calcination temperature by 50°C to 100°C; rinsing the wet filtercake with deionized water; and basing the amount of excess $Mg(OH)_2$ used in the process on a molar quantity as opposed to a percent of stoichiometry.

Wet Filtercake Volume: The physical properties and volume of the wet filtercake affect the filtration rate, the frequency at which the filter must be scraped, and the muffle furnace/calciner throughput. Testing with surrogates showed that under some feed conditions, the volume of the wet filtercake will limit the number of precipitator batches that can sequentially be processed before the filtercake is removed.

In addition to the feed composition, factors that affect the volume of the filtercake include initial solution acidity, excess $Mg(OH)_2$, flocculating agent dosage, and neutralization rate [tied to the excess $Mg(OH)_2$ to some extent]. The type and concentration of solution impurities will also affect the wet filtercake volume; however, these effects have not been investigated. To reduce the volume of the wet filtercake, the following strategies can be used: decrease excess $Mg(OH)_2$; eliminate the flocculating agent; and avoid diluting a solution to an initial acidity < 2 M HNO_3. However, it is likely that operating sequences for certain feed solutions will need to be modified to include more frequent filtercake removal.

Cerium Surrogate Confirmation: The use of cerium IV as a surrogate for plutonium IV allowed a large number of tests to be conducted quickly at a much lower cost. Testing with actual PFP solutions is ultimately needed to confirm the trends identified from the results of the simulant testing.

A prototype sparge reactor system was designed, built, and provided to PFP for bench-scale testing with actual solutions. Testing will be underway in July through September 2000.

Other Potential Issues/Challenges

Neutralization and Filtration Time: When the initially acidic solutions are neutralized to a pH of 6.8, the precipitation is complete. The time required for neutralization to take place, and subsequent slurry filtration, affects the rate at which PFP solutions can be processed. The filtration time is influenced by the initial acidity and cerium concentration of the solution, the neutralization rate, and the number of batches filtered before the filtercake is removed. Neutralization time has also been shown to affect the quality of the calcined product.

The neutralization rate can be controlled by limiting the amount of excess $Mg(OH)_2$ added to the solutions and by changing the sparge (mixing rate). There is a concern that the neutralization rate above a pH of 4 in the prototype reactor is significantly slower than observed in the beaker tests for solutions containing high cerium concentrations. Further evaluation of both parameters is needed. The flocculating agent dosage may influence the neutralization rate, but it also requires further investigation. A reasonable filtration rate can be achieved by maintaining the initial solution acidity to between 1.5 and 2.3 M HNO_3; controlling the neutralization rate to optimum values; minimizing the quantity of water used to rinse the filtercake; and frequently removing the filtercake from the filter.

Foaming and plugging: Foaming in the sparge reactor has been observed during previous small-scale testing of the process with PFP solutions. However, significant foaming has not been observed during the extensive testing with simulants, conducted with high purity $Mg(OH)_2$ and with and without flocculating agents. Plugging of the sparge reactor outlet line was observed at RFETS and during one simulant test at PNNL using the prototype test system. In the simulant test, the plug was removed by sparging air through the line.

At this time, a resolution strategy for foaming is not warranted. If foaming does occur in the full-scale system, then using a higher purity $Mg(OH)_2$ reagent, decreasing the air sparge rate (reducing process throughput), or adding anti-foaming agents should be considered. Further testing is recommended to better understand the conditions that are conducive for plugging and to develop a refined recovery strategy.

Gel Formation: In laboratory beaker tests, gel formation was observed at several solution compositions. In the laboratory system, the gel reduced the rate of neutralization and resulted in poor mixing. During testing using the same solution compositions in the prototype test system, gel was again observed, but satisfactory mixing was achieved with the air sparge.

While operators should be aware of the potential for gel formation, further testing with simulants is not warranted.

Filtrate Quality: To meet disposal requirements, the filtrate must contain less than 1 mg/L plutonium. Based on the literature and test data, the plutonium concentrations in the filtrate will meet the applicable requirements unless the solutions contain complexants, or if filter breakthrough is significant. No further evaluation is necessary unless complexants are present or filter breakthrough occurs.

Solids in Filtrate After Neutralization to pH > 12: Disposition of filtrate to the Hanford DSTs requires that centrifuged solids be less than 5 volume percent. Testing has shown that the neutralized filtrate will need to be significantly diluted to meet this criterion. The testing also showed that the predominantly $Mg(OH)_2$ solids are sticky, difficult to handle, and could adhere to vessel walls. It is therefore recommended that neutralization and dilution of the filtrate be conducted just before the stream is transferred to the DSTs.

Impurities in PFP Solutions: PFP solutions are known to contain appreciable quantities of impurities, including uranium, iron, permanganate, potassium, chromium, nickel, boron, cadmium, gadolinium, aluminum, and tributyl phosphate (and its degradation products). Some of these impurities, most notably uranium, iron and aluminum, are at concentrations comparable to the plutonium. These solutions could have a very serious impact on the process operability and the ability to meet the product quality requirements. It is highly recommended that testing be conducted on simulants with the major impurities.

Table S.1. Summary of Assessment of Technical Issues and Resolution Strategy

Technical Issue and Significance	Assessment Recommendations
Key Process Operability and Product Quality Issues/Technical Challenges	
Filter Breakthrough *Process Operability Issue* Surrogate testing has shown that significant quantities of precipitate can break through planned 25-µm filter. Breakthrough increases precipitate load on 1-µm filter, requires more frequent removal, and may result in Pu carry-over.	➢ Evaluate different filter media. ➢ Evaluate effects of ripening/settling time. ➢ Evaluate using minimal flocculating agent (~1 mg/L). ➢ Evaluate effect of vacuum level.
Loss-on-Ignition (LOI) of Calcined Product *Product Quality Issue* The DOE-STD-3013-99 limit for moisture content (or weight loss if using LOI method) of oxide packaged in sealed containers is <0.5%. LOIs for calcined filtercake at RFETS for the $Mg(OH)_2$ process averaged about 1.7%. Surrogate testing has shown LOI criterion is unlikely to be met for some of the PFP solutions. Failure to meet LOI criterion will decrease the process throughput as material is reprocessed.	➢ Perform calcination at a higher temperature. ➢ Further evaluate calcination temperature. ➢ Provide a minimal amount of rinsing (one filtrecake volume). ➢ Dilute acid to > 1 M whenever possible. ➢ Use Fluka BioChemika $Mg(OH)_2$ (high purity reagent). ➢ Optimize excess $Mg(OH)_2$ to minimize LOI; ~ 0.1 M excess $Mg(OH)_2$ rather than 10% excess based on stoichiometry. ➢ Do not add flocculating agent. ➢ Evaluate adding alkali salt to solution.
Calcined Filtercake Volume *Product Quality Issue* Vault storage capacity for calcined filtercake is limited. Volume impacts storage and handling costs. Average bulk density of calcined product should be at least 2 g/cm^3. Testing at RFETS, PFP, and PNNL (with surrogates) has shown that a bulk density of 2 g/cm^3 will not be achieved for many of the PFP solutions unless baseline process is modified.	➢ Provide a minimal amount of rinsing (one filtercake volume). ➢ Dilute acid to > 1 M whenever possible ➢ Evaluate calcination temperature. ➢ Use Fluka BioChemika $Mg(OH)_2$ (high purity and very reactive). ➢ Optimize excess $Mg(OH)_2$ to maximize density [use ~ 0.1 M excess $Mg(OH)_2$]. ➢ Further evaluate excess $Mg(OH)_2$. ➢ Control neutralization rate. ➢ Evaluate flocculating agent. ➢ Evaluate alternative drying strategies.
Wet Filtercake Volume *Process Operability Issue* The wet filtercake volume affects filtration rate and the number of precipitation batches that can be added to the filter before filtercake must be removed. The planned three batches before filtercake removal will not be possible for some solutions because of the large volume of filtercake.	➢ Where possible use an initial acid concentration between 2.0 and 2.5 M HNO_3. ➢ Optimize excess $Mg(OH)_2$ to optimize neutralization rate. ➢ Control neutralization rate. ➢ Evaluate using low concentrations of flocculating agent. ➢ Re-evaluate filtration operating strategy.
Use of Cerium Simulant *Simulant Confirmation Issue* Recommendations and conclusions from PNNL testing are based on the use of a cerium simulant. Trends developed from cerium data need to be confirmed with solutions containing plutonium in $Mg(OH)_2$ process.	➢ Conduct tests using prototype system with PFP solutions containing plutonium.

Table S.1. Summary of Assessment of Technical Issues and Resolution Strategy (continued)

Technical Issue Significance	Assessment Recommendations
Other Operability Issues	
Neutralization Time (to pH 6.8) Neutralization time limits the rate at which precipitator batches can be processed. It also can affect the filtration properties of the slurry and the quality of the calcined product.	➢ Optimize excess $Mg(OH)_2$ to optimize neutralization time (use ~ 0.1 M excess). ➢ Use Fluka BioChemika $Mg(OH)_2$ (very reactive and high purity). ➢ Evaluate neutralization rate vs. air sparge rate (i.e., mixing). ➢ Evaluate adding lower concentrations of flocculating agent.
Filtration Time Filtration time affects the rate at which precipitator batches can be processed. The baseline strategy for operating the filtration system will not work for some solutions. More frequent filtercake removals will be needed.	➢ Where possible, adjust initial solution acidity to between 1.5 and 2.3 M HNO_3. ➢ Rinse with 1 filtercake volume or less. ➢ Minimize addition of flocculating agent. ➢ Conduct trade-off study on exposure time vs. filtration time for adding slurry from two or more precipitators before changing filter.
Foaming During Neutralization Foaming in the precipitators limits the air sparging rate, which limits the neutralization rate and maximum capacity of precipitator. Severe foam may increase the volume of the wet filtercake.	➢ Use Fluka BioChemika $Mg(OH)_2$ (very reactive and high purity). ➢ Only very minor foaming occurred during surrogate testing with and without flocculating agents. ➢ Evaluate foaming during confirmation tests with PFP solutions.
Plugging in Precipitation Vessel Drain Line Plugging was observed at RFETS and in several simulant tests. Plugging will adversely affect process throughput and will increase dose to workers.	➢ Evaluate flow of settled slurry in the prototype precipitation vessel and outlet. ➢ Include design provisions and procedures for removal of plugs.
Gel Formation Gel formation during neutralization was observed during simulant tests. Gel could adversely affect neutralization and filtration times, and could contribute to plugging.	➢ Carefully observe for signs of gel formation when processing PFP solutions. ➢ Evaluate simulant solutions containing impurities.
Filtrate Quality Challenges	
Plutonium Concentration in the Filtrate Pu concentration in the filtrate must be <330 mg/L to meet tank waste acceptance criteria. Waste with Pu concentrations between 1 mg/L and <330 mg/L may be disposed in the tanks if the solution meets the criticality criterion.	➢ Simulant testing (and literature) indicates that very low concentration of Pu remains dissolved in filtrate. However, if filter breakthrough issues are not adequately addressed, Pu could escape with filtrate. ➢ If complexants are present in solutions, this issue should be further evaluated.
Solids in Filtrate After Neutralization to pH > 12 Disposition of filtrate to Hanford DSTs requires the centrifuged solids in the stream be less than 5 vol%. Testing has shown significant dilution will be necessary to meet criterion.	➢ Dilute filtrate. ➢ Do not neutralize and dilute until just before transfer, as solids are sticky and adhere to vessel walls.

Table S.1. Summary of Assessment of Technical Issues and Resolution Strategy (continued)

Technical Issue Significance	Assessment Recommendations
Process Challenges Resulting from Solution Impurities	
Solution Impurities The effects of small quantities of various impurities in the PFP solutions on the process operability and product quality are unknown. Almost no testing has been performed on solutions with impurities.	➢ Evaluate effects of individual and mixtures of impurities.
Uranium Precipitation The behavior of PFP solutions containing high concentrations of U and relatively low concentrations of Pu is unknown. No testing has been performed on solutions containing high levels of uranium.	➢ Evaluate solutions containing uranium to optimize process conditions.

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1.0 Introduction/Approach

The overall mission of the plutonium solutions processing program at the Hanford Plutonium Finishing Plant (PFP) is to stabilize the plutonium present in nitric acid solutions as an oxide form suitable for storage under the U.S. Department of Energy (DOE) standard DOE-3013-STD-99 (DOE 1999). In addition, the remaining aqueous solutions must be treated for dispositioning to the Hanford waste storage tanks. At PFP, nitric acid solutions bearing plutonium nitrate will be neutralized with magnesium hydroxide [$Mg(OH)_2$], and the resulting plutonium-bearing sludge will be calcined and packaged for storage. The baseline processing steps include:

- neutralizing PFP solutions with $Mg(OH)_2$, adding flocculating agent, and precipitating plutonium-bearing slurry at near-neutral pH (~7 to 9)
- filtering the precipitate and rinsing the wet filtercake to remove occluded salts
- drying the wet filtercake on a hot plate at ~500°C
- calcining the dried filtercake in a muffle furnace at 950°C
- treating the filtrate solution and rinse waters with sodium hydroxide (NaOH) to pH >12 for dispositioning to the Hanford double shell tanks (DSTs).

The reactions taking place in the precipitation step can generally be described by the following equations:

$$Pu(NO_3)_{4(aq)} + 2\,Mg(OH)_{2(s)} \rightarrow Pu(OH)_{4(s)} + 2\,Mg(NO_3)_{2(aq)} \tag{1}$$

$$2\,HNO_{3(aq)} + Mg(OH)_{2(s)} \rightarrow Mg(NO_3)_{2(aq)} + 2\,H_2O \tag{2}$$

In addition, polymeric plutonium hydroxide will begin to form once the acidity drops below about 0.5 M HNO_3. The first reaction is important because it provides the precipitate solids that, along with unreacted $Mg(OH)_2$, make up the solids inventory in the wet filtercake. The second reaction is important because the soluble magnesium nitrate is a component of the interstitial liquid in the wet filtercake. It accounts for 55% to 80% of the total inventory of magnesium in the wet filtercake.

Subsequent drying and calcining evaporates the water from the wet filtercake, forming magnesium nitrate solids that denitrate to form magnesium oxide according to the reaction:

$$Mg(NO_3)_{2(s)} \rightarrow MgO_{(s)} + 2\,NO_{2(g)} \tag{3}$$

The magnesium and plutonium hydroxides form their respective oxides according the reactions:

$$Pu(OH)_{4(s)} \rightarrow PuO_{2(s)} + 2\,H_2O_{(g)} \tag{4}$$

$$Mg(OH)_{2(s)} \rightarrow MgO_{(s)} + H_2O_{(g)} \tag{5}$$

These reactions are completed upon drying the wet filtercake at 500°C for 2 hr. Subsequent calcining at 950°C for 2 hr causes minor sintering of the solids, reducing their internal surface area and increasing their density. Calcining at the higher temperature also decreases loss-on-ignition (LOI) properties.

The solution stabilization process to be implemented at PFP is based on one previously built and operated at the Rocky Flats Environmental Technology Site (RFETS) to stabilize similar nitric acid solutions containing plutonium and contaminants. However, while the equipment and operating strategy being employed at PFP are similar to RFETS, the processing objectives and feed streams are different. At RFETS, the key processing goal was to produce a filtrate containing less than 4 mg/L plutonium. At times this goal was met by adding a great excess of $Mg(OH)_2$. Also, due to criticality constraints, all solutions processed at RFETS contained less than 25 g/L plutonium. At PFP, the key processing objectives are focused on meeting vault storage constraints by reducing the calcined filtercake volume; meeting the DOE-STD-3013-99 stabilization acceptance criterion moisture limit (or weight loss if using the LOI method) of <0.5% for oxide packaged in sealed containers; obtaining a minimum 30% PuO_2 concentration in the calcined product to meet DOE Nuclear Materials Stabilization Program requirements; and providing an acceptable means for dispositioning the process filtrate. Consequently, the work described in this report to optimize the process for PFP [including maximizing the plutonium concentration in the feed and minimizing the added $Mg(OH)_2$] was needed to ensure the most successful deployment.

In December 1999, Fluor Hanford, Inc. (FHI), who manages the PFP, requested that Pacific Northwest National Laboratory (PNNL) perform a technology evaluation for the $Mg(OH)_2$ precipitation process and recommend a test program to resolve outstanding issues. This evaluation is included as Appendix A of this report. As a result of that evaluation and discussions with PFP staff, several issues were identified that could impact process operability and calcined product quality. These issues are summarized below:

- *Loss-on-Ignition Properties of Calcined Product from Muffle Furnaces*. Results at RFETS suggest that the <0.5% moisture limit (or weight loss) for oxide packaged in sealed containers could not be met. An LOI averaging less than 2% was routinely achieved at RFETS.

- *Bulk Density and Volume of Calcined Filtercake*. To minimize the volume of plutonium oxide powder, and thus the number of 3013 containers that must be stored, the bulk density (plutonium basis) of the calcined filter cake must be maximized. Previous testing of the $Mg(OH)_2$ process at PFP and RFETS resulted in a calcined plutonium oxide powder bulk density ranging from about 0.4 to 1.1 g/cm^3. To stay within existing vault space constraints at PFP, the average bulk density of the calcined product must be greater than or equal to 2 g/cm^3.

- *Foaming in the Precipitators*. To maintain high process operability, the precipitators using $Mg(OH)_2$ are to be operated in a manner to minimize foaming.

- *Plutonium Concentration in the Filtrate*. Plutonium concentration in the filtrate must be minimized with a goal of <1 mg Pu/L (maximum throw-away limit and maximum for solutions going to waste handling at PFP).

- *Solids Volume in the Filtrate After NaOH Treatment*. To meet the waste acceptance criteria for disposal to the Hanford DSTs, the volume of the suspended solids in the NaOH-treated filtrate must be less than 5% (centrifuged solids basis).

In addition, some areas affecting the operability of the process were targeted for limited evaluation. These areas included parameters such as nominal nitric acid and plutonium loading in the feed solutions, the method of adding $Mg(OH)_2$, filter performance and filtration strategies, and drying and calcining methods.

PNNL was then requested by the PFP Stabilization Project to conduct the test program discussed here to develop data for addressing these issues. PNNL approached this program through a three-phase testing strategy to investigate the key issues and process parameters in a timely manner. The first phase consisted of a series of beaker tests using simulant solutions, with Ce^{4+} as a surrogate for Pu^{4+}. [Cerium was also successfully used in early process development work at RFETS and Los Alamos National Laboratory (LANL).] This first phase provided important experience and reduced both cost and time for the overall test program. The second phase consisted of a limited number of tests in a bench-scale prototype version of the PFP precipitation vessel to verify the scaleability of the data from the beaker tests and to further investigate the effects of sparge rate on other operating parameters. In the third phase, being coordinated through FHI, PNNL built a second prototype precipitation system for testing with actual solutions at PFP.

Section 2.0 of this report provides an assessment of the specific technical challenges and issues associated with the process, and is organized based on severity: key issues, other operability issues, filtrate quality challenges, and challenges from solution impurities. Appendix B provides an overview of the testing strategy, equipment, and procedures used in the first two phases of the test program. Appendices C through G discuss the tests and results for the following test series for the first two test phases for FY2000:

- *Source Testing (Appendix C)* - selecting a preferred commercial source of $Mg(OH)_2$ reagent for the process (beaker tests)
- *Neutralization Rate Testing (Appendix D)* - establishing optimum neutralization rates with respect to product quality criteria (beaker tests)
- *Baseline Testing (Appendix E)* - providing baseline data over a broad range of initial cerium and HNO_3 concentrations for evaluating the effect of solution composition on key operating parameters and product quality (beaker tests)
- *Rinsing Tests (Appendix F)* - investigating the potential benefits and consequences of rinsing filtercake with water to remove dissolved species prior to drying and calcining (beaker tests)
- *Prototype Testing (Appendix G)* - investigating the operability of the process using a prototype neutralization/precipitation reactor system.

The laboratory- and bench-scale testing was conducted with cerium (IV) as a surrogate for plutonium in solutions consisting of cerium nitrate in nitric acid. The concentrations evaluated included 0.052 M, 0.105 M, 0.157 M, and 0.209 M cerium, which corresponded to 12.5 g/L, 25 g/L, 37.5 g/L, and 50 g/L of plutonium. The majority of tests were conducted using 1.0 M, 2.0 M, and 3 M HNO_3, with several tests conducted at 0.69 M, 1.5 M, and 2.5 M in the baseline test matrix to better understand observed trends. Tests using 0.052 M cerium were performed to obtain data for solution concentrations comparable to that anticipated in PFP solutions currently scheduled to be treated first in the full-scale system. The nitric acid and cerium concentrations given in this report refer to their initial concentrations before the addition of $Mg(OH)_2$.

2.0 Assessment of Issues

The approach used by PNNL to better understand and address technical issues and process challenges that could affect the $Mg(OH)_2$ process operability and calcined product quality consisted of several components:

- evaluating the previous testing results, the process chemistry, and the literature to understand how the process operation and performance are affected by feed composition and operating parameters
- assessing the performance of the PFP $Mg(OH)_2$ process under baseline flowsheeet conditions through testing
- evaluating processing refinements and options to improve performance and throughput
- identifying parameters and process issues that warrant further evaluation.

The following specific issues were evaluated through a series of laboratory- and bench-scales tests: filter breakthrough, LOI properties of calcined filtercake from muffle furnaces, calcined filtercake volume, wet filtercake volume, use of cerium simulant, neutralization time, filtration time, foaming of solution during neutralization, plugging in the precipitation vessel outlet, plutonium concentration in the filtrate, volume percent solids in filtrate after neutralization, solution impurities, and uranium precipitation. Each issue is discussed separately in this section. Those identified but not evaluated include effects of solution impurities on the process and testing to confirm that plutonium will behave similar to cerium.

2.1 Key Process Operability and Product Quality Challenges

This section discusses four issues that, if left unresolved, have the potential to seriously undermine the process operability and the ability of the calcined product to meet requirements: filter breakthrough, LOI, calcined product volume, and wet filtercake volume. The fifth item in this section, cerium surrogate confirmation, is essential to verify that trends and resolutions developed from simulant testing are applicable to the processing of the actual PFP solutions.

2.1.1 Filter Media and Breakthrough

For successful implementation of the $Mg(OH)_2$ process, nearly all of the precipitate (and plutonium) must be captured on the primary 25-µm polypropylene filtercloth. Some precipitate breakthrough can be tolerated, provided that the quantity is small and that it will be retained on the 1-µm polypropylene polishing filter cartridge.

During the laboratory and bench-scale testing, most of the filtrations were performed at 20 in. Hg vacuum using Whatman #41 ashless paper filters (nominal pore size ~25 µm). With the Whatman #41 filter paper, essentially no precipitate passed through the filter, regardless of the test conditions. However, a limited series of filtration tests were performed using prototypical filtercloth materials.

The performance of filter media became an issue when a 25-µm polyester fiber filter from Knight Corp., Houston, Texas (vendor for filtercloth to be used in the process), failed to adequately retain solids during testing. The slurry filtered very rapidly at less than 2 in. Hg vacuum, and approximately half of the solids passed through the filter. The filtrate was passed through the same filter (containing some filtercake) twice at very low vacuum before it was clear. Any increase in the vacuum during the refiltering operation caused solids to break through. Rinsing the filtercake also caused it to pass through the filter until the filter media appeared clean.

Filtration tests were also conducted using 10-µm and 1.0-µm polypropylene filter media from Knight Corp. The finer filter media performed progressively better in terms of retention and maximum operable vacuum pressures, but were still very unsatisfactory with respect to breakthrough.

A 1.6-µm glass fiber filter (Whatman GF/A) was much better at retaining solids than any of the polypropylene filters and performed nearly as well as the ~25-µm Whatman 41 ashless paper filter in terms of solids retention. A 0.45-µm MSI Magna nylon membrane filter performed better than the paper filter in terms of solids retention, but it had a much slower filtration rate.

An abbreviated review of literature indicates that part of the problem with the polypropylene filters is they are rated based on a percentage of solids of a certain size passing through the filter media. Ratings typically range from 90% to 99% depending on the vendor, and the testing methods may vary. In addition, the fibers can move if the pressure differential across the filter is varied, causing solids to slough off and penetrate through the filter. In some polymer fiber filters, the fibers are glazed or otherwise fused to fix the position of the fibers.

The process supervisor for the $Mg(OH)_2$ process at RFETS was contacted about past experiences with filter breakthrough. [Personal communication from M. McCullough, RFETS, to A.J. Schmidt, PNNL, on June 7, 2000.]. Early in the deployment of the process at RFETS, precipitate did pass through their 25-µm filter and through three 5-µm polishing filters. The breakthrough problems were eliminated by providing a 20-min settling period after neutralization. During the settling period, the precipitate flocs/crystals grew in size. RFETS also tried using a 5-µm filtercloth in the primary filter. This filtercloth resulted in significantly longer filtering times and did not substantially improve the filtrate quality. Also, for most of the process, a 20-µm polypropylene (15-oz/yd) filtercloth was used that was glazed on one side (Style 7409 Lambports Filter Media, Cleveland, Ohio).

Filter breakthrough must be addressed before process startup. A more detailed investigation of other filter media is needed [including hardened paper, polymers with fused fibers (glazed), and glass fibers with binders and at nominal pore sizes ranging to below 1 µm], along with testing of flocculating agents and an evaluation of the effects of a settling/ripening period before filtration. At this time, a settling/ripening period is not included in the process flowsheet at PFP.

2.1.2 Weight Gain/Loss-on-Ignition Properties

Loss-on-ignition testing is used to estimate the amount of moisture on a cooled calcined filtercake before it is sealed into a 3013 can for storage. Moisture content is important because radiolysis will decompose the water into hydrogen [and oxygen gas], which accumulates in the sealed can and thereby increases the internal pressure of the can contents, and possibly deform the can. To meet the DOE-STD-3013-99 stabilization criterion moisture limit (or weight loss if using LOI), moisture in the calcined product must be less than 0.5%. Results from LOI testing at RFETS and laboratory testing at PNNL suggest that at certain feed conditions [Pu, HNO_3, and excess $Mg(OH)_2$ concentrations], the LOI criterion is unlikely to be met using currently planned operating procedures. If frequent failures occur, the process throughput will decrease because material will need to be reprocessed. Potential LOI failure is a near-term issue that will impact the success of the process startup.

Strategies that improve the LOI include calcining at temperatures 50°C to 100°C higher than the baseline temperature (950°C); basing the amount of excess $Mg(OH)_2$ used in the process on a molar quantity as opposed to a percent of stoichiometry [i.e., minimize $Mg(OH)_2$ to optimize process]; performing minimal rinsing of the wet filtercake to remove $Mg(NO_3)_2$; and appropriate blending/diluting of solutions to be processed.

The LOI test provides a good estimate of the moisture content. However, CO_2 adsorption to form carbonates and weight loss due to further aging of the calcined sample during the test will also contribute to the LOI value.

The LOI depends on the composition of the calcined material, the calcination time and temperature, the humidity of the ambient air, the time of exposure to the ambient environment, and the total mass and manner in which the material is stored during exposure. Measuring the weight of calcined samples upon removal from the desiccator where they had been cooled, and after exposure to ambient conditions for a period of time (weight gain), can be used to estimate the subsequent LOI of these samples.

Weight measurements were taken on samples that had been dried at 500°C for 2 hr followed by calcination at 950°C for 2 hr and cooling in a desiccator. These measurements were taken when the samples were removed from the desiccator and after they remained exposed to ambient conditions for 1 hr. The samples typically ranged from 2 to 7 g and appeared as coarsely divided material or a single monolith in the crucibles. Many of the samples were also weighed after 24 hr of exposure. Several samples were calcined at 1000°C instead of 950°C. Samples of Fluka BioChemika $Mg(OH)_2$ and ceric nitrate reagents were also processed through the drying and calcining sequence that was used for test samples.

Figures 1 and 2 show the effect of the solution composition on the 1-hr and 24-hr weight gain, respectively. The cerium concentration appears to have a minor effect on the weight gain, although there was considerable scatter of the data at each condition evaluated. The weight gain also appears to undergo a slight decrease between 1 and 2 M HNO_3, and then a significant increase (about double) between 2 and 3 M HNO_3. This behavior is likely due to the phenomenon to be discussed in Section 2.1.4, where there is a significant decrease in the volume of wet filtercake between 1 and 2 M HNO_3. This decrease reduces the total amount of $Mg(NO_3)_2$ in the filtercake interstitial liquid, even though the concentration is greater. The weight gain at 0.209 M HNO_3 between 0.69 and 1 M HNO_3 does not exhibit this trend, because the wet filtercake volume does not vary significantly in this acid range.

The neutralization rate also has a significant effect on the weight gain. The results of tests on the effects of neutralization rate (Figure 3) suggest that the weight gain undergoes a minimum value for pH 2-4 time intervals between 2 and 5 min. The time required for the solution to pass from pH 2 to pH 4 was chosen as the key neutralization interval because it spans the pH range where significant precipitation occurs.

Figure 4 also suggests that the presence of a relatively small quantity of alkali salt (KNO_3) has a significant impact on the weight gain. According to these results, derived from both beaker and prototype system testing, the addition of 0.1 M of the salt decreased the weight gain by a factor of 1.6. Further tests would be required to determine the minimum amount of alkali required to achieve the effect, as well as the effect of rinsing.

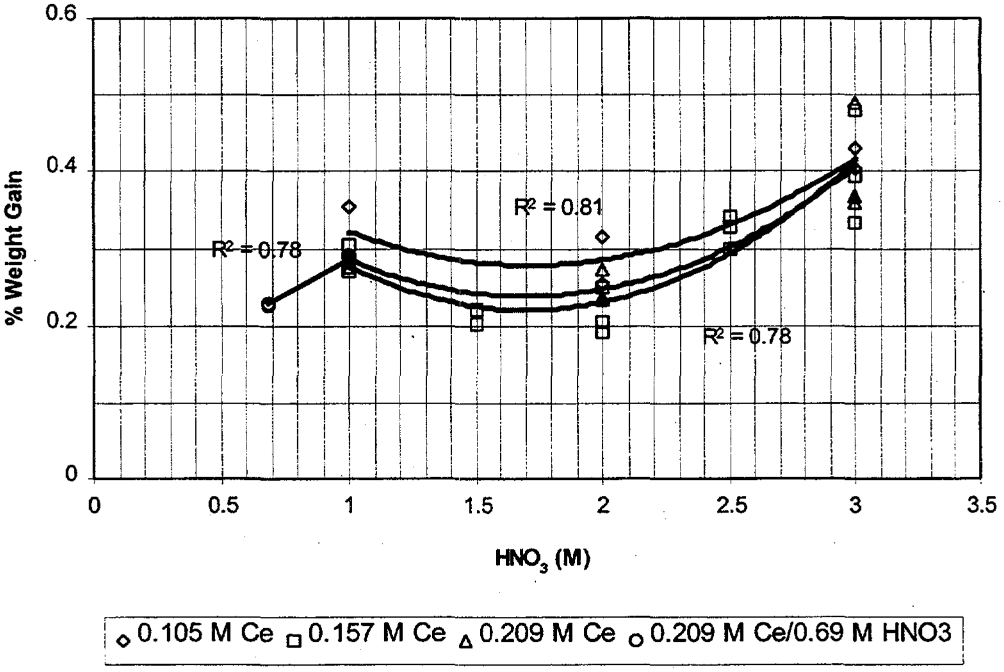

Figure 1. Calcined Product Weight Gains After 1 Hr vs. Initial HNO_3

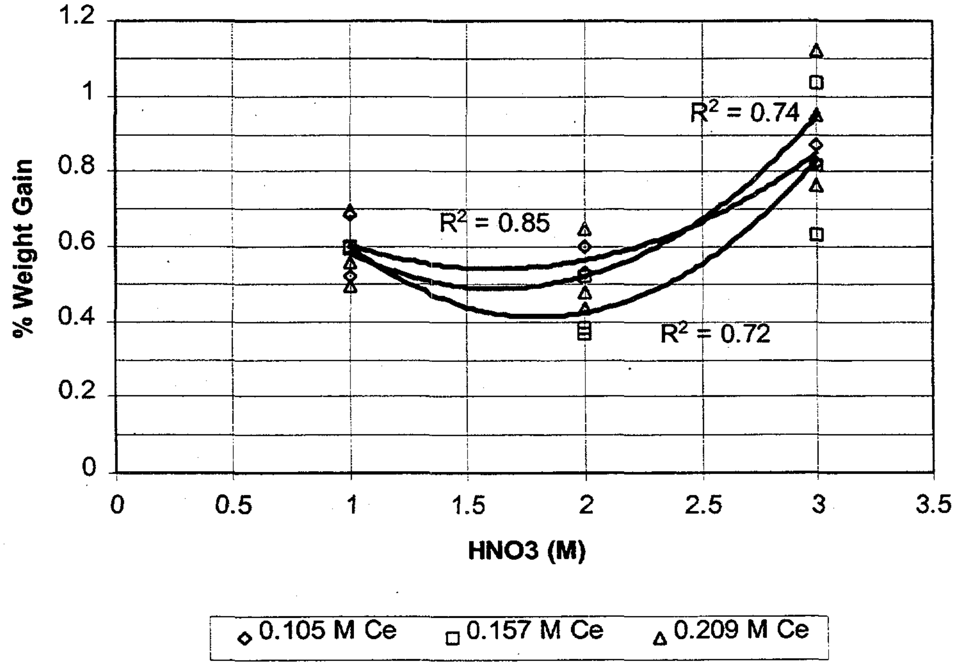

Figure 2. Calcined Product Weight Gains After 24 Hr vs. HNO_3

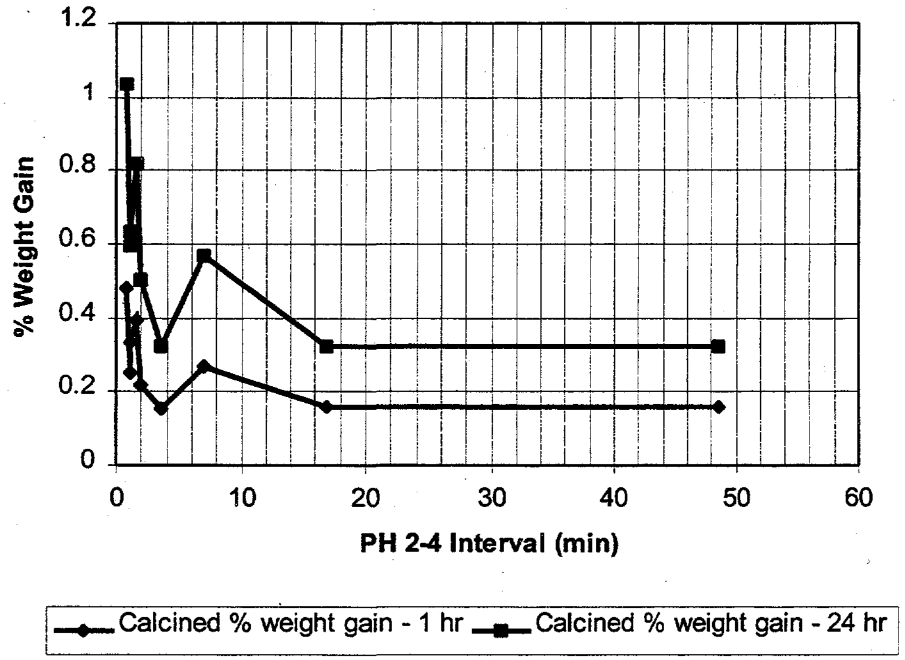

Figure 3. Effect of Neutralization Rate on Weight Gain for 0.157 M Ce/3 M HNO_3

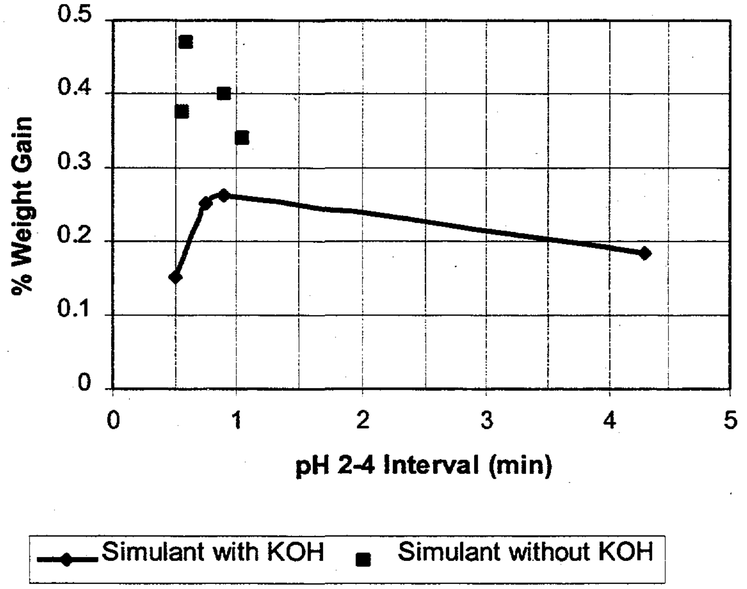

Figure 4. Effect of Neutralization Rate on Weight Gain for 0.052 M Ce/3 M HNO_3 With and Without 0.1 M KOH Added

The methods used for drying wet filtercake and the calcination temperature were examined in limited testing to determine if they affect the weight gain and the density (see Section 2.1.3) of the calcined product (Table 1). The wet filtercake from selected tests was split, with half dried on a hot plate and half dried in a furnace and calcined at 950°C. The weight gain of the filtercake that was dried and crumbled to a coarse powder on the hot plate was ~50% of the weight gain from the sample dried in the furnace (Table 1). Further tests are needed to confirm this trend under different conditions of rinsing and solution composition. However, the single result suggests that drying on a hot plate is a reasonable practice for minimizing the weight gain.

Table 1. Effect of Drying Method and Calcining Temperature on Weight Gain and Density

Test Conditions	Drying Conditions	Calcining Conditions	1-Hr Weight Gain, %	24-Hr Weight Gain, %	Calcined Tapped Density, g/L
0.157 M Ce/2.5 M HNO_3 single sample – recalcined (950°C, 1000°C)	Oven set at 500°C for 2 hr	950°C for 2 hr	0.30	NA	NA
		1000°C for 2 hr	0.22	0.58	2.15
0.209 M Ce/1 M HNO_3 two filtercakes rinsed once with one filtercake volume of DI water – recalcined (950°C, 1000°C)	Oven set at 500°C for 2 hr	950°C for 2 hr	0.22	0.42	2.71
		1000°C for 2 hr	0.14	0.22	2.82
0.052 M Ce/3 M HNO_3 – split sample	Oven set at 500°C for 2 hr	950°C for 2 hr	0.40	NA	NA
		1000°C for 2 hr	0.32	0.78	1.49
0.052 M Ce/3 M HNO_3 prototype tests average of 3 tests – split sample	Oven set at 500°C for 2 hr	950°C for 2 hr	0.40	0.77	1.67
		1000°C for 2 hr	0.31	0.46	1.69
0.209 M Ce/1 M HNO_3 Rinsed once with one filtercake volume of DI water	Oven set at 500°C for 2 hr	950°C for 2 hr	0.151098	0.28	2.87
	Hotplate drying at highest setting (~450°C)	950°C for 2 hr	0.088876	0.18	2.75

A limited number of tests were also conducted with the simulant, but without KNO_3 added, to determine the effect of the calcining temperature on the weight gain. In these tests wet filtercake samples were split with half calcined at 950°C and half calcined at 1000°C and samples calcined at 950°C and then recalcined at 1000°C. It was found that increasing the calcining temperature by 50°C reduces the 1-hr weight gain by 20% to 33% (Table 1).

2.1.3 Calcined Filtercake Volume

Because the available vault storage space at PFP is limited, it is critical that the volume of the calcined material generated from the $Mg(OH)_2$ process be minimized. If the average calcined filtercake density is less than 2 g/cm^3, then vault storage space will not be adequate. Previous testing with actual solutions at PFP and testing at RFETS resulted in densities of calcined product well below 2 g/cm^3. Additionally, PNNL testing with surrogates revealed operating conditions that can result in a low-density calcined product.

Strategies to reduce the volume of the calcined filtercake or increase the bulk density include increasing the calcination temperature by 50°C to 100°C; rinsing the wet filtercake with deionized water; and basing the amount of excess $Mg(OH)_2$ used in the process on a molar quantity as opposed to a percent of stoichiometry.

The volume of calcined filtercake depends on both the mass of filtercake and its density. The mass of the filtercake depends on both the mass of precipitated solids and the mass of dissolved solids in the interstitial liquid of the wet filtercake. The mass of precipitated solids for a specific solution is fixed by the concentration of cerium in the solution, which precipitates quantitatively as $Ce(OH)_2$ and excess $Mg(OH)_2$ added to the solution beyond that required to neutralize the acid and precipitate the cerium. The latter increases with increasing cerium and acid concentration in the starting solution because it is based on 8% of the stoichiometric requirements to neutralize the solution to a pH of 7. As the stoichiometric requirements increase, the quantity of excess $Mg(OH)_2$ correspondingly increases. The mass of dissolved solids, in turn, depends on the volume of the wet filtercake (due to its porosity), as well as the concentration of the dissolved species $[Mg(NO_3)_2]$ in the interstitial liquid.

Figure 5 shows how the volume of the calcined filtercake varies with both the cerium and nitric acid concentration in the initial solution. The volume of calcined filtercake increases with increased cerium concentration at all acid concentrations. On the other hand, the sensitivity of the calcined filtercake volume to changes in the acid concentration depends on the cerium concentration, with the higher cerium concentrations producing a much greater volume increase between 2 and 3 M acid concentrations.

The calcined product weight, as shown in Figure 6, remains fairly constant between 1 and 2 M HNO_3 for all three cerium concentrations evaluated. This implies that the increase of excess $Mg(OH)_2$ in the filtercake is compensated by a decrease in the $Mg(NO_3)_2$ in the interstitial liquid accompanying a decrease in the wet filtercake volume. At the same time, the density of the calcined filtercake decreases with decreasing HNO_3 concentrations for all three cerium concentrations, as shown in Figure 7. The net result is a modest increase in the calcined filtercake volume as the initial HNO_3 concentration is increased from 1 M to 2 M (Figure 5).

Between 2 and 3 M HNO_3 the filtercake mass increases due to an increase in the wet filtercake volume (increasing the interstitial liquid inventory), the $Mg(NO_3)_2$ concentration in the interstitial liquid, and an increase in the excess $Mg(OH)_2$. The density of the calcined filtercake also increases for the 0.105 and 0.157 M cerium concentrations so that the net effect is a leveling off of the calcined filtercake volume with increasing initial acidity of the solution (Figure 7). At 0.209 M cerium, however, the density continues to decrease between 2 and 3 M HNO_3, causing an increasing rate of volume increase with acid concentration (Figure 5). The cause for the different behavior of the calcined filtercake for the higher cerium and acid concentrations was not further evaluated, except to note that x-ray diffraction analysis did not reveal any phases other than CeO_2 and MgO in the calcined filtercake.

The neutralization rate was also found to have a small but significant effect on the bulk and tapped density and volume of the calcined filtercake. An examination of the calcine density and calcine volume vs. the pH 2-4 time interval during the source test series and neutralization test series (Figure 8) suggested an apparent tapped volume minimum at a time interval of about 1 to 3 min, even though the density of the calcined filtercake was relatively constant. Similar test results were obtained from the prototype system using a simulant (0.052 M Ce/0.1 M KNO_3/3 M HNO_3), as shown in Figure 9. The limited data available from the prototype tests suggest that time intervals less than 1 min could cause a substantial increase in the calcined filtercake volume (as much as 100%).

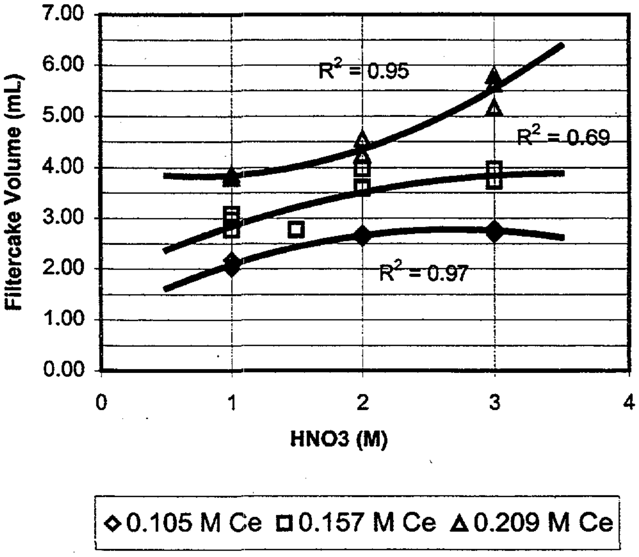

Figure 5. Calcined Filtercake Volume vs. HNO_3 Concentration (Initial Solution = 200 ml)

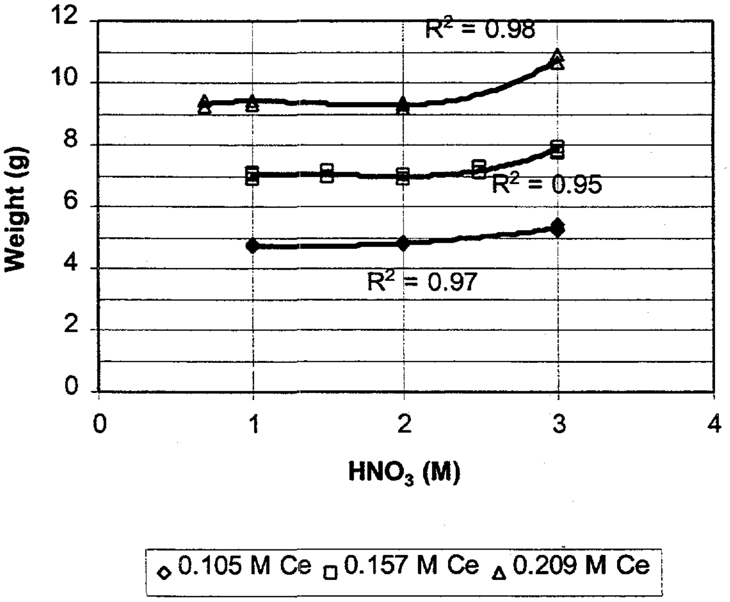

Figure 6. Calcined Filtercake Weight vs. HNO_3 Concentration (Initial Solution = 200 ml)

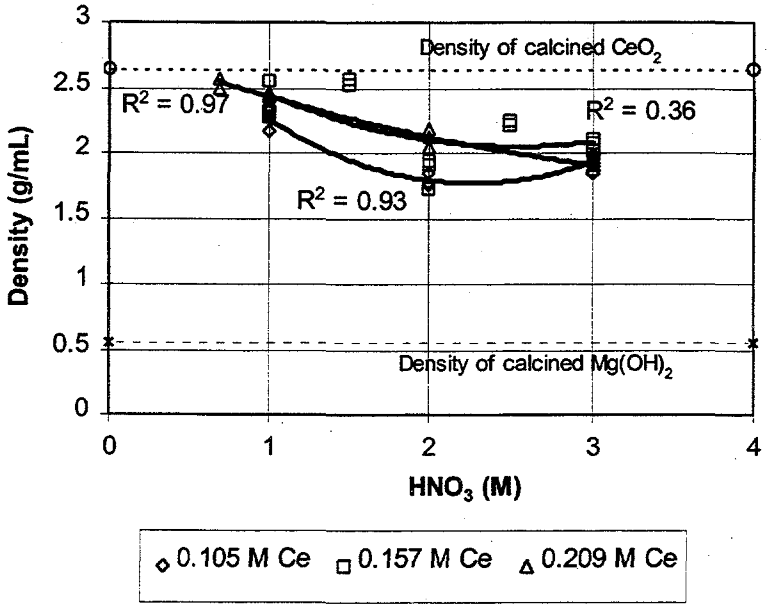

Figure 7. Calcined Filtercake Density vs. HNO_3 Concentration

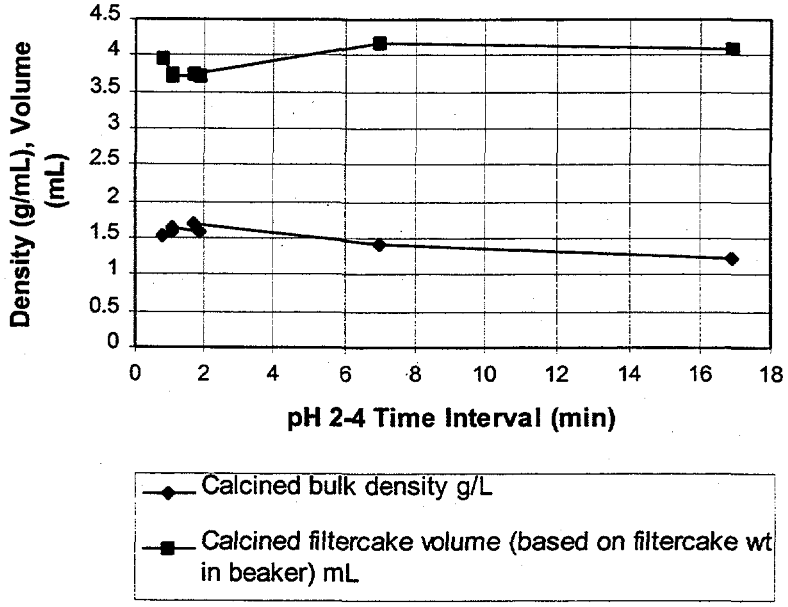

Figure 8. Calcined Filtercake Volume vs. pH 2-4 Time Interval – Neutralization Test Series

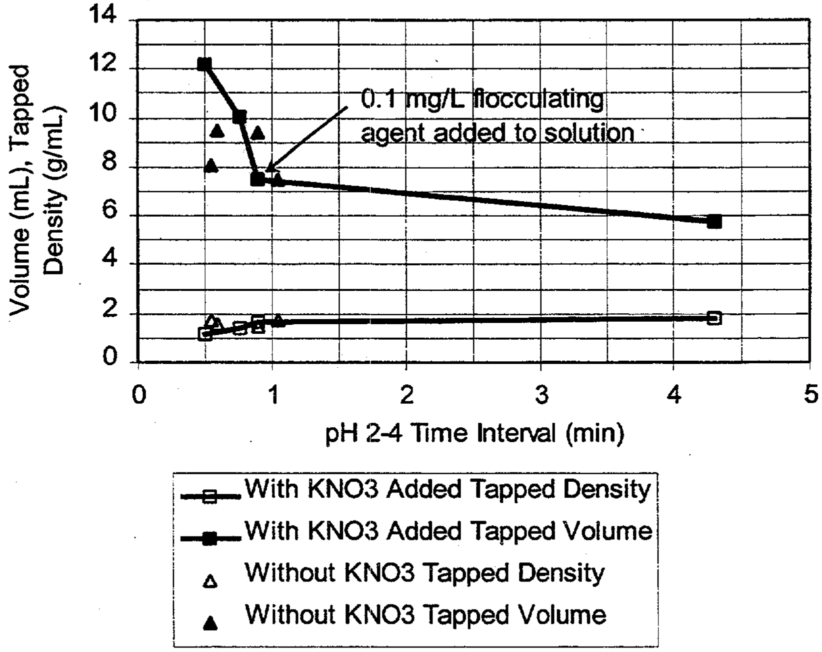

Figure 9. Calcined Filtercake Tapped Density and Volume vs. pH 2-4 Time Interval for Simulant – 0.052 M Ce/3 M HNO_3 (Tests Conducted in Prototype Reactor)

The addition of a flocculating agent was briefly examined to determine whether it potentially affects the volume of the calcined filtercake. A plot of the calcined volume vs. pH 2-4 interval (Figure 9) suggests that the presence of a flocculating agent in one of the tests did not have a pronounced effect on the calcined filtercake volume relative to the more pronounced effect of the pH 2-4 time interval, even though the volume of the wet filtercake was about 50% greater for this particular test. The concentration of flocculating agent used was consistent with the baseline process flowsheet (i.e., about 100 times greater than is typically added to a precipitation system).

The effects of the drying method on density were investigated using wet filtercake from a rinsing test (0.209 M Ce/1 M HNO_3 – that was rinsed with one filtercake volume of deionized water), which was split into two samples before drying. One split sample was dried in a furnace for 2 hr at 500°C, and the other split sample was dried on a hot plate for 2 hr at the highest setting (at least 450°C as measured by a thermocouple placed in the middle of a sample) with periodic stirring to crumble the material to a coarse powder. Both split samples were then calcined in the furnace at 950°C. The samples had densities that differed from their average value by about 2%.

The effect of calcination temperature on product density was examined (Table 1). The filtercakes from several tests were split with one split calcined at 950°C and the other at 1000°C. The average densities of the calcined split samples differed by less than 4%.

2.1.4 Wet Filtercake Volume

The physical properties and volume of the wet filtercake have an impact on the filtration rate, the frequency at which the filter must be scraped, and the muffle furnace/calciner throughput. The filtercake volume also affects the subsequent calcined filtercake volume and LOI properties, as well as the filtration time.

Testing with surrogates has shown that under certain planned operating conditions (e.g., 50 g/L plutonium and 1 M HNO_3), the volume of filtercake generated will likely exceed the physical capacity of the available volume within the process filtration system (when processing three batches). Excessive wet filtercake volume adversely affects the filtration rate and increases the number of boats that must be calcined.

Besides the feed composition, factors that affect the volume of the filtercake include initial solution acidity, excess $Mg(OH)_2$, flocculating agent dosage, and neutralization rate [tied to the excess $Mg(OH)_2$ to some extent]. The type and concentration of solution impurities will also affect the wet filtercake volume; however, these effects have not been investigated. The following strategies can be used to reduce the volume of the wet filtercake: decrease excess $Mg(OH)_2$; eliminate the flocculating agent; and avoid diluting a solution to an initial acidity < 2 M HNO_3. However, it is likely that operating sequences for certain feed solutions will need to be modified to include more frequent filtercake removal.

Analysis of the filtercake from the baseline tests, as shown in Figure 10, indicates it reaches a minimum volume between 2.0 and 2.5 M HNO_3 in the feed. However, there is considerable scatter in the data, particularly for the 0.157 M cerium concentration, which is attributed to the challenge of accurately measuring the volume of the wet filtercake. Figure 11 shows the effect of the feed acidity on the weight of the filtercake, which is more accurately measured and should be closely correlated to the filtercake volume. It can be seen that the mass of the filtercake decreases significantly through contraction of the filtercake between 1 and about 2.3 M HNO_3, although the total inventory of $Mg(OH)_2$ has increased and the concentration of $Mg(NO_3)_2$ is greater. The filtercake texture also changed from a crystalline to a more clay-like appearance and behavior.

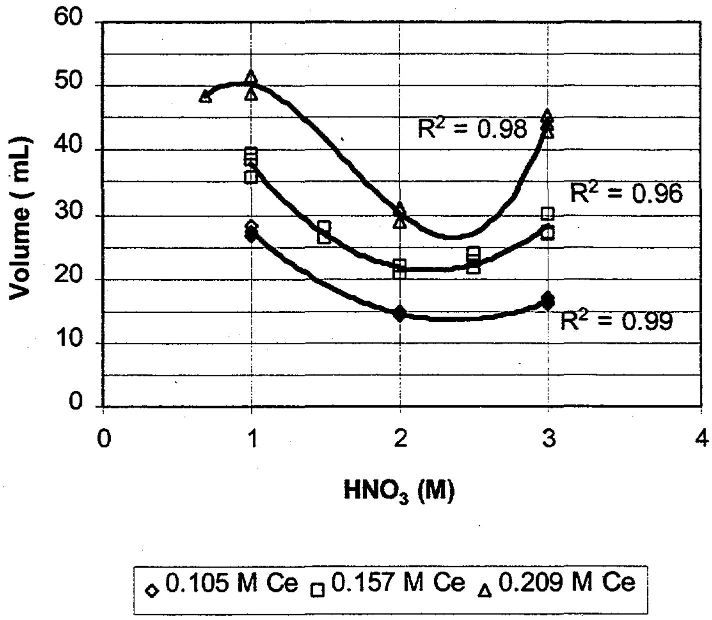

Figure 10. Wet Filtercake Volume vs. HNO_3 Concentration (Initial Solution = 200 ml)

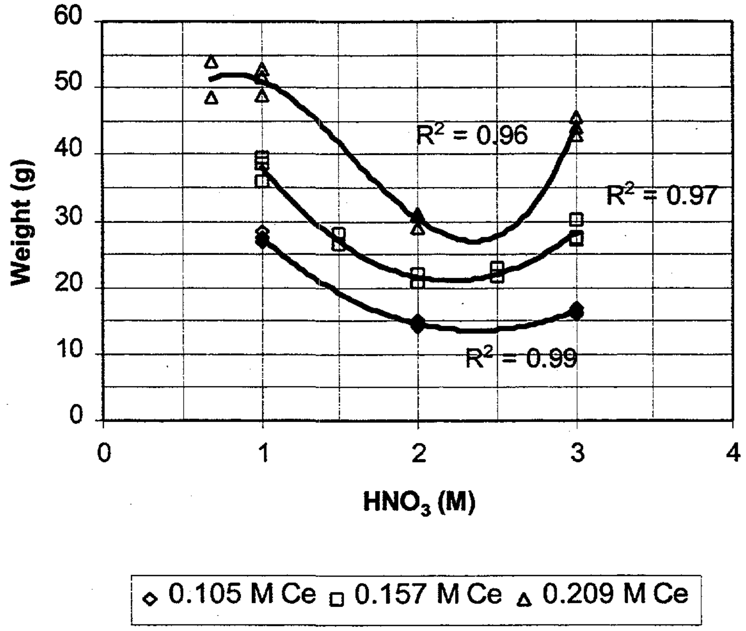

Figure 11. Wet Filtercake Weight vs. HNO_3 Concentration

2.1.5 Cerium Surrogate Confirmation

The use of cerium as a surrogate allowed a large number of tests to be conducted quickly at a much lower cost. At RFETS and LANL, Ce(IV) was used as a surrogate for Pu(IV) to evaluate the $Mg(OH)_2$ process for treating HNO_3 solutions containing plutonium. Cerium(IV) is the best available surrogate for Pu(IV) for the simulant tests because the chemical reactions are similar, producing a $CeO_2 \cdot xH_2O$ precipitate analogous to the $PuO_2 \cdot xH_2O$ precipitate (Cotton and Wilkinson 1988). The physical characteristics of the dried cerium precipitate are expected to be representative of the precipitate containing $PuO_2 \cdot xH_2O$, and the $Mg(OH)_2$ should contribute to the calcined product density in a proportional manner. However, testing with actual PFP solutions is ultimately needed to confirm the trends identified from the results of the simulant testing.

A prototype sparge reactor system was designed, built, and provided to PFP for bench-scale testing with actual solutions. Testing will be underway in July through September 2000.

2.2 Operability Challenges

This section describes issues related to operability and throughput of the process: neutralization time, filtration time, foaming, plugging, and gel formation. Recommended resolutions are also discussed.

2.2.1 Neutralization Time

Neutralization time refers to the amount of time needed to neutralize the acidic solutions to a pH of 6.8, at which time the precipitation is complete. The processing time required to perform the neutralization and subsequent slurry filtration affects the rate at which PFP solutions can be processed. It has also been found to affect the weight gain and density properties of the calcined filtercake, as discussed in Sections 2.1.2 and 2.1.3.

Three primary parameters affect the neutralization rate:

- reactivity of the $Mg(OH)_2$ [determined from the source of $Mg(OH)_2$]
- amount of excess $Mg(OH)_2$ added to the solution
- mixing rate.

Ideally, the $Mg(OH)_2$ used in the precipitation should be reactive so that the other two factors provide the means to control it.

The reactivity of the $Mg(OH)_2$ is related to its preparation method. Material with a small particle size and high internal surface area will be more reactive than material with larger particles. Tests were conducted with $Mg(OH)_2$ from several vendor sources, as well as two vendor sources of MgO that will hydrate to $Mg(OH)_2$ when added to solutions. Of the materials tested, the Fluka BioChemika $Mg(OH)_2$ was found to have the fastest neutralization rate.

Excess $Mg(OH)_2$ is required because the material has a low solubility limit as a solution approaches a pH of 7, and relatively slow dissolution kinetics (related to particle size porosity and internal surface area). Increasing the $Mg(OH)_2$ inventory above that required for neutralization to pH 7 provides a greater surface area for dissolution, thereby increasing the rate of replenishment of OH^- in the solution. At the same time, the neutralization rate increases as the mixing rate increases, because OH^- is more effectively removed from the particle surface. In turn, the OH^- concentration near the particle surface is reduced where dissolution is taking place.

Data from the baseline tests were evaluated to investigate the effect of excess $Mg(OH)_2$ on the neutralization rate. While all baseline tests used 8% excess $Mg(OH)_2$, different combinations of cerium and acid concentrations produced different stoichiometric requirements on a molar concentration basis and, in turn, different excess quantities $Mg(OH)_2$ on a molar basis.

Beaker tests (200 mL of solution in a 400-mL beaker) were conducted with a Corning stir-plate operated at about 80% of the maximum stirring rate, which was needed to achieve acceptable neutralization rates. Figure 12 shows how the pH 2-4 time interval varied with excess $Mg(OH)_2$. There appears to be a significant correlation between the pH interval time and the excess $Mg(OH)_2$. This figure also suggests that 0.09 M excess $Mg(OH)_2$ and above will achieve pH 2-4 time intervals of less than 2 min for the beaker tests.

The inverse of the pH 2-4 time intervals was used to calculate an average neutralization rate over this critical pH range for the baseline test series. Comparing the neutralization rate to the excess $Mg(OH)_2$ showed a fairly good linear correlation between the neutralization rate and the excess $Mg(OH)_2$.

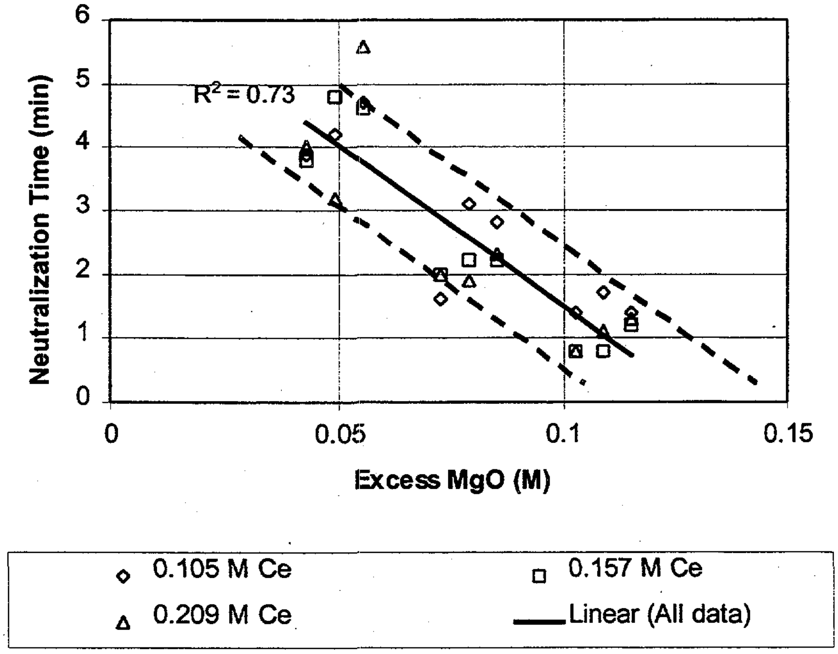

Figure 12. The pH 2-4 Neutralization Time vs. Excess $Mg(OH)_2$

Including either the initial acid concentration or the inverse of the cerium concentration significantly improved the correlation. The best empirical correlation was:

$$\frac{1}{\text{(pH 2 - 4 time interval)}} \propto \frac{[\text{excess Mg(OH)}_2]^{1.2}}{(0.05 - [\text{Ce}])} \qquad (6)$$

This correlation is shown in Figure 13. The linear trend-line R^2 squared value is 0.71 using Microsoft Excel 2000 software. The factor in the denominator of the correlation includes a constant (0.05) to account for the limiting rate for neutralization of pure nitric acid and is based on one experiment neutralizing 3 M HNO_3 with 8% excess $Mg(OH)_2$. If the nitric-acid-only data point is included in the set, a correlation with slightly different constants produces an R^2 of 0.85 with the Y intercept set to zero.

The inverse relationship of the neutralization rate with the cerium concentration is believed to be caused by its buffering effect in this pH range where cerium hydroxide precipitation takes place. The first order relationship of the neutralization rate with the initial acid concentration is believed to reflect an effect of temperature (i.e., heat of acid neutralization) on the neutralization rate because, over the interval of interest, the actual acid concentration would be the same for all experiments (limited only by the ability of the pH probe to measure the actual pH during a transient condition).

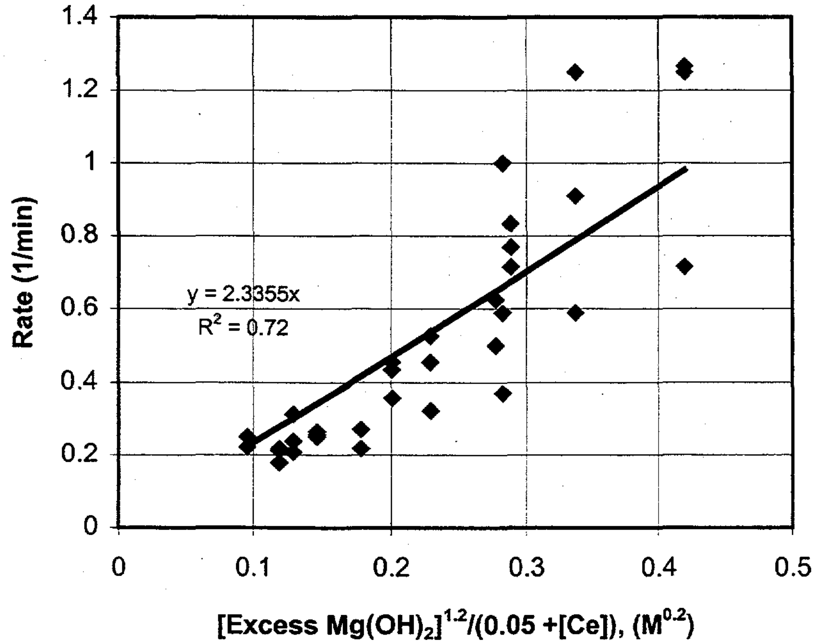

Figure 13. Correlation of Neutralization Rate (pH 2-4) and Excess $Mg(OH)_2$

While there is a relatively good fit between the data and the correlation, there is still considerable scatter in the data. This scatter is probably due to variations in the mixing characteristics for individual experiments. Even though the mixing rate was constant, there was considerable size variation in the $Mg(OH)_2$ solids agglomerations. The sizes varied with the initial acid concentration and from the ways the solid became wetted after addition to the beaker. The relationship may be suitable for estimating adjustments in the amount of excess $Mg(OH)_2$ needed once the pH 2-4 time interval has been measured for one batch of solution, pending verification of the correlation with plutonium and in the larger-scale reactor. Further testing is needed to confirm this correlation and the general relationship between molar excess $Mg(OH)_2$ and the neutralization rate. Similar tests using a flocculating agent are also needed to determine whether its presence affects the neutralization rate.

A limited number of tests using the prototype system were conducted to investigate the effect of the air sparge flow rate on the neutralization time. Tests were conducted using two simulants 0.052 M Ce/0.1 M KNO_3/3.0 M HNO_3 and 0.209 M Ce/1.0 M HNO_3. It was determined that higher air sparge flow rates were required for the 0.209 M Ce/1 M HNO_3 simulant (300 mL/min sparge rate) to achieve pH 2-4 time interval comparable to the same simulant in the beaker tests than for the 0.052 M Ce/0.1 M KNO_3/3.0 M HNO_3 simulant (80 mL/min). Furthermore, it was found that the neutralization rate decreased markedly above a pH of about 4 for the 0.209 M Ce/1 M HNO_3 simulant even at a 300-mL/min air sparge flow rate, resulting in much longer time required to achieve a pH of 7 (Figure 14). This effect was not evident in the other simulants, except at a very low air sparge flow rate of 50 mL/min. Further evaluation is needed to determine the significance of this phenomenon.

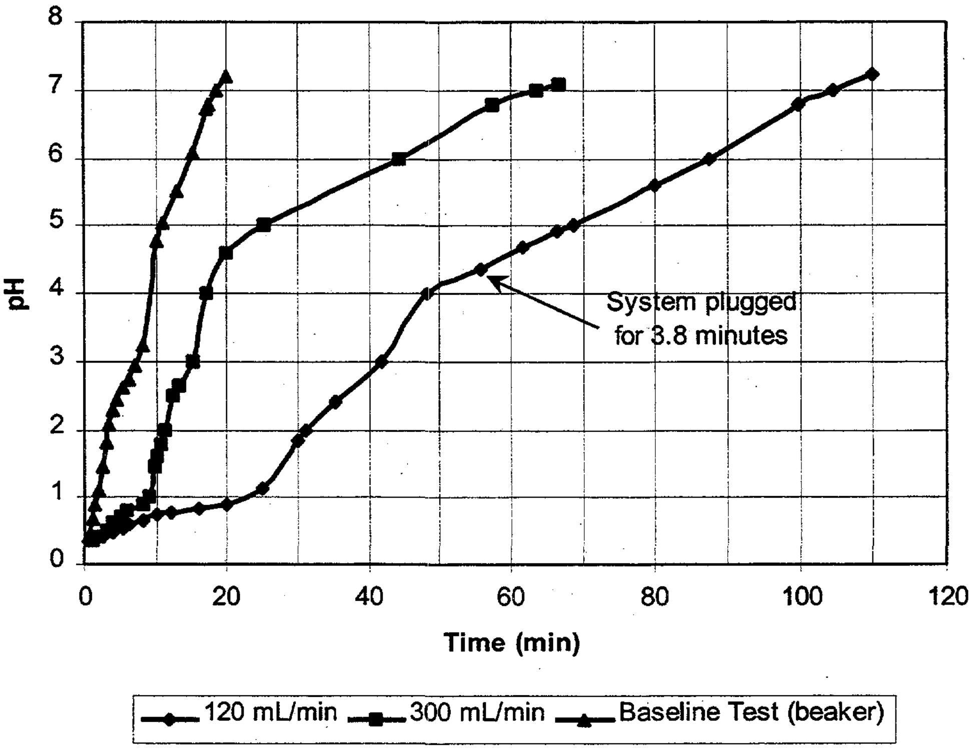

Figure 14. Effect of Air Sparge Rate on Neutralization Rate for 0.209 M Ce/1 M HNO_3

2.2.2 Filtration Time

The filtration time depends on several factors including, but not limited to, the total mass of the solids and liquid in the slurry, the filter area, and the pore structure of the filtercake being formed. The total mass of the liquid in the slurry affects the filter time by establishing how much fluid will pass through the filter, which should increase the filtration time as the amount of liquid increases. Similarly, the mass of solids affects the filtration time because as the filtercake is formed, a greater mass of solids produces a greater thickness of filtercake, which in turn increases the resistance to flow. The filter area influences the filtration time in two ways. First, an increased filter area decreases the thickness of the filtercake for a given mass of solids. Second, increased filter area increases total flow of liquid through the filter for a given flow per unit area of filter surface.

The pore structure of the filtercake depends on a number of factors, including the particle size distribution, particle shape, and particle surface charge effects. The particle size distribution for the filtercake produced from neutralization of the cerium/nitric acid solutions is influenced by the initial particle size distribution of the $Mg(OH)_2$, the degree of uniformity of $Mg(OH)_2$ solids dissolution, and the rate of neutralization. The latter affects both the propensity to form polymeric hydrous cerium oxide and the crystal growth of crystalline hydrous cerium oxide. The uniformity of dissolution is affected in part by the formation of precipitate on the curd-like solids particles upon wetting in the solution, causing a diffusion barrier to the internal solids in the curd. This barrier may be affected to some extent by the mixing rate.

Quantifying the filtration time depends on the degree of dewatering desired. The total filtration time for all tests was based on filtering to a <1 drip/min filtration rate using a 70-mm-diameter filter. However, in many cases, the filtercake partially lifted from the filter as the filtercake compressed due to dewatering. A second measurement was the time required for filtering the slurry to the point where the surface of the resulting filtercake was mostly uncovered and had not begun compression. This measurement is expected to provide a better estimate of the effects of various parameters on the filtering properties of the slurry. Figure 15 shows the relationship of these two measurements for the baseline tests. It can be seen that the total filtration time was roughly twice that required to uncover the filtercake surface.

The data from the baseline test series was evaluated to investigate the effects of the cerium and initial acid concentrations on the filtration rate. The cerium concentration would be expected to increase the filtration time by increasing the total mass of solids [both $Ce(OH)_4$ and $Mg(OH)_2$] to be filtered. Higher initial solution acidity would also be expected to increase the total solids because of the excess $Mg(OH)_2$ added. Higher acidity also increases the neutralization rate, which would decrease the particle size of the cerium oxide and reduce the likelihood of producing polymeric hydrous cerium oxide. Furthermore, increasing the acid concentration also changes the electrolytic strength of the solution, which can affect the intraparticle separation in the filtercake.

Figure 16 shows the effect of the cerium concentration on the filtration time for the various acid concentrations. There is a general trend of increasing filtration time with increasing cerium concentration in 1 and 3 M HNO_3 solutions. However, there does not appear to be a similar trend at 2 M HNO_3. Furthermore, the figure shows the minimum filtration time occurs for all cerium concentrations at 2 M HNO_3.

Figure 17 presents the data slightly differently by comparing the filtration time with the solution acidity. Additional data at 1.5 and 2.5 M HNO_3 at 0.157 M cerium, and 0.69 M HNO_3 at 0.209 M cerium were also evaluated to better develop any trends. From this figure, there is a minimum filtration time between about 1.6 and 2.2 M HNO_3, with the minimum shifting to the lower values at lower cerium concentrations. It also appears that the filtration time begins to either level off or decrease below 1 M HNO_3 for the 0.209 M cerium solutions, which is consistent with the wet filtercake weight and volume, which also level off below 1 M HNO_3. Qualitatively, the decrease in the filtration time from 1 to 2 M HNO_3 is accompanied by a change in the texture of the wet filtercake (more crystalline-like at 1 M HNO_3 and more clay-like at 2 M HNO_3) and a significant decrease in the wet filtercake volume. Apparently, an increased resistance of the pores to flow does not accompany the contraction of the filtercake. Between 2 and 3 M HNO_3 the filtercake maintains its texture while increasing its filtercake thickness, resulting in an increased filtration time. Between 0.69 and 1.0 M HNO_3 the texture of the wet filtercake also appears to remain about the same and may account for the increased filtration time in this region.

The neutralization rate also appears to affect filtration rate. Qualitatively it was noted that tests conducted at the same test conditions, but with significantly different pH 2-4 time intervals, had filtration rates that differed in a fairly consistent manner. The baseline data were evaluated to compare the filtration rates at different pH 2-4 time intervals. As shown in Figure 18, there does appear to be a trend of longer filtration times for pH 2-4 time intervals that decrease below about 2 min, and a less pronounced increase in filtration times for pH 2-4 time intervals above 3 min. As indicated earlier, the lowest filtration rates occur at 2 M HNO_3. However, there is considerable overlap of acid values (2, 2.5, and 3 M HNO_3) in the

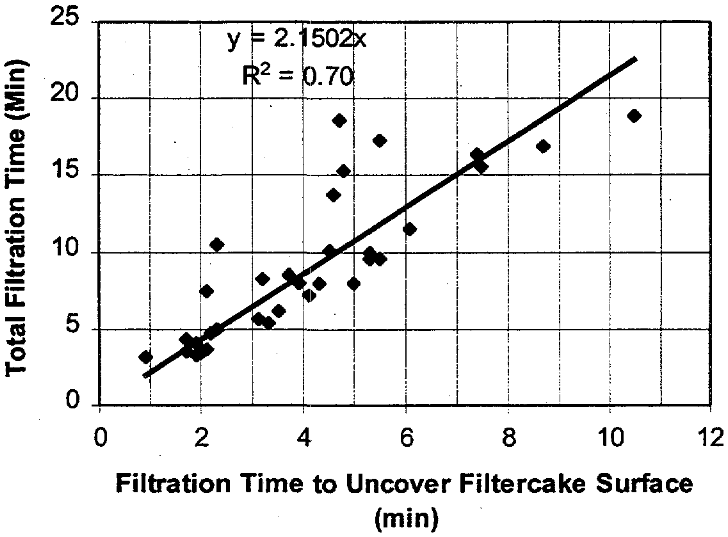

Figure 15. Total Filtration Time vs. Filtration Time to Uncover Filtercake Surface

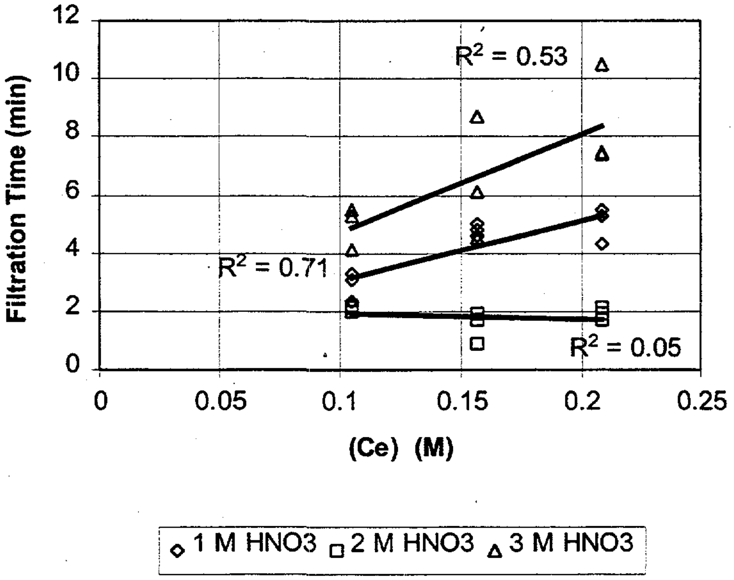

Figure 16. Filtration Time vs. Cerium Concentration

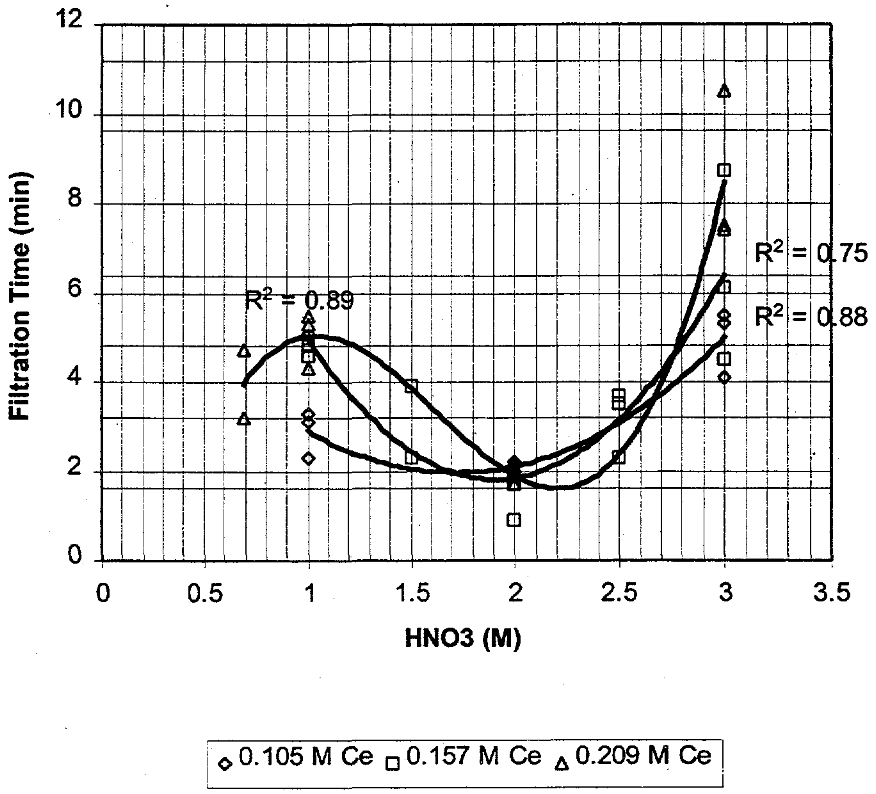

Figure 17. Filtration Time vs. HNO_3

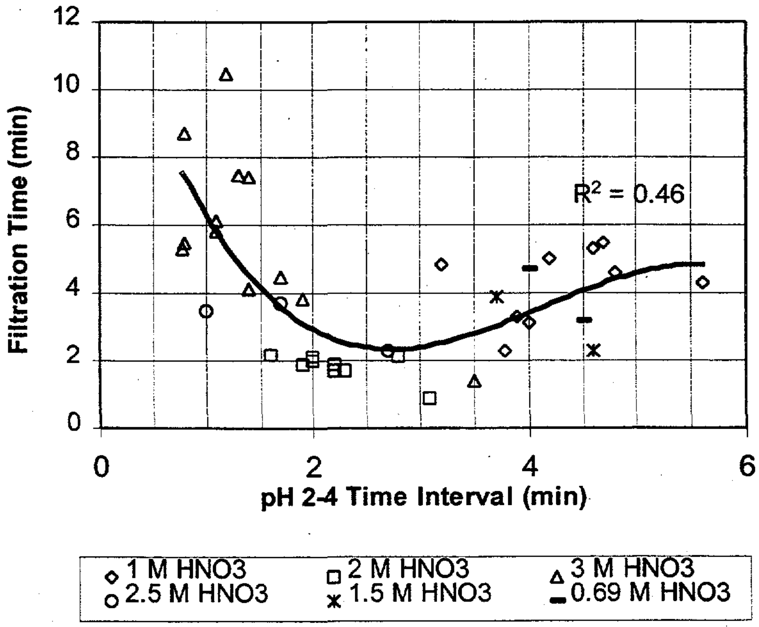

Figure 18. Filtration Time vs. pH 2-4 Interval

pH 2-4 time interval range of 1.5 to 3, suggesting that the apparent effect is not exclusively an artifact of the initial solution acidity. The implication of this figure is that the filtration rate is affected by both the neutralization rate and the initial acid concentration. This trend was also observed in prototype system tests with the simulant, which had very short neutralization times as shown in Figure 19. At the lower pH 2-4 time intervals, the effect is likely due to the formation of smaller $Ce(OH)_4$ particles in the precipitate that offer greater resistance to filtration.

Several tests were conducted as part of the filtercake rinsing test series in which the slurries from two or three separate batches of precipitate were added to the same filter. In some tests, each batch of slurry was filtered until there was no flow through the filter and the filtercake was compressed and cracked before the next batch was added to the filter. In other tests, each batch of slurry was filtered only until the filtercake surface was uncovered but not compressed before the next batch of slurry was added. In both cases, rinse water was added to the filter after the last batch of slurry had been filtered to the point where the surface was just uncovered.

The results of these tests, illustrated in Figures 20 and 21, show several important trends. First, the filtration time for a second slurry layered on top of an uncompressed filtercake takes three times as long as the time to filter only one slurry. Similarly it takes, approximately twice as long to filter a second slurry on top of a compressed filtercake as it does to filter a second slurry on top of an uncompressed filtercake. For the 0.105 M Ce in 3 M HNO_3 solution, the filtration of a third filtercake takes approximately 1.9 times as long to filter as the second filtercake for both uncompressed or compressed filtercakes. The rinsing time is also impacted by the number of filtercakes. In the case of the 0.105 M Ce/3 M HNO_3 solution, rinsing time through three filtercakes increased by a factor of 6 (relative to the time required to rinse a single filtercake) for both uncompressed and compressed filtercakes. For the 0.209 M Ce/1 M HNO_3 solution, the average rinse time through two filtercakes increased 2.4 times (relative to the time required to rinse a single filtercake) for both sets of filtercakes.

The filtration time data show that process throughput could potentially be increased by removing the filtercake between each precipitator batch filtered. For example, the total filtration time to filter three slurries by filtering each on a separate filter (or scraping the filter between filtrations), will take about 3x10=30 min, not counting the time to set up between filtrations. In comparison, it will require between 75 and 120 min for the 0.105 M Ce/3 M HNO_3 solution to filter all three slurries on the same filter. These differences allow for between 45 and 90 min to change two filters between filtrations if only one slurry is placed on each filter or to scrape a single filter between slurries. For the 0.209 M Ce/1 M HNO_3 solution, the total time for filtering two slurries individually, not including the setup time between filtrations, is about 40 min. Filtering the two slurries on the same filter will require between 65 and 80 min. These differences allow for between 25 and 40 min to change out or scrape one filter between filtrations if only one slurry is placed on each filter. In addition, with the 0.209 M Ce/1 M HNO_3 solution, more operator time is required to incrementally add slurry to the filter system as free board is lost (i.e., occupied by voluminous filtercake). With the present PFP filter design there is insufficient free board to add a third slurry to the filter, even in very small increments, because the volume of uncompressed filtercake from three slurries is greater than the capacity of the filter.

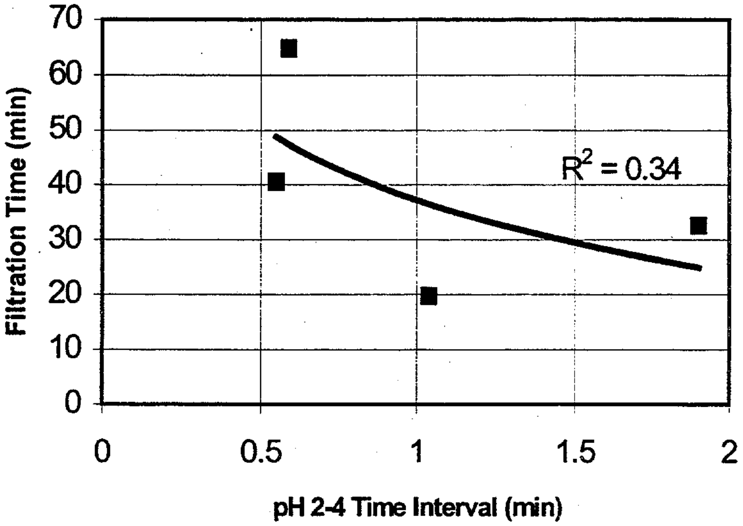

Figure 19. Filtration Time vs. pH 2-4 Time Interval – Very Short Neutralization Times

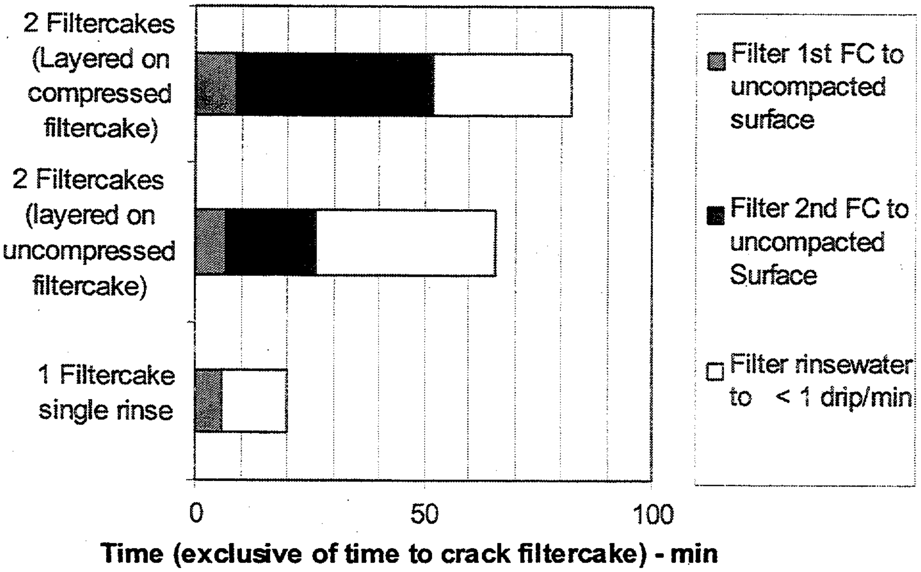

Figure 20. Filtration Times for Stacked Filtercakes Rinsed with 1 Volume of a Single Compacted Filtercake (0.209 M Ce/1 M HNO_3)

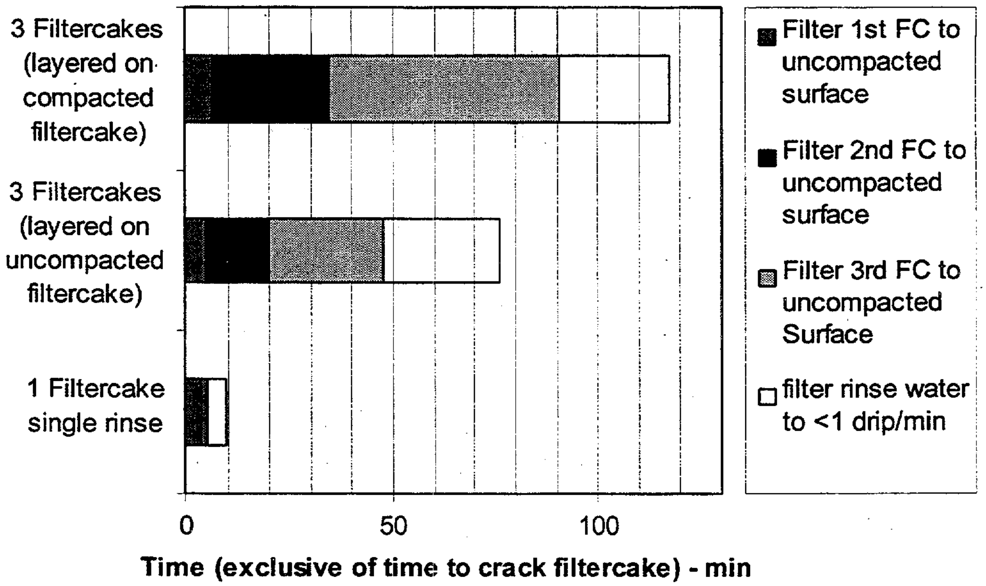

Figure 21. Filtration Times for Stacked Filtercakes Rinsed with 1 Volume of the Total Compacted Filtercake (0.105 M Ce/3 M HNO_3)

2.2.3 Foaming and Plugging in the Precipitator

Foaming in the sparge reactor has been observed during previous small-scale testing of the process with PFP solutions. However, significant foaming has not been observed during the extensive testing with simulants, conducted with high purity $Mg(OH)_2$ and with and without flocculating agents. Plugging of the sparge reactor outlet line was observed at RFETS and during one simulant test at PNNL. In the simulant test, the plug was removed by sparging air through the line.

At this time, a resolution strategy for foaming is not warranted. If foaming does occur in the full-scale system and it appears to be the result of chemical reaction, then the quality of the $Mg(OH)_2$ reagent should be evaluated to determine if it contains an appreciable quantity of carbonates. Also, it may be possible to mitigate foaming by decreasing the air sparge rate (reducing process throughput) or by adding anti-foaming agents. Further testing is recommended to better understand the conditions conducive for plugging and to develop a refined recovery strategy.

2.2.4 Gel Formation in the Precipitator

Gel formation and associated mixing problems were observed for several of the tests during baseline testing. Gel formation is a transient behavior occurring shortly after the yellow precipitate first forms at a pH of about 2 and continuing until a pH of about 5 when the precipitate turns tan. In the beaker tests, gel formation caused stratification of the pH in the 400-mL beaker, where pH was comparatively lower in regions where there was no mixing. As shown in Table 2, gel formation resulting in mixing problems was not observed at any of the solution acidities for the 0.105 M Ce (IV) solutions (Ce concentrations corresponding to Pu at 25g/L). However, there were more significant mixing problems at 0.157 M Ce(IV) (Pu equivalent, 37.5 g/L) at 1 and 3 M HNO_3, and at 2 M HNO_3 for the 0.209 M Ce(IV) solution (Pu equivalent 50 g/L). Gel formation was severe at 1 and 3 M HNO_3 for the 0.209 M Ce(IV) solutions, to the extent that most of the slurry did not mix.

In the prototype reactor system, the air sparge was able to effect good solids mixing even in the presence of thick gel. However, it was previously noted (Section 2.2.1) that the neutralization rate did significantly decrease above a pH of 4 for a simulant that produced significant gel formation. This may or may not directly relate to gel formation, because the reduced neutralization rate persisted well after the gel disappeared. Depending on how other constituents behave, gel formation may adversely affect neutralization time in the full-scale system at PFP. However, based on its apparent lack of impact to the performance of the prototype system, no further investigation of gel formation with simulants is warranted at this time, except in conjunction with investigations into the air sparge flow rate effects on the neutralization rate above a pH of 4 for certain simulants.

2.3 Filtrate Quality and Disposition

The filtrate must meet certain requirements for disposition to the Hanford DSTs, including limits on plutonium concentration and suspended solids.

2.3.1 Plutonium Concentration in the Filtrate

Plutonium concentration in the filtrate is limited to <330 mg/L to meet tank waste acceptance criteria. Waste with plutonium concentrations between 1 mg/L and < 330 mg may be transferred to the tanks if the solution meets the criticality criterion. Waste with < 1 mg/L plutonium concentration can be transferred without special considerations for criticality.

Table 2. Observed Conditions for Gel Formation

Pu Equivalent Concentration	1 M Nitric	2 M Nitric	3 M Nitric
25 g/L	No gel	No gel	No gel
37.5 g/L	Moderate gel	No gel	Moderate gel
50 g/L	Extensive gel	Slight gel	Extensive gel

When the slurry from the precipitation vessel is filtered, plutonium can report to the filtrate as residual dissolved species, particularly if complexants are present in the feed solution. Plutonium can also report to the filtrate as uncaptured precipitate, either plutonium hydroxide precipitate or plutonium adsorbed on uncaptured $Mg(OH)_2$ solids.

Filtrate samples from the baseline tests were analyzed to determine whether the filtrate contained unacceptably high soluble cerium concentrations. All filtrate samples were passed through a 0.5-µm syringe filter to removed particulates. All of the samples had cerium concentrations at or near the detection limit of 1 ppb. These concentrations suggest that filtrate passing through a 0.5-µm polishing filter will likely be suitable for the waste storage tanks, provided there are no trace quantities of plutonium complexing organics in the feed. Tests with actual waste will be needed to determine whether plutonium is being complexed.

2.3.2 Volume Percent Solids in the Filtrate Following Neutralization

The current suspended solids limit for transferring liquids at PFP to the Hanford DSTs is 5 vol% centrifuged solids. The filtrate from the $Mg(OH)_2$ precipitation process will contain dissolved solids as $Mg(NO_3)_2$ at a concentration directly related to stoichiometric requirements needed to neutralize the feed solution to a pH of about 7 and precipitate the cerium (plutonium) nitrate salts in the solution as hydroxide. The $Mg(NO_3)_2$ concentrations expected in the process filtrate will vary from about 1 to 1.5 M. Therefore, upon further neutralization to pH 12 or higher to meet DST requirements, the resulting slurry will contain roughly 1 to 1.5 M $Mg(OH)_2$ solids.

Filtrates from the baseline tests range from 0.71 to 1.91 M $Mg(NO_3)_2$. Figure 22 shows the results of settling and centrifugation tests of the filtrates neutralized to pH 13, as well as selected filtrate samples that were first diluted with 0.1 M NaOH to concentrations less than 0.5 M nitrate, as would be necessary for tank farms disposal. The samples with a nitrate concentration ranging from 0.7 to 1.5 M need to be diluted by about 14X to 30X, to approximately 0.05 M nitrate, to achieve the 5 vol% solids concentration limit. This testing also showed that the predominantly $Mg(OH)_2$ solids are sticky and difficult to handle. It is therefore recommended that neutralization and dilution of the filtrate be conducted just before the stream is transferred to the DSTs.

Achieving the desired dilution of the filtrate can be accomplished by diluting the feed prior to precipitation, diluting the filtrate, or recycling the $Mg(OH)_2$ produced by neutralizing the filtrate, either individually or in any combination. However, diluting solutions will necessarily decrease the quantity of cerium (plutonium) processed per precipitation batch and may not be a desirable approach. Recycling the $Mg(OH)_2$ was not evaluated in this study, but may be impractical anyway because the filtrate would need to be centrifuged to separate the supernate from the solids (it does not filter very well), and dry it. The

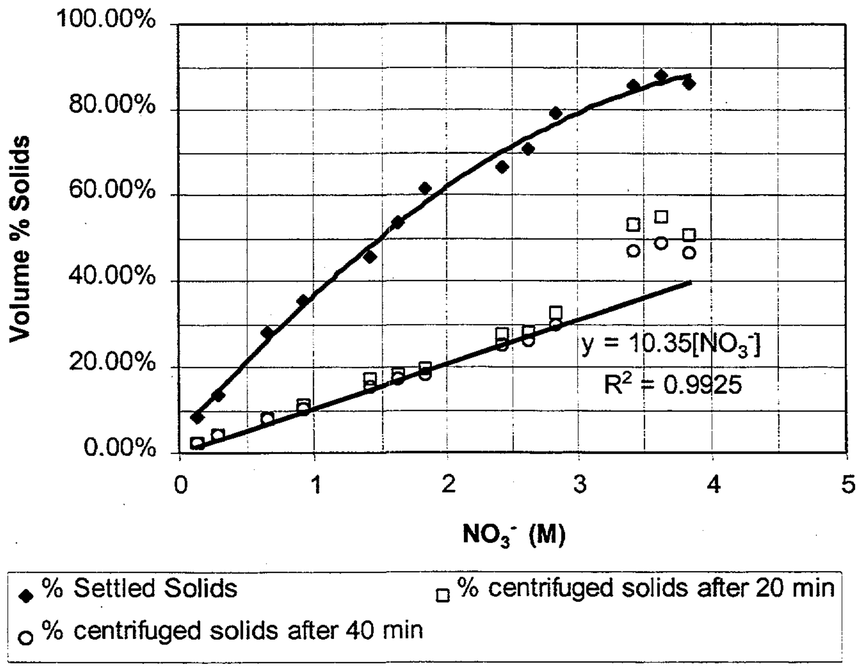

Figure 22. Settled Centrifuged Solids of Neutralized (pH ~13) Filtrate vs. Initial HNO_3 Concentration

solids will also necessarily contain $NaNO_3$ from the interstitial liquid remaining in the centrifuged solids, which may build up in the system to unacceptably high levels. Diluting the filtrate with deionized water is considered to be the most viable alternative, provided the added volume of water does not create a storage problem.

2.4 Solutions Containing Impurities

PFP solutions are known to contain appreciable quantities of impurities, including uranium, iron, permanganate, potassium, chromium, nickel, boron, cadmium, gadolinium, aluminum, and tributyl phosphate (and its degradation products). Some of these impurities, most notably uranium, iron and aluminum, are at concentrations comparable to the plutonium. These solutions could have a very serious impact on the process operability and the ability to meet the product quality requirements. Because of funding constraints and limited information on impurity concentrations, the effects of solution impurities were not investigated as a part of this evaluation. It is highly recommended that testing be conducted on simulants with the major impurities.

3.0 References

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Appendix A

Assessment and Optimization of Magnesium Hydroxide Process for Treatment of PFP Nitric Acid Solutions

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Assessment and Optimization of Magnesium Hydroxide Process for Treatment of PFP Nitric Acid Solutions

Summary

The overall mission of the plutonium solutions processing program at the Plutonium Finishing Plant (PFP) is to stabilize the plutonium in an oxide form suitable for storage under the US-DOE 3013 standard (DOE 1999)[a], and to treat and dispose of the remaining solutions to the Hanford tanks. At PFP, nitric acid solutions bearing plutonium nitrate will be neutralized with magnesium hydroxide [$Mg(OH)_2$], and the resulting plutonium-bearing sludge will be calcined.

The magnesium hydroxide treatment process to be implemented at PFP is based on a process previously built and operated at Rocky Flats Environmental Technology Site (RFETS), and will encompass the following steps:

- neutralizing and precipitating plutonium-bearing sludge at near-neutral pH (~7 to 9) by treating plutonium-bearing nitric acid solutions with $Mg(OH)_2$
- filtering and rinsing the sludge to remove occluded salts
- calcining the sludge at ~1000°C
- treating the filtrate solution and rinse waters with sodium hydroxide (NaOH) to pH >12 so it can be dispositioned to the Hanford double shell tanks (DSTs).

This report describes the approach proposed by Pacific Northwest National Laboratory (PNNL) to support the operation and enhance the performance of the PFP magnesium hydroxide process. In developing this approach, previous work at RFETS and the results of preliminary tests at the Hanford Plutonium Process Support Laboratory (PPSL) were reviewed. Several challenges impacting process throughput and quality goals were identified:

- *Foaming in the precipitators.* To maintain high process operability, the precipitators using $Mg(OH)_2$ are to be operated in a manner to minimize foaming.

- *Bulk density of calcined filter cake.* To minimize the volume of plutonium oxide powder and thus the number of 3013 containers that must be stored, the bulk density (plutonium basis) of the calcined filter cake must be maximized. Previous testing of the $Mg(OH)_2$ process at PFP and RFETS resulted in a calcined plutonium oxide powder bulk density ranging from about 0.4 to 1.1 g/cm^3. To stay within existing vault space constraints at PFP, the average bulk density of the calcined product must be greater than or equal to 2 g/cm^3.

- *Loss on ignition (LOI) properties of calcined product from muffle furnaces.* The 3013 stabilization acceptance criteria limit moisture content (or weight loss, if using the LOI method) of oxide to be packaged in any type of sealed container to less than 0.5%. Results at RFETS suggest that this limit could not be met, although an LOI averaging less than 2% was routinely achieved.

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[a] U.S. Department of Energy (DOE), 1999, *DOE Standard, Stabilization, Packaging, and Storage of Plutonium-Bearing Materials*, DOE-STD-3013-99 (http://tis.eh.doe.gov/techstds/standard/std3013/std301399.pdf), Washington, DC.

- *Plutonium concentration in the filtrate.* Plutonium concentration in the filtrate must be minimized with a goal of <1 mg Pu/L (maximum throw-away limit and maximum for solutions going to waste handling in 241-Z).
- *Solids volume in the filtrate after NaOH treatment.* To meet the Waste Acceptance Criteria for disposal to the Hanford DSTs, the volume of the suspended solids in the NaOH-treated filtrate must be less than 5%.

In addition to addressing the above challenges, aspects related to the design and efficient operation of the magnesium hydroxide process using PFP solutions must be resolved. The design and operation aspects generally affect processing throughput and include parameters such as nominal nitric acid and plutonium loading in the feed solutions, the method of adding $Mg(OH)_2$, and filtration and drying rates.

The proposed PNNL approach to support PFP plutonium solution treatment has several components:

- Evaluate the previous testing results, the process chemistry, and the literature to understand how the process operation and performance are affected by feed composition and operating parameters.
- Through testing, assess the performance of the PFP magnesium hydroxide process under baseline flowsheet conditions.
- Determine and quantify processing refinements and options to improve process performance and throughput.

The preliminary findings from the evaluation of the process chemistry and processing challenges are summarized. A review of the pertinent chemistry indicates that plutonium in the feed solutions likely will be in the +4 oxidation state. The plutonium will precipitate as its hydrous oxide during $Mg(OH)_2$ treatment. Transition metal and aluminum impurities in the feed solutions will precipitate, with the plutonium hydrous oxide, as hydroxide solids during the $Mg(OH)_2$ neutralization step. Magnesium hydroxide will form ternary oxides with plutonium and uranium present in the +6 oxidation state. Fluoride will precipitate as MgF_2. Any excess $Mg(OH)_2$ also will be retained as solid in the filter cake. The interstitial liquid in the filter cake is expected to contribute a significant quantity of soluble magnesium nitrate that will dry to form $Mg(NO_3)_2$ solid and calcine to MgO. The presence of large concentrations of MgO in the calcined products is expected to be the primary cause of the low bulk density. Strategies to reduce the quantity of magnesium salts in the filter cake include decreasing the initial acid concentration of the feed solution, decreasing the amount of excess $Mg(OH)_2$ added, improving filter cake rinsing before calcinations, and changing the properties of the precipitate formed during neutralization.

Foaming observed in the precipitator during RFETS processing probably was due to the use of air sparging for mixing, air entrainment in the finely dispersed, low-density, dry $Mg(OH)_2$ solid resting on top of the feed solution, and carbonate impurities in the $Mg(OH)_2$. Decreasing the feed solution acid concentration is one known method to reduce foaming. Pre-wetting the $Mg(OH)_2$ solids, decreasing the rate of solids addition, and using low carbonate $Mg(OH)_2$ may also reduce foaming.

The solubility of plutonium hydrous oxide is below 1 mg/L above a pH of about 5.5, which suggests that neutralizing the solution to a pH of 6 or greater should produce a suitably low plutonium concentration in the filtrate, assuming that the solution achieves near-equilibrium conditions prior to filtering. The presence of excess $Mg(OH)_2$ and/or iron hydroxide can be expected to decrease the filtrate's plutonium concentration because both species have good cation adsorption properties. Any oxidation of Pu^{4+} to form the +6 oxidation state could result in higher filtrate plutonium concentrations because of the higher solubility of the +6 state precipitates. In addition, if a finely dispersed precipitate is produced, then some plutonium may pass through the filter along with the supernatant. The proper selection and dosage of flocculating agent and the use of a sub-micron filter downstream are two methods to minimize this latter effect.

Moisture content (LOI) in the calcined filter cake depends on the types of chemicals present in the calcined product as well as the available surface area. Hygroscopic compounds (e.g., the alkali oxides and hydroxides) readily react with moisture and carbon dioxide from the air. The concentration of hygroscopic compounds in the calcined filter cake can be decreased by not adding the hygroscopic impurities to the feed and by rinsing the filter cake to remove these compounds. Moisture also adsorbs on surfaces inside the pores of the calcined material. Increasing the calcination time and temperature reduces particle surface area and controls moisture adsorption.

Treatment of the filtrate with NaOH to a pH >12 for discharge to the tanks will produce a significant quantity of precipitate (as much as 30 vol%) composed almost entirely of $Mg(OH)_2$ solid but with only trace quantities of plutonium and other heavy metals. Strategies to reduce the amount of precipitate in the NaOH-treated filtrate include decreasing the amount of $Mg(OH)_2$ added in the process. Solids concentrations can be decreased by diluting the filtrate either during rinsing or as a separate step.

PNNL proposes a three-phase testing approach to investigate the key process parameters. The first phase consists of a series of tests using simulant solutions, with Ce^{4+} as a surrogate for Pu^{4+}, and includes an evaluation of the key parameters affecting the process. This phase is expected to provide important experience prior to performing tests with actual solutions, and reduce both cost and time for the overall test program. The results of the tests using simulant solutions will be used to design a more limited set of tests with genuine PFP process solutions in the second phase. The second phase tests will be used to confirm the results of the simulant tests and to obtain the key data needed to design and operate the process at PFP. The third phase will consist of large- or full-scale process tests.

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1.0 Introduction

Plutonium being stored at Hanford's Plutonium Finishing Plant (PFP) must be stabilized for long-term storage and eventual shipment to the Savannah River Site for final disposition. The PFP is located in the 200 West Area of the Hanford Site, and is currently operated by Fluor Hanford, Inc. (FHI). At PFP, approximately 5000 liters of plutonium in nitric acid solutions will be stabilized using a magnesium hydroxide [$Mg(OH)_2$] precipitation process. This process is based on a similar process built and operated at the Rocky Flats Environmental Technology Site (RFETS). The precipitate from the process will be converted to an oxide in muffle furnaces.

Under Contract 5381-4 (January 27, 2000), the Pacific Northwest National Laboratory (PNNL) is providing process development/optimization support for the magnesium hydroxide stabilization process. The first milestone under the contract was to devise a testing strategy to investigate the processing challenges identified during preliminary testing conducted at the Hanford Plutonium Process Support Laboratory (PPSL). The identified processing challenges include process throughput, foaming in the precipitator, a low bulk density for calcined product, and a high solids volume in the filtrate after neutralization. This report describes the magnesium hydroxide process chemistry, summarizes results of prior related studies, and provides the testing strategy to identify process conditions that minimize or eliminate the challenges and result in optimum throughput rates to meet process goals. An evaluation of alternative technologies for the stabilization of plutonium/nitric acid solutions is not included within the scope of this document.

Several sources of information were examined to assess the magnesium hydroxide process and develop the testing strategy:

- published studies by Los Alamos National Laboratory in developing magnesium hydroxide as a neutralizing agent for plutonium-bearing solutions at RFETS
- experience gained at RFETS in applying the neutralization process to their plutonium solutions
- experience of PPSL personnel in laboratory scoping work with pure plutonium nitrate in nitric acid solutions
- vendor information on magnesium hydroxide application to acid neutralization and heavy metal precipitation
- published chemical literature related to plutonium, magnesium, and other PFP solution constituents under expected process conditions.

From the assessment of the available information on the process and processing issues, a three-phase testing approach was recommended:

1. testing with simulant solutions, using Ce^{4+} as a surrogate for Pu^{4+}

2. a more limited set of tests with genuine PFP process solutions

3. full-scale process tests at the PFP.

The proposed Phase 1 laboratory testing program, described in this document, includes the following testing campaigns. The results from each test series will be used to establish conditions for the subsequent test series:

- shakedown tests (to help define laboratory equipment and techniques)
- testing of various magnesium hydroxide reagents (magnesium hydroxide qualities can affect foaming, neutralization rates, and plutonium solids filtration rate and density; in addition, the form of magnesium hydroxide, added as a powder or as an aqueous slurry, can affect process operability)
- testing the rate of magnesium hydroxide reagent addition (to test foaming, neutralization rates, and plutonium solids filtration rate and density)
- testing the direction of magnesium hydroxide reagent addition (reverse strike) (to test foaming, neutralization rates, and plutonium solids filtration rate and density)
- baseline tests to determine the effects of nitric acid and cerium(IV) concentrations on precipitation and filtration times, calcined product bulk density, filtrate composition and volume (after neutralization).
- flocculent tests (to identify optimum flocculating agents and quantities to minimize filtration times)
- addition of excess or alternative neutralizing agent; testing addition of sodium hydroxide after magnesium hydroxide addition to decrease time to achieve target pH
- filter cake rinsing tests (to determine the effects of rinsing on entrained magnesium salt content and calcined filter cake density and hygroscopicity)
- filter cake drying and calcination protocol (to determine the effects of these parameters on the calcine density
- tests of the effects of other constituents (e.g., uranium, fluoride, iron) in the PFP process solutions.
- test alternative neutralization methods to supplant some of the magnesium hydroxide used to neutralize nitric acid with water-soluble hydroxides (sodium, potassium) to decrease magnesium hydroxide solids quantities sent to tank farms.

The results of these tests will be used in Phase 2 of the proposed laboratory testing program, in which key data for designing and operating the PFP process will be obtained with actual PFP solutions. In Phase 3, large- or full-scale process tests will be conducted.

2.0 Process Chemistry Description

The treatment process for stabilizing PFP plutonium-bearing solutions consist of four steps:

- precipitation of plutonium-bearing sludge at near neutral pH (~7 to 9) by treating plutonium-bearing nitric acid solutions with magnesium hydroxide [$Mg(OH)_2$]
- separation of the sludge and rinsing the sludge free of occluded salts
- sludge drying and calcination at ~1000°C
- treatment of the supernatant solution and rinse waters with NaOH to pH >12 for disposal of the NaOH-treated material to the tank farms.

The individual treatment steps and anticipated process outcomes and potential impacts determined by PNNL are described in the following sections. The major technical *Findings* are summarized at the beginning of each section.

2.1 Precipitation

Findings: A number of commercial manufacturers market magnesium hydroxide (in powder and aqueous slurry forms) and magnesium oxide powder for use in acid neutralization and heavy metal precipitation. These products are specially formulated for ease of handling and reactivity, and thus are recommended to be used in the testing and plant applications.

The use of magnesium hydroxide to neutralize acidic, heavy metal-bearing solutions is rooted in several favorable attributes when compared with neutralization by sodium hydroxide, NaOH (Kirk-Othmer 1993). First, $Mg(OH)_2$ has lower equivalent weight for acid neutralization than NaOH and thus requires less mass of chemical. Second, the neutralization proceeds more slowly, because dissolution of $Mg(OH)_2$ is first required. This slow dissolution allows time for the heavy metal hydroxide precipitates to grow in particle size and provides a more easily settled and filtered solid cake. The higher charge of the Mg^{2+} ion compared with the Na^+ ion is more effective for removing the negative surface charge of the precipitate, which aids floc formation. The $Mg(OH)_2$ is much less corrosive to skin than NaOH, improving the safety in handling. Finally, because the $Mg(OH)_2$ buffers to around pH 9, it prevents re-solubilization of certain amphoteric metals (such as aluminum), which can occur by using a stronger base such as NaOH.[a] As might be expected, as the pH increases, the rate of $Mg(OH)_2$ dissolution decreases. Thus, the time required to reach higher pH (e.g., 6-8) can be long unless the $Mg(OH)_2$ has high surface area or excess $Mg(OH)_2$, or stronger bases (e.g., NaOH, calcium hydroxide) are added to accelerate the pH adjustment.

Commercially available $Mg(OH)_2$ powders and slurries are created and marketed for heavy metal precipitation and acid neutralization [e.g., FloMag® MHP powder and FloMag® H slurry, both by Martin Marietta Magnesia Specialties, http://www.magspecialties.com/wtrbroch.htm; Aquamag® SW powder and Aquamag® NW 63 slurry, by Premier Chemicals (http://www.premierchemicals.com/)]. The $Mg(OH)_2$ in these products is formulated to be reactive and the slurry to be readily re-suspended and have good flow properties. Magnesium oxide, MgO, also may be used for heavy metal precipitation and acid neutralization. This material, essentially dehydrated $Mg(OH)_2$ prepared by precipitating $Mg(Cl)_2$ in alkali, is also available commercially (e.g., FloMag® HP and HP-ER powders, Martin Marietta Magnesia Specialties; MAGOX® powder, Premier Chemicals). The higher surface area of the FloMag® HP MgO

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[a] Re-dissolution of aluminum hydroxide by pH adjustment above about 10 is not a disadvantage to processing the PFP solutions.

(~30 m^2/g) compared with FloMag® MHP $Mg(OH)_2$ powder (~10 m^2/g) enhances its relative reactivity. For ease in application, the MgO powder usually is slurried in water first. Agitation must be maintained to prevent settling. The process to prepare an active calcium hydroxide/magnesium hydroxide mixture and use of the mixture to neutralize metal-bearing acid solutions is the partial subject of a patent application by Martin Marietta Magnesia Specialties (Gibson and Wajer 1998). The addition of calcium hydroxide is useful to achieve higher pH of neutralization.

2.1.1 Plutonium Precipitation by Reaction with Magnesium Hydroxide

Findings: Plutonium is expected to be present in its tetravalent oxidation state in PFP process solutions. This oxidation state should precipitate readily as pH is increased by magnesium hydroxide addition and reach the target filtrate concentration (<1 mg Pu/L) above about pH 5.5. However, in low concentrations of nitric acid (<1 M), disproportionation of the tetravalent plutonium to the tri- and hexavalent oxidation states occurs, which can cause unacceptably high losses of plutonium to the filtrate as a result of the higher solubility of hexavalent plutonium. High losses also might be expected if hexavalent plutonium is present because of chemical oxidation or prior high-temperature treatment of the process solution. Testing must be performed to examine the thoroughness of plutonium removal from solution, particularly for the hexavalent state.

Because of alpha self-radiolysis [which produces species such as NO and H_2O_2 that stabilize Pu(IV)] and the stabilization by nitrate complexing Pu(IV) is the oxidation state expected in strong nitric acid solutions of weapons-grade or commercial power reactor fuels-isotopic-grade plutonium over extended storage periods (Sheppard 1968; Kazanjian and Horrell 1972; Cuillerdier et al. 1989). With much higher alpha radiolytic rates (as produced by ^{238}Pu), significant Pu(VI) concentrations can be produced [see, for example, Vasil'ev et al. (1985)]. However, because such high radiolysis rates are unlikely even for aged materials containing in-grown ^{241}Am, Pu(IV) is the preponderant oxidation state expected in >1 M HNO_3 PFP process solutions.

In dilute nitric acid solutions (i.e., below about 1 M HNO_3), Pu(IV) disproportionates with increasing extent to give trivalent, hexavalent, and, eventually, pentavalent plutonium [Pu(III), Pu(VI), and Pu(V), respectively]. As shown in Reaction 1, the degree of disproportionation to give Pu(III) and Pu(VI) depends on $1/[H^+]^4$. Because of nitrate complexation of Pu(IV), the dependency is closer to $1/[H^+]^{5.3}$. The time required to achieve disproportionation equilibrium in <1 M HNO_3 is about 15-20 hours. The plutonium valence distribution as a function of HNO_3 concentration is shown in Figure 1 (Artyukhin et al. 1959; Connick 1954; Weigel et al. 1986; Toth et al. 1990). Disproportionation is an equilibrium process. Hence, even in 1 M HNO_3, Pu(VI) constitutes about 0.0045% of the total plutonium (calculated based on Connick 1954). This corresponds to ~2 mg Pu(VI)/L in a 50 g Pu/L solution.

$$3\ Pu^{4+} + 2\ H_2O \leftrightarrow 2\ Pu^{3+} + PuO_2^{2+} + 4\ H^+ \qquad \text{(Rxn 1)}$$

The (III) and (VI) oxidation states also can be found in nitric acid solutions under strongly oxidizing [e.g., with permanganate] or reducing [e.g., with hydroxylamine] conditions. Neither of these conditions is likely in the well-aged PFP solutions, however.

The Pu(IV) nitrate precipitation chemical reaction with $Mg(OH)_2$ is:

$$Pu(NO_3)_{4\,(aq)} + 2\ Mg(OH)_{2\,(s)} + x\ H_2O \rightarrow PuO_2{\cdot}xH_2O_{\,(s)} + 2\ Mg(NO_3)_{2\,(aq)} + 2\ H_2O \qquad \text{(Rxn 2)}$$

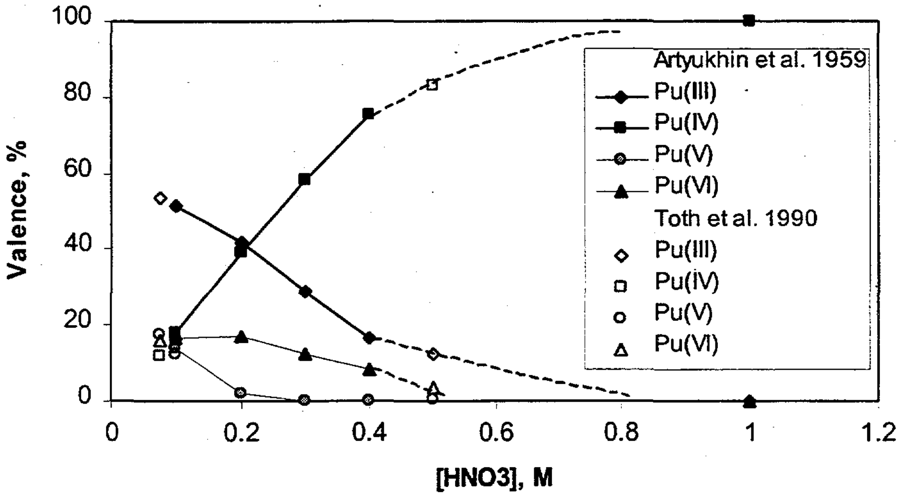

Figure 1. Plutonium Valence State Distribution as a Function of Nitric Acid Concentration (solid points at 1 M HNO_3 derived from Connick 1954)

Therefore, solid $Mg(OH)_2$ reacts with dissolved $Pu(NO_3)_4$ to produce solid hydrated plutonium oxide ($PuO_2 \cdot xH_2O$), dissolved $Mg(NO_3)_2$, and some water. There is no indication in the technical literature of formation of ternary oxides or hydroxides of Pu(IV) and magnesium [e.g., $MgPuO_3$] by precipitation (Weigel et al. 1986; Cunningham 1954). Rather, the discrete oxides PuO_2 and MgO are found when acidic plutonium/magnesium nitrate solutions are precipitated by ammonium hydroxide and the washed precipitates calcined (Kurina and Moseev 1997). In those same tests, metal concentrations in the pH 10.5 ammonia solution were less than 1 mg/L ($<4\times10^{-6}$ M Pu) and 1.5 g/L ($\sim6\times10^{-2}$ M Mg) after 4 hours of digestion at 40-42°C and standing for 1 day.

The solubility of $PuO_2 \cdot xH_2O$ in aerated aqueous solution decreases strongly with increasing pH (Figure 2). The goal plutonium solution concentration in the supernatant of the precipitation step is <1 mg Pu/L. With thorough solid/liquid phase separation, this concentration (about 4×10^{-6} M) is attained at about pH 5.5. The plutonium solubility decreases about one order of magnitude for each unit pH increase up to pH 8, where the concentration in well-clarified solutions is about 10^{-8} M or about 0.002 mg Pu/L. In dilute solution, the terminal pH attainable by $Mg(OH)_2$ is about 10.5. However, with neutralization of higher concentrations of HNO_3, significant $Mg(NO_3)_2$ concentrations are developed. Mass action effects of the dissolved Mg^{2+} lower the pH attainable by $Mg(OH)_2$ such that with 1 M Mg^{2+}, only a final pH of 9 can be reached.

The Pu(VI) and Pu(III) could be expected to precipitate to different extents than Pu(IV) in $Mg(OH)_2$ treatment to produce pH-neutral solutions. Hexavalent plutonium [Pu(VI)] precipitates with magnesium ion to form a ternary oxide. One likely reaction is:

$$2\ PuO_2(NO_3)_{2\,(aq)} + 5\ Mg(OH)_{2\,(s)} \rightarrow MgPu_2O_{7\,(s)} + 4\ Mg(NO_3)_{2\,(aq)} + 5\ H_2O \qquad \text{(Rxn 3)}$$

based on expected analogous reactions of magnesium with U(VI) (the exact plutonium compound was not identified in early work). The solid phase produces a plutonium concentration in 6 M NH_4OH (pH ~11) of about 18-40 mg/L, or $(8\text{-}18)\times10^{-5}$ M (Cunningham 1954, p. 402). The fraction of plutonium present as $PuO_2(NO_3)_2$ in the PFP feed solutions likely will be small because Pu(IV) normally forms by extended

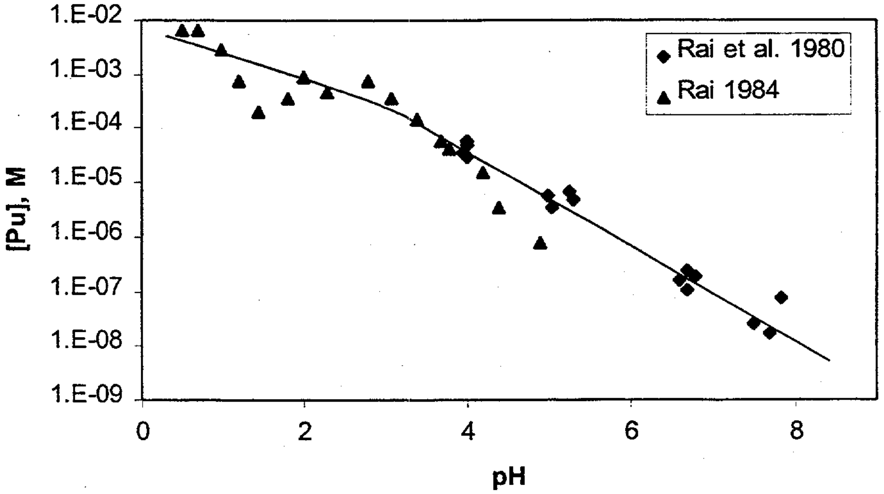

Figure 2. Plutonium Concentrations over Plutonium(IV) Hydrous Oxide in Aerated Waters as a Function of pH

storage in strong nitric acid. Nevertheless, if significant Pu(VI) is present in any stream, perhaps due to remaining strong oxidants, high-temperature treatment, or disproportionation, higher losses of plutonium to the filtrate can be expected than otherwise would be found in pure Pu(IV) solutions. Filtrate losses caused by the presence of Pu(VI) likely would be decreased by coprecipitation for any process solutions that contained U(VI).

In the absence of a strong chemical reductant, plutonium present as Pu(III) in the nitric acid solution will rapidly air oxidize to Pu(IV) when made neutral or alkaline and thus behave like Pu(IV).

2.1.2 Other Reactions with Magnesium Hydroxide

Findings: Nitric acid and many polyvalent metallic components in the PFP process solutions consume magnesium hydroxide reagent. Most of the magnesium hydroxide required for reaction with the nitric acid and polyvalent metals will report to the filtrate as magnesium nitrate solution, whereas excess magnesium hydroxide, if used, will report to the solid. The quantity of magnesium nitrate in the filtrate could be decreased by an equivalent replacement with sodium hydroxide. The reactions of magnesium hydroxide and sodium hydroxide with nitric acid are similarly energetic and will raise solution temperatures about 12°C per mole nitric acid per liter. The reaction of magnesium oxide with nitric acid will raise temperatures about 18°C per mole nitric acid per liter. The replacement of some portion of the magnesium hydroxide requirement by sodium hydroxide or other base, as a means to decrease magnesium oxide content in the calcined solid product, should be investigated.

The PFP process solutions contain nitric acid and other materials that react with $Mg(OH)_2$. A nominal PFP process solution composition is presented in Table 1. Besides the elements listed in Table 1, aluminum, americium, calcium, and fluoride also are known to be present in various PFP process solutions. The reactions of the other components with $Mg(OH)_2$ are considered in this section.

Table 1. Nominal Concentrations of Components in PFP Process Solutions (DOE 1996)

Element	Concentration	
	g/L	M
H^+	7	7.0
Plutonium	99	0.40
Uranium	23	0.10
Potassium	5.2	0.13
Iron, nickel, chromium	<0.5	<0.01
Manganese	4.3	0.08
Chloride	3	0.09

The nitric acid present in the PFP solutions reacts with $Mg(OH)_2$ according to Reaction 4:

$$2\ HNO_{3\,(aq)} + Mg(OH)_{2\,(s)} \rightarrow Mg(NO_3)_{2\,(aq)} + 2\ H_2O \qquad \text{(Rxn 4)}$$

The trivalent metal nitrate salts $Fe(NO_3)_3$, $Al(NO_3)_3$, and $Am(NO_3)_3$ may be present with plutonium in some of the stored plutonium-bearing nitric acid solutions and will react, like Pu(IV), to form insoluble solids and dissolved $Mg(NO_3)_2$ (Reaction 5). In addition, $Fe(OH)_3$ is a particularly effective carrier precipitant for plutonium and can help achieve even lower plutonium solution concentrations than shown in Figure 2 (Fedoseev et al. 1998).

$$2\ (Fe,Al,Am)(NO_3)_{3\,(aq)} + 3\ Mg(OH)_{2\,(s)} \rightarrow 2\ (Fe,Al,Am)(OH)_{3\,(s)} + 3\ Mg(NO_3)_{2\,(aq)} + 2\ H_2O \qquad \text{(Rxn 5)}$$

As alluded in describing Reaction 3, uranyl nitrate $[UO_2(NO_3)_2]$ present in the PFP process solutions reacts with $Mg(OH)_2$ to produce a magnesium diuranate such as MgU_2O_7 (Reaction 6 based on Merritt 1971). The actual precipitating phase depends on the precipitation conditions.

$$2\ UO_2(NO_3)_{2\,(aq)} + 5\ Mg(OH)_{2\,(s)} \rightarrow MgU_2O_{7\,(s)} + 4\ Mg(NO_3)_{2\,(aq)} + 5\ H_2O \qquad \text{(Rxn 6)}$$

Calcium nitrate $[Ca(NO_3)_2]$, potassium nitrate (KNO_3), and sodium nitrate ($NaNO_3$) are other salts often found in PFP solutions to be processed. These are salts of stronger bases [i.e., $Ca(OH)_2$, KOH, and NaOH] than $Mg(OH)_2$. Therefore, they will not react with $Mg(OH)_2$ and will remain in solution unchanged by addition of $Mg(OH)_2$.

The precipitation behavior of a solution containing plutonium, iron, aluminum, and uranium as a function of increasing pH was determined based on the published solubilities of $PuO_2{\cdot}xH_2O$ (taken from Figure 2), amorphous $Fe(OH)_3$ and gibbsite [crystalline $Al(OH)_3$] (Lindsay 1979), and calcium uranate (Brownsword et al. 1990; no data have yet been found for the magnesium diuranate system). The result (Figure 3) indicates that the solubility decreases with increasing pH to a minimum solubility at pH 9 to 10. The iron has a lower solubility than plutonium over the entire pH range of interest.

Fluoride and chloride (F^- and Cl^-) also occur in some PFP solutions. The fluoride, present as hydrofluoric acid (HF) once the metal-fluoride complexes are destroyed by hydrolysis, reacts with $Mg(OH)_2$ to produce MgF_2 precipitate (Reaction 7). The chloride salts of all metals found in the PFP process solutions are soluble and have no effect on $Mg(OH)_2$ consumption.

$$Mg(OH)_{2\,(s)} + 2\ HF_{(aq)} \rightarrow MgF_{2\,(s)} + H_2O \qquad \text{(Rxn 7)}$$

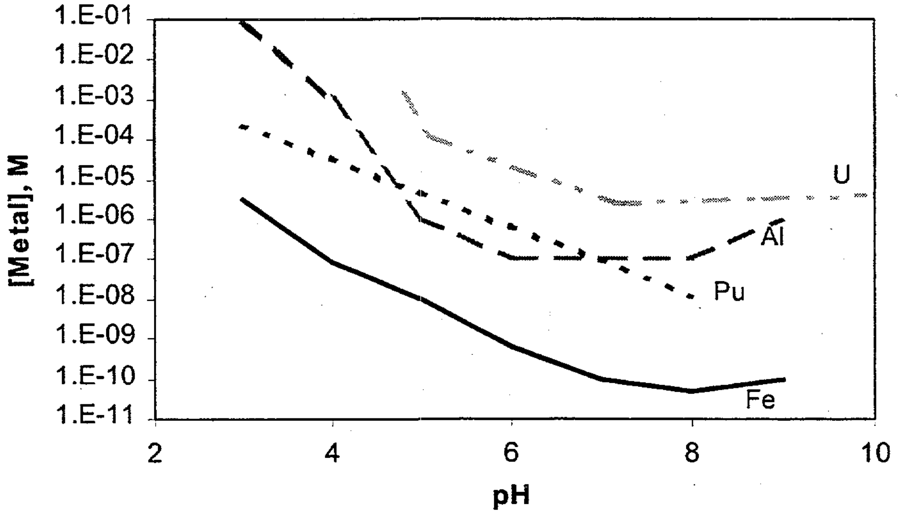

Figure 3. Metal Concentrations as a Function of pH

Reactions 2 through 7 identify the principal consumers of the $Mg(OH)_2$ neutralizing reagent. Accordingly, the molar quantity of $Mg(OH)_2$ required to achieve complete neutralization of PFP solutions is one-half the total molar amount of nitrate from $Pu(NO_3)_4$, HNO_3, and $(Fe,Al,Am)(NO_3)_2$, plus about 1.25 times the amount of nitrate associated with U(VI) and Pu(VI), plus the one-half of the total molar amount of fluoride. Any $Mg(OH)_2$ added in excess of that required in Reactions 2 through 7 will remain as $Mg(OH)_2$ and will report, with PuO_2, $Fe(OH)_3$ and other precipitates, to the solid phase.

The quantity of $Mg(OH)_2$ required could be reduced by decreasing the amount of HNO_3 in the feed solutions. Three techniques to decrease free HNO_3 are identified:

- reductive denitration of HNO_3 [e.g., with sucrose, formic acid, or formaldehyde (Smith et al. 1999)].
- evaporation and distillation of HNO_3 [distillation curves of HNO_3 and water from acidic plutonium nitrate solutions are described by Harmon et al. (1961)]. Evaporative concentration is more effective for concentrated plutonium solutions (in which both the solution and distillate ultimately reach about 6.6 M HNO_3), but can produce a significant fraction of Pu(VI). The Pu(VI) then must be chemically reduced to Pu(IV) to achieve thorough plutonium precipitation.
- neutralization of free HNO_3 with NaOH or other base (e.g., KOH, NH_4OH). The course of titration of HNO_3 with NaOH could be followed under plant conditions by monitoring solution electrical conductivity. At acid concentrations around 1 M, electrical conductivity, corrected for the effects of temperature, reflects HNO_3 concentration and is relatively independent of $NaNO_3$ concentration (Mikhailov and Ivukova 1982).

Of these options, neutralization treatment with NaOH or other base is easiest to apply.

Magnesium nitrate is the product of reaction of $Mg(OH)_2$ with nitric acid and acidic nitrate salts. The crystalline salt is present as the hexahydrate $[Mg(NO_3)\cdot 6H_2O]$ at room temperature and has a solubility in water of about 3.9 M at 25°C (Linke 1965). Thus, assuming the volume does not change upon mixing, $Mg(OH)_2$ can neutralize 7.8 M HNO_3 to produce a clear (solids-free) solution. The solubility of $Mg(NO_3)_2\cdot 6H_2O$ is about 20% higher at 80°C, so the possibility exists that the product solutions warmed by the heat of neutralization of HNO_3 with $Mg(OH)_2$ may produce $Mg(NO_3)\cdot 6H_2O$ crystals on cooling.

Neutralization of HNO_3 with $Mg(OH)_2$ is exothermic (produces heat). The enthalpy of the neutralization reaction (i.e., Reaction 4) was calculated to be -58 kJ/mole HNO_3 based on enthalpy of formation data (Wagman et al. 1982). Under adiabatic conditions and starting with 2 M HNO_3, this heat is sufficient to raise the solution temperature about 27°C. To a first approximation, the temperature increase is proportional to the HNO_3 concentration. Thus, a temperature increase of ~100°C (i.e., to boiling) could be expected if 8 M HNO_3 were neutralized with magnesium hydroxide. If NaOH rather than $Mg(OH)_2$ is used for the neutralization, the enthalpy change will be similar. If MgO is used instead, the enthalpy change is -77 kJ/mole HNO_3 [the increased heat output is caused by slaking the MgO to $Mg(OH)_2$]. The amount of heat produced by using MgO for the neutralization would raise the temperature of 2 M HNO_3 by about 36°C instead of 27°C if $Mg(OH)_2$ were used.

2.2 Filter Cake Separation and Rinsing

Findings: Rinsing and removal of salts present in the interstitial liquid of the plutonium-bearing filter cake are important in achieving the desired high-density plutonium oxide product for 3013 can storage. Means to improve precipitate particle growth and coagulation, and to achieve thorough salt washing without peptization, must be investigated.

The $PuO_2 \cdot xH_2O$ (present as a moist solid) and accompanying $(Fe,Al,Am)(OH)_3$, $Mg_2U_2O_7$, and MgF_2 will be separated from the $Mg(NO_3)_2$ solution by filtration. The sludge solids should be washed to remove the salt-bearing interstitial solution so that the salts do not excessively dilute the PuO_2 product meant for storage or cause other problems in calcination (as discussed in the following section).

Even with good washing, some interstitial liquid will likely remain entrapped in the moist solid filter cake. Magnesium nitrate, soluble alkali, and alkaline earth metal nitrates [$Ca(NO_3)_2$, $NaNO_3$, KNO_3] and the corresponding chlorides will be present in the interstitial liquid. Extended washing with water to remove all salts is not desirable because peptization (de-agglommeration and re-suspension) of the solids would occur, making solid/liquid phase separation difficult. Instead, initial washing with water (to remove most of the magnesium nitrate) followed by a rinse with a dilute electrolyte solution (such as 0.01 M NaOH) could be used to remove most of the nitrate salts without re-dissolving or re-suspending the precipitates. A better rinsing agent might be an ammonium hydroxide/ammonium nitrate (NH_4OH/NH_4NO_3) solution buffered to about pH 7, because it would provide ionic strength to maintain particle coagulation, dissolve some excess $Mg(OH)_2$, and leave no condensable residue in the solid cake.

Despite the particle growth afforded by the use of magnesium hydroxide, the multivalent metal hydrous oxides, hydroxides, and MgF_2 formed by the precipitation step still will have small particle sizes. For example, the iron hydroxide and sodium diuranate ($Na_2U_2O_7$) crystallite particles created by NaOH neutralization (to 0.01 to 1 M excess NaOH) of $Fe(NO_3)_2$ and $UO_2(NO_3)_2$ in nitric acid have size distributions centered at 2 to 5 nanometers or 0.002 to 0.005 μm (Krot et al. 1998). Conditions that increase the crystallite particle size and the agglomeration of the fine crystallites will decrease filtration times and improve process throughput.

Several methods are identified to improve solids agglomeration and dewatering and enhance filtration. First, heating/digestion steps could be used to grow and ripen the crystals to increase their particle sizes. Heating also would dewater the precipitates by converting the hydroxides and hydrous oxides to denser oxides. Second, flocculating agents could be used. The flocculating agents could be added in the filtration step or in the rinse for the filter cake. Also, a reverse-strike neutralization (i.e., addition of plutonium/nitric acid solutions to magnesium hydroxide suspension) could result in larger crystal sizes.

2.3 Filter Cake Drying and Calcination

Findings: Water-soluble salts retained in the moist washed filter cake, by themselves or in reacting with the metal precipitates, can produce clinkers and cause problems in achieving desired loss-on-ignition values for the calcined cake. Methods to enhance removal of interstitial salts must be developed.

Heating will be used to dry the moist filter cake (initial drying in a beaker on a hotplate has been suggested for plant operations). The dried solids then will be fired in a muffle furnace for some hours at about 950-1000°C to produce, ideally, a PuO_2 powder according to the DOE 3013 standard (DOE 1999). The PuO_2 will be accompanied by Fe_2O_3, Al_2O_3, MgF_2, and MgO formed by dehydration of any excess $Mg(OH)_2$.

Any $Mg(NO_3)_2$ salt present in the interstitial liquid in the moist filter cake will dry at room temperature to form $Mg(NO_3)_2{\cdot}6H_2O$. With heating, $Mg(NO_3)_2{\cdot}6H_2O$ decomposes to form basic nitrates such as $Mg(NO_3)_2{\cdot}4Mg(OH)_2$. Further heating above about 400°C produces MgO and gaseous oxides of nitrogen (Kirk-Othmer 1993). Calcium nitrate salt also decomposes with heating to form its respective oxide. Reactions of magnesium and other nitrate salts with the metal oxides during the drying and calcination steps must be considered.

As described previously, the discrete oxides PuO_2 and MgO form when acidic plutonium/magnesium nitrate solutions are precipitated by ammonium hydroxide and the washed oxide/hydroxide precipitates are calcined (Kurina and Moseev 1997). With insufficient washing and the presence of some nitrate, however, oxidizing conditions imposed by 1000°C thermal decomposition of the residual nitrate may oxidize the plutonium and form the compound $MgPuO_4$ or, in the presence of $Ca(NO_3)_2$, $CaPuO_4$ (speculation based on Keller 1972, 1973). The MgU_2O_7 when heated to 1000°C in air forms $MgUO_4$ and U_3O_8.

Moist sodium nitrate begins to decompose on heating above about 400°C to give NaOH. The NaOH then can react with Fe_2O_3 and Al_2O_3 to form the respective ternary oxides $NaFeO_2$ and $NaAlO_2$. In contrast, NaOH does not react with MgO (D'Ans and Löffler 1930). The NaOH also can react with Fe_2O_3 and PuO_2, under the oxidizing conditions imposed by the decomposing nitrates and the air environment, to give Na_2FeO_4 (D'Ans and Löffler 1930) and substances such as Na_4PuO_5 and Na_6PuO_6 (Keller 1972, 1973). Potassium nitrate would be expected to calcine and react to form ternary oxides in a manner analogous with $NaNO_3$.[a] The $NaFeO_2$, $NaAlO_2$, and Na_2FeO_4 ternary oxides are hygroscopic (collect water from humid air), and the Na_4FeO_4 further decomposes in moist air to give NaOH, $Fe(OH)_3$, and oxygen gas. Similar reductive decomposition of sodium/potassium/magnesium/calcium-plutonium ternary oxides might be expected in moist room temperature air. The low-melting NaOH and KOH also can act as cementing agents for the oxide powders to form clinkers during calcination processing.

In summary, calcines containing alkali (Na, K) and alkaline earth (Mg, Ca) oxides/hydroxides will be unstable to reactions, manifested as weight changes, if left exposed to moist glovebox air. Furthermore, complete conversion of plutonium to the PuO_2 product expected by extended calcination of plutonium-bearing materials in air may not occur. Uptake of water on the high surface area (hydr)oxides (e.g., PuO_2, Fe_2O_3, Al_2O_3, MgO, NaOH) can occur and likewise be manifested as weight increase upon exposure of the dried oxides to moist glovebox air. The strong alkali oxides and hydroxides also can adsorb carbon dioxide from the air to give the respective carbonates (e.g., $MgCO_3$, Na_2CO_3).

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[a] Lithium plutonates can be formed by direct reaction of $LiNO_3$ with PuO_2; Li_4PuO_5 at 500-800°C and Li_3PuO_4 at 900°C. At 1000°C, the Li_3PuO_4 formed at 900°C decomposes, leaving PuO_2 (Yamashita et al. 1992).

The chloride salts (e.g., $MgCl_2$, $CaCl_2$, NaCl, KCl) should be relatively inert in the calcination step and have low volatilities (their boiling points are 1400°C or higher). However, volatilization of chloride salts observed in heating Pu-bearing scrap to 800-950°C to meet the DOE 3013 criteria (page 29 of DOE 1999) has been sufficient to cause difficulties in achieving a steady final weight for LOI testing. The chloride salt vapors also can cause corrosion in the furnace. Finally, the chloride salts are hygroscopic to varying degrees and will adsorb water from moist air at room temperature after calcination.

The deleterious effects of interstitial salt (clinker formation, inherent hygroscopicity or reaction to form hygroscopic compounds, water and CO_2 uptake, volatilization problems in LOI) can be minimized by thorough removal of soluble alkali and alkaline earth salts from the filter cake.

2.4 Sodium Hydroxide Treatment of the Supernatant Solution

Findings: Magnesium nitrate present in the filtrate will precipitate completely as magnesium hydroxide when made alkaline for discharge to the tank farms. The resulting slurry may have to be diluted to meet waste tank acceptance criteria and to achieve pumpability. Decrease in the magnesium hydroxide demand at the acid neutralization and metal ion precipitation step (for example, by replacement with sodium hydroxide) would help decrease the slurry quantities destined for tank farm disposal and should be investigated.

The $Mg(NO_3)_2$ filtrate and rinse waters will be treated with NaOH solution to reach a goal pH >12 (i.e., at least 0.01 M NaOH) to meet acceptance criteria for wastes discharged to the Hanford tanks. The NaOH addition will produce $Mg(OH)_2$ slurry in $NaNO_3$ solution:

$$Mg(NO_3)_{2\,(aq)} + 2\ NaOH_{(aq)} \rightarrow Mg(OH)_{2\,(s)} + 2\ NaNO_{3\,(aq)} \qquad \text{(Rxn 8)}$$

The precipitation of $Mg(OH)_2$ is virtually complete above about pH 10 [Figure 4; note also that the pH of a saturated solution of $Mg(OH)_2$ is 10.5]. The precipitation will remain complete at pH >12 because $Mg(OH)_2$ is only weakly amphoteric (Gmelin 1939) and requires molar concentrations of alkali and heat to dissolve appreciably. Thus, the molar quantity of $Mg(OH)_2$ produced for discharge to tank farms will match the quantity of $Mg(OH)_2$ introduced in the metal precipitation/acid neutralization step, plus any $Mg(OH)_2$ produced from magnesium nitrate present in the PFP wastes, minus any magnesium lost as MgF_2, $MgPu_2O_7$, and MgU_2O_7 and in the interstitial liquid of the $PuO_2{\cdot}xH_2O$ filter cake. The $Mg(OH)_2$ solids will be bulky and difficult to pump to tank farms. The solids also will have to be diluted to below 5 vol% to meet the tank farms disposal criteria. Consequently, any decrease in magnesium hydroxide demand at the acid neutralization/metal ion precipitation step, achieved most conveniently by decreasing HNO_3 concentration, would have a commensurate effect on decreasing $Mg(OH)_2$ solids requiring disposal to tank farms. Alternatively, the $Mg(OH)_2$ solids created by NaOH treatment of the supernatant solution could be recycled to neutralize more PFP feed solution. However, the $Mg(OH)_2$ solids with entrained NaOH and other materials would be poorly characterized compared with fresh $Mg(OH)_2$ reagent for use in subsequent plutonium precipitation operations.

Calcium nitrate [$Ca(NO_3)_2$] in the filtrate will react with NaOH similarly to $Mg(NO_3)_2$, though at a somewhat higher pH, and will produce $Ca(OH)_2$ precipitate and dissolved $NaNO_3$:

$$Ca(NO_3)_{2\,(aq)} + 2\ NaOH_{(aq)} \rightarrow Ca(OH)_{2\,(s)} + 2\ NaNO_{3\,(aq)} \qquad \text{(Rxn 9)}$$

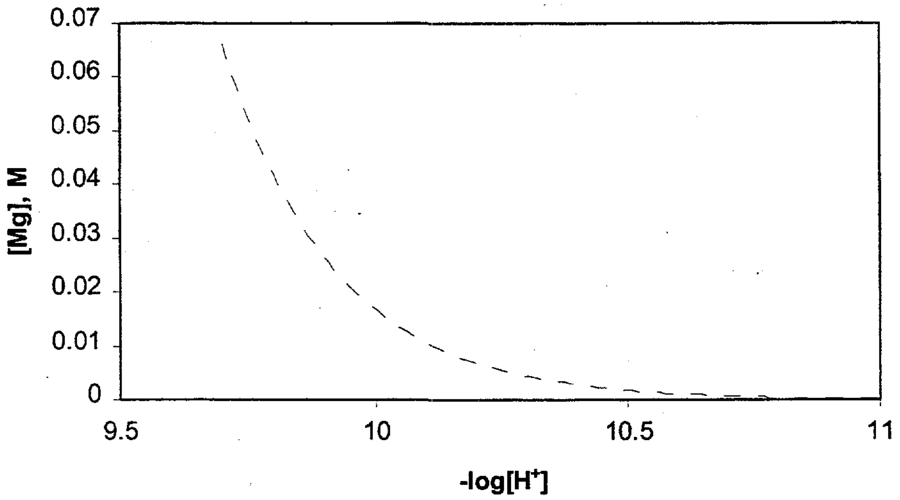

Figure 4. Magnesium Concentration in 1 M $NaNO_3$ as a Function of the Negative Logarithm of Free H^+ Concentration (similar to pH) (taken from Einaga 1981)

Other nitrate salts ($NaNO_3$, KNO_3) are very soluble. However, the possibility exists that the ~5 M $NaNO_3$ solubility in water could be exceeded if saturated (~3.9 M) $Mg(NO_3)_2$ were treated with 50% (~19 M) NaOH.

3.0 Characterizing the Acid Concentrations of PFP Processing Solutions

The total alkali required to achieve the pH in which plutonium solution concentrations are lowest (~6-8; see Figure 3), but for which excess $Mg(OH)_2$ is not used, must be known to achieve efficient neutralization. This value, the total alkali demand, is determined by titrating a measured volume of the process solution with a standardized NaOH solution. The pH of the vigorously mixed solution is recorded as a function of NaOH solution volume added. The number of equivalents of NaOH required to reach the target pH (~pH 8) is identical to the number of equivalents of $Mg(OH)_2$ or NaOH plus $Mg(OH)_2$ required to reach the same pH.

The free acid concentration in the PFP solution is another key parameter for neutralization processing because it describes how much NaOH can be substituted for $Mg(OH)_2$ [to avoid excessive disposal of $Mg(OH)_2$ slurry to tank farms]. The free acid is part of the total alkali demand, but does not include the alkali consumed by precipitation of the hydrolyzable metal ions (e.g., Pu^{4+}, Fe^{3+}, Al^{3+}, UO_2^{2+}). The free acid represents the sum of the concentrations of HNO_3 and HF. The following steps are used to determine the free acid concentration:

- Prepare a ~1 M ammonium oxalate [$(NH_4)_2C_2O_4$] buffer solution and adjust the pH to about 4.5.
- Add about 20 mL of the ammonium oxalate buffer into a beaker and measure the pH.
- Add a known volume of PFP process solution to the buffer and mix vigorously.
- Titrate the buffer with standardized NaOH solution to reach the pH found before PFP solution addition.

The hydrolyzable metals precipitate or are complexed as their oxalates and do not react with the NaOH titrant.

4.0 Process Challenges

Preliminary process testing of the magnesium hydroxide process with actual PFP solutions identified a number of challenges associated with the operation and efficacy of the process. In this section, these challenges are examined, and the underlying contributing factors are discussed, along with potential options for resolution.

4.1 Process Operation Times (Throughput)

The key process steps that will impact the overall processing rate are discussed below.

4.1.1 Acid Neutralization

In the acid neutralization step, the main impact on processing throughput is the time to add and completely mix the $Mg(OH)_2$ with the acid solution and the time for the $Mg(OH)_2$ to dissolve and reach the target pH. For the baseline approach, solid $Mg(OH)_2$ will be added to the top of the precipitation tank in three roughly equal doses. Plutonium does not begin to precipitate until the acid concentration is below about 0.3 M. Assuming 3 M HNO_3 initially, about 70% of the $Mg(OH)_2$ (the first two steps) will be added before significant plutonium precipitation occurs. Most of the plutonium precipitate will form over a pH range from about 0.5 to 2 with the residual levels being removed as the pH is further increased (see Figure 2). Significant transient behavior in the precipitation vessel is expected due to localized high and low acid concentrations as solids are slowly distributed throughout the acid solution by mixing. According to vendor data (Dow 1998), the dissolution of the specially formulated finely particulate and high surface area $Mg(OH)_2$ is fairly rapid, although not as rapid as that occurring with a concentrated NaOH solution. For example, $Mg(OH)_2$ added as a slurry will neutralize a 0.2 M sulfuric acid solution to a pH of 6 in about 2 minutes. The rate is limited by the rate of dissolution of the $Mg(OH)_2$ and the maximum hydroxide ion solution concentration of about 10^{-4} M (pH ~10) established by the solubility of $Mg(OH)_2$. In contrast, concentrated NaOH solutions react almost instantly, limited only by how fast the two solutions can mix.

One potential problem with adding $Mg(OH)_2$ as a solid is that it has a very low bulk density and will float on the process solution. Dry $Mg(OH)_2$ powder also can be expected to resist wetting like most other insoluble solids. Intimate mixing becomes difficult, and localized variations in pH around clumps of $Mg(OH)_2$ will occur.

Mixing problems can be overcome by adding the $Mg(OH)_2$ as an aqueous slurry. At least two companies (Martin Marietta and Dow) sell $Mg(OH)_2$ as a ~59 wt% slurry. The slurry has a density of ~1.5 g/mL, somewhat higher than the ~1.2 g/mL density of the process solutions. The water within the $Mg(OH)_2$ slurry is equivalent to about 10 vol% of the initial 3 M HNO_3-50 g Pu/L solution volume and thus constitutes a small addition to the volumes to be processed. The use of $Mg(OH)_2$ slurry also allows better control of the addition rate to facilitate the growth of $PuO_2 \cdot xH_2O$ particles in the critical pH range.

4.1.2 Filtration

Use of a $Mg(OH)_2$ slurry permits a reverse strike (acid addition to base) to be performed. When the acid is added to the $Mg(OH)_2$ slurry, the pH will approach neutrality from the alkaline side and maintain $PuO_2 \cdot xH_2O$, $Fe(OH)_3$, $Al(OH)_3$, and other solid product particles in suspension during the entire neutralization process. This may aid particle growth and produce a more easily filtered solid. Tests are needed to determine the relative benefits of using a $Mg(OH)_2$ slurry instead of a $Mg(OH)_2$ dry powder to treat the acidic PFP process solutions.

The filtration time also might be decreased if precipitate digestion at higher temperatures and flocculating agents are used. In addition, according to RFETS experience, settling and decantation of the supernatant solution, filtration of the settled solids, removal of the filter cake, and filtration of the decantate is faster than direct filtration of the entire slurry (see appendix).

4.1.3 Calcination

The greatest contributor to the calcination time likely will be the water content in the filter cake. Methods that enhance dewatering of the filter cake (e.g., centrifugation and decantation) will directly decrease the calcination time. If sufficient glovebox space is available, overnight air-drying of the filter cake followed by drying in ovens may decrease the amount of time the filter cake must spend in the muffle furnaces.

4.2 Foaming During Precipitation

Foaming has been observed at RFETS when HNO_3 solutions at concentrations greater than 3 M are neutralized with $Mg(OH)_2$ powders. Additionally, significant foaming occurred during preliminary testing (using actual PFP solutions) of the $Mg(OH)_2$ process at the Hanford Plutonium Processing Support Laboratory (PPSL).[a] The cause of the phenomenon has not been identified, but may lie in a combination of factors:

- low density and wet-ability of the $Mg(OH)_2$ powder
- positive surface charge of the powder
- fine powder particle size, which entrains air when added to the top of the acid as a solid
- carbonate impurities in the $Mg(OH)_2$.

The process solution surface tension (dependent on other materials in the process feed [b]), rapid exothermic reactions, and the air-sparge mixing rate may also contribute to foam formation.

Parameters that may be examined to minimize foam generation include the initial acid concentration, the form of magnesium hydroxide used in neutralization (solid or slurry), the direction of addition [$Mg(OH)_2$-to-acid, acid-to-$Mg(OH)_2$], the $Mg(OH)_2$ particle size, the purity of the $Mg(OH)_2$, and air sparge rate.

4.3 Plutonium Concentration in the Filtrate

The filtrate has two plutonium concentration limits that affect transfer to the 241-Z facility. The maximum plutonium concentration that is acceptable is 330 mg/L based on criticality safety. However, the target for the process is to limit the plutonium concentration in the filtrate to less than 1 mg/L (throw-away limit). Filtrates between these limits may be transferred if they meet other criteria that affect criticality potential. Plutonium concentration in the filtrate will be determined in part by the efficiency of

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[a] Personal communication. SA Jones (FHI) to AJ Schmidt (PNNL), February 3, 2000.

[b] Ion exchange resins may have contributed to foaming. Ion exchange resins, used extensively in prior plant operations at RFETS, are composed of long-chain organic molecules with quaternary ammonium and sulfonate terminal functional groups. Decomposition of the resins releases the constituent monomers which themselves have detergent qualities and thus are foam formers.

other process solution components (e.g., iron or coagulating agents) to carry plutonium to the precipitate and by the ability of the filters to capture the precipitate. As proposed, the $Mg(OH)_2$-treated acid will be passed through a 25-µm filter to remove the bulk of the precipitate, and the filtrate will be polished through a 1-µm polishing filter.

4.4 Density of the Calcined PuO_2 Product

Preliminary testing of the $Mg(OH)_2$ hydroxide process with PFP solutions at PPSL resulted in final calcine product bulk densities ranging from 0.4 to 1.1 g/cm^3.[a] These bulk density results were significantly lower than the minimum target bulk density of 2 g/cm^3.

Several factors may affect the density of the plutonium oxide product:

- precipitation, digestion, and flocculation
- the calcination temperature
- the compaction properties of the calcined oxide product
- the possible effect of particle size on the bulk density
- the composition of the precipitate being calcined.

The precipitation process temperature and time at temperature also can influence the particle size and density. Higher temperatures and greater digestion times normally increase particle size and can increase particle densities because the species re-crystallize more rapidly and lose water from their structures. Flocculating agents can increase apparent particle size in the solid/solution separation step and possibly influence the size of the calcined particles.

As shown in Table 2, both the bulk density and the tapped bulk density depend on the calcination temperature. For example, PuO_2 prepared from plutonium hydroxide increases its density by 40% upon increasing calcining temperature from 240°C to 800°C. The density increases by about 5% to 20% upon tapping the solids to a constant volume.

Particle size can significantly impact the physical behavior of a slurry. In slurry suspensions, the surface/volume ratio increases with decreased particle size, producing a greater drag on a settling particle, as well as increasing the quantity of water wetting the particle surface relative to its weight. The effect of particle size on the bulk density of a dry solid is less obvious. Particle shape and particle size distribution both affect the packing density. However, the nominal particle size should not affect it. Equally important is the nature of the bridges between irregular-shaped agglomerates of particles in the precipitate. As the precipitate dries and is calcined, the bonding strength between agglomerates can increase and make packing more difficult to achieve. This is especially true if clinkers form because of low-melting components in the calcine that act to fuse dry, non-melting particles together. The moisture content and heating rate are important because as water vaporizes or solids decompose to produce gases (e.g., NO_x), an outward pressure is developed on the pores of the material. If the rate of gas evolution is too great, the solid may expand (like popcorn), leaving voids in the solids. Lower heating rates and initial moisture contents may minimize this effect. Grinding the calcined particles also may be effective to increase bulk or tap density, particularly if sintering or caking has occurred.

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[a] Personal communication. SA Jones (FHI) to AJ Schmidt (PNNL), February 3, 2000.

The composition of the precipitate being calcined also affects the density of the calcined product. For example, as seen in Table 1, plutonium nitrate calcined at 800°C has about 90% and plutonium oxalate about 37% of the density of plutonium hydroxide calcined at the same temperature. Another compositional factor that could affect the density of the calcined product is the amount and type of impurity in the wet precipitate. Impurities can be both precipitated solids or solids dissolved in the interstitial liquid. After vacuum filtration, the filter cake will contain 30 to 50 wt% solids based on values typically achieved by drying intact filter cakes. If the solids cake is not washed prior to evaporating the water, it will contain a substantial amount of dissolved solids, consisting of 1.9 M magnesium nitrate (based on the nominal 3 M HNO_3-50 g Pu/L PFP process solution). Calculation shows that this amount of $Mg(NO_3)_2$ can contribute 20 to 50 wt% of the dried filtered solids. If excess $Mg(OH)_2$ is added to ensure reaching the desired pH, even more of the solids will be magnesium compounds.

Table 2. Bulk and Tap Densities of PuO_2 Prepared in Different Ways (ARHCO 1980)

Starting Material	**Decomposition Temperature, °C**	**Bulk Density, g PuO_2/mL**	**Tap Density, g PuO_2/mL**
Pu nitrate	240	1.7	2.1
	400	1.9	2.4
	600	1.7	1.8
	800	2.9	3.6
	1000	--	--
Pu peroxide	240	3.5	4.1
	400	3.8	4.3
	600	3.9	4.4
	800	4.5	4.8
	1000	4.9	5.8
Pu(IV) oxalate	240	1.0	1.4
	400	1.1	1.5
	475*	2.0	2.5
	600	1.2	1.5
	800	1.4	1.7
	1000	1.7	2.3
Pu hydroxide	240**	2.9	3.2
	400**	3.7	4.2
	600**	3.5	4.0
	800	3.2	3.7
	1000	3.8	4.2
Pu metal	Unknown	4.8	5.3

* Maximum values for eight measurements, tapped to constant density. From letter, R. D. Fox to G. W. Upington, ARHCO, August 30, 1972.

** Average of two or more measurements. Other data are single measurements. From RFP-503, "Properties of Plutonium Dioxide," I. D. Moseley and R. O. Wing.

The contribution of interstitial $Mg(NO_3)_2$ and excess $Mg(OH)_2$ to the solids to be packaged in the 3013 containers is significant because the bulk density of the resulting MgO is about 1/10 that of calcined PuO_2

(0.3 g/mL[a] vs. ~3.0 g/mL, respectively). A dried and calcined precipitate mixture containing 80 wt% PuO_2 and 20 wt% MgO will have a net density of about 1.07 g/mL, assuming the two volumes are additive. The postulated densities of PuO_2/MgO mixtures as a function of MgO content are plotted in Figure 5.

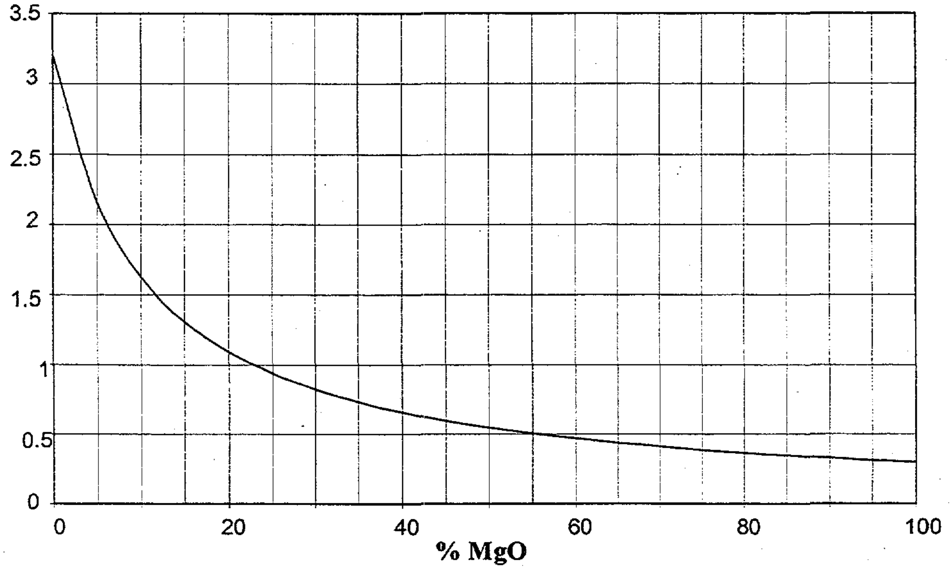

Figure 5. Postulated Density of Blended PuO_2/MgO Powders Mixtures

The amount of moisture in the filter cake prior to calcining, the geometry of the filter cake being dried, and the heating rate may also affect the density of the resulting calcine material.

Based on the above properties, it is necessary to determine the influence of digestion time and temperature on the calcined density of the vacuum-dried filter cake. The effects of MgO/plutonium ratio in the mixture resulting from acid process solution neutralization also must be investigated. Chemical compound analysis of the filter cake prior to calcining is recommended to identify and determine the relative abundance of interstitial salts.

4.5 Suspended Solids Content of the NaOH-Treated Filtrate

The filtrate produced after treatment of the PFP process solutions will primarily be a $Mg(NO_3)_2$ solution. Assuming that $Mg(OH)_2$ was used to neutralize 50 g Pu/L in 3 M HNO_3 to a pH of about 6, there will be approximately 1.9 M (282 g/L) $Mg(NO_3)_2$ dissolved in the solution. Treatment of the filtrate with 19 M NaOH solution for discharge to tank farms will produce a slurry of about 110 g $Mg(OH)_2$/L (assuming negligible volume increase). The commercial-grade $Mg(OH)_2$ slurry, FloMag® H, a stabilized high-density slurry, is about 960 g $Mg(OH)_2$/L and has no standing free liquid. On this basis, the $Mg(OH)_2$ slurry to be sent to the tank farms would be 11 vol% or less settled $Mg(OH)_2$ solids. The suspended solids content can be decreased by dilution or by reducing the amount of HNO_3 that is neutralized by $Mg(OH)_2$. The latter could be accomplished by denitration methods or by neutralizing the acid using an alkali hydroxide (such as NaOH) to achieve an initial HNO_3 concentration of about 1 M prior to addition of $Mg(OH)_2$.

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[a] For example, FloMag® HP MgO has a bulk density of about 0.35 g/mL.

Tests are needed to establish the settled solids content of the NaOH-treated filtrate under the baseline $Mg(OH)_2$ addition conditions and under alternative strategies in which NaOH is substituted for part of the $Mg(OH)_2$ demand during the acid neutralization step.

4.6 Calcined Product Moisture Adsorption

Moisture adsorption on the calcined product is expected to be an important contributor to meeting (or not meeting) the LOI criterion for 3013 disposition (DOE 1999). Moisture adsorption depends on the types of compounds present in the product calcine, the design time and temperature for calcining the material, and possibly the geometry of the precipitate as it is being calcined. Section 2.3 describes how composition affects the moisture adsorption of the calcine product. The pore structure of the calcined product also can affect its deliquescence. Part of the porosity is due to the micropore structure and is reflected in the internal surface area of the solids. These surfaces also contribute to adsorption of moisture. This pore structure will decrease if sufficiently high calcining temperatures are achieved to cause sintering. For $Mg(OH)_2$, this mechanism begins to become significant at calcining temperatures above about 700°C and is essentially complete at temperatures above 1500°C (Mellor 1946). As more sintering takes place, the internal surface area decreases.

The moisture adsorption on the calcined product material will be documented for each test. Correlation of moisture adsorption with parameter variations will be examined to identify the conditions leading to lower water uptake by the calcined product.

5.0 Testing Program

This section outlines the proposed testing strategy to characterize and optimize the magnesium hydroxide precipitation process for treatment of PFP plutonium nitrate solutions. First, testing will be performed to determine operability and efficacy of the process under current baseline flowsheet conditions. Next, identified process adjustments and options will be tested to improve process throughput, operability, and product quality.

In Section 2.0 (Process Chemistry) and Section 4.0 (Process Challenges), a large number of process parameters and options were identified that may impact the overall process performance. Evaluation of every parameter and option through testing using actual PFP solutions would require significant resources (time and funding). Consequently, for the recommended testing approach, nonradioactive simulants will be used to identify the operating parameters and options that will have the greatest impact on the process performance. To the extent practicable, these key parameters will also be optimized with the simulant solutions. Results from the simulant testing will be confirmed by performing tests with the actual PFP solutions.

Testing with simulated PFP solutions can be initiated immediately. It is expected that the results from the simulant tests will be used to focus the subsequent testing at PPSL and Radiochemical Processing Laboratory (RPL) with actual PFP solutions.

5.1 Tests with Simulated PFP Process Solutions

Testing with simulated PFP process solutions is proposed to investigate multiple process variables in a timely and cost-effective framework. The purpose of these tests is to reduce the number of parameters and range of process conditions that need to be investigated using radioactive solutions, while at the same time exploring those parameters that are reasonably expected to affect process operation, calcined filter cake density, and filtrate solids content.

At RFETS, Ce(IV) was used as a surrogate for Pu(IV) to evaluate their $Mg(OH)_2$ process for treating HNO_3 solutions containing plutonium. Cerium(IV) is the best available surrogate for Pu(IV) for the proposed experiments because the chemical reactions are similar and produce a $CeO_2 \cdot xH_2O$ precipitate analogous to the $PuO_2 \cdot xH_2O$ precipitate (Cotton and Wilkinson 1988). The dried filter cake would consist of the precipitate and $Mg(NO_3)_2$ salts within the interstitial liquid. The physical characteristics of the dried cerium precipitate should be representative of the precipitate containing $PuO_2 \cdot xH_2O$, and the $Mg(OH)_2$ should contribute to the calcined product density in a proportional manner.

While the testing outlined below appears to be sequential, the results from each series of tests will be used to establish conditions for the subsequent tests. Because of the interdependency of the process parameters, some iterative testing will be required to optimize the process.

All tests using simulants will nominally be performed using 200 mL of solution containing the desired nitric acid and $Ce(NO_3)_4$ concentration equivalent to that of $Pu(NO_3)_4$ in a 500-mL beaker. Most tests are expected to follow the baseline test conditions of 3 M nitric acid concentration solution, cerium concentration corresponding to 25 g Pu/L, and $Mg(OH)_2$ added at 110% of stoichiometric requirements for neutralization of the solution to pH 7.

Thirty minutes of mixing will be accomplished using a magnetic stirrer. A low rate of air sparging will be provided in addition to the stir bar as necessary to investigate the effect of selected parameters on foaming. BetzDearborn polyfloc AP1110 will be added to the solution which will be briefly mixed and filtered in a Buchner funnel using a 25-µm filter. The filter cake will be dried and calcined. Filtrate will be measured and sampled as needed.

The following set of data will be obtained for each test, as appropriate:

- feed composition
- feed volume
- feed mass
- $Mg(OH)_2$ mass
- $Mg(OH)_2$ addition rate
- solution mixing rate and time
- solution temperature
- flocculent type and dose
- mixing rate and time
- sparge rate
- final pH
- filtration time
- filter cake rinse solution composition volume
- wet filter cake mass
- filtrate mass
- filtrate volume
- filtrate composition
- optical particle size distribution (optional).

The following data will be collected for tests involving drying and calcining of filter cake:

- surface temp of hot plate
- drying time
- dry filter cake mass
- muffle furnace temp
- calcine time
- calcine product mass and density
- moisture adsorption (deliquescence) of product
- calcine product composition.

The test program will include shakedown test series followed by ten test series to investigate the following parameters:

- shakedown testing
- $Mg(OH)_2$ source
- $Mg(OH)_2$ addition rate
- direction of addition of acid solution to $Mg(OH)_2$ slurry (reverse strike)
- process baseline (Pu and acid concentration)
- flocculating agents

- excess neutralizing reagent addition
- rinsing
- drying and calcining conditions
- other cations
- alternative neutralization methods.

The first four test series will be conducted to quickly determine the optimum processing conditions for the neutralizing step, with respect to the source of $Mg(OH)_2$, and the rate and method of adding it to the acid. The results will be used to make recommendations for further evaluation at PPSL so that an early decisions can be made on the preferred method of combining the acid solution and the $Mg(OH)_2$.

The next seven test series will be conducted to determine the effects of key variables on the processing time, calcined filter cake density, and the solids content of the filtrate.

After completing the laboratory testing series, tests will be performed to determine the effects of process scale on processing.

5.1.1 Shakedown Tests

Three shakedown tests are planned to help gain experience with the equipment and procedures. These tests are expected to follow the baseline test conditions described above. Protocols for filtration, drying, calcined density measurement, and data collection will be confirmed during these tests.

5.1.2 $Mg(OH)_2$ Source Effects

The source of $Mg(OH)_2$ can affect the performance of the process because of differences in the purity, particle size and calcining history. In addition, commercially available products (Table 3) come in both powder and slurry forms, which provides more options for handling the material in the PFP process.

Tests will be conducted to determine the preferred source of $Mg(OH)_2$ material to be used in all subsequent tests and to determine whether there are any advantages of adding $Mg(OH)_2$ as a slurry (Table 4). The three criteria to be used to compare products are 1) foam generation, 2) pH reduction rate (as a measure of the neutralization rate), 3) and filterability. Tests will be conducted using nominal feedstock conditions (3 M nitric acid, Ce concentration equivalent to 25 g Pu/L) to evaluate alternative sources of $Mg(OH)_2$. Tests will be conducted with and without the baseline flocculating agent addition (BetzDearborn Polyfloc AP1110). Several different magnesium hydroxide and magnesium oxide powders and magnesium hydroxide aqueous slurries will be tested (Table 3). Stabilization of the aqueous slurries may be accomplished by use of dispersants, which themselves may contribute to foam formation.

Tests will consist of combining and mixing the magnesium hydroxide or oxide with the acid solution while measuring pH in the mixture. Air will be gently sparged into the mixture to test for the propensity of the mixture to generate foam. At the conclusion of mixing, the flocculating agent will be added, if called for in the test, and the mixture will be filtered (using the filter material of choice for the process) to test the filtration rate.

Each material will be tested with and without the addition of the flocculating agent. If it is determined that the slurry formulations do not perform as well as the dry solids, then up to four tests will be performed using slurries made from the solids to determine whether stabilizers in the slurry products are

Table 3. Magnesium Hydroxide and Oxide Qualities

Quality	**Product and Properties**					
	Martin Marietta, FloMag®			**Premier Chemicals**		
Name	MHP	H	HP	AquaMag® SW	AquaMag® NW 63	MAGOX®
Material	$Mg(OH)_2$ powder	$Mg(OH)_2$ aq. slurry	MgO powder	$Mg(OH)_2$ powder	$Mg(OH)_2$ aq. slurry	MgO powder
Purity, wt%	98.6	98.6 62.0 solids	98.0	>96	93 63 solids	93.7
CaO, wt%	--	0.7	--	0.9	4.4	3.4
Surface Area, m^2/g	10	--	30			
Particle Size, µm	--	2.0-4.0	5	4		
Wet screen, % past 325 mesh	99.6	99.8	99	98.0	--	97.0
Viscosity, cps	--	250	--	--	500	--

contributing to poor performance. Duplicate tests will be run as necessary to determine the best product and addition method.

If it appears that adding $Mg(OH)_2$ as a slurry is better than adding it as a powder, confirmation tests will need to be performed with actual PFP solutions by staff at PPSL so that PFP staff can consider incorporating the change into the baseline flowsheet.

Table 4. Effects of $Mg(OH)_2$ Source - Test Matrix

Test ID	**$Mg(OH)_2$ Description**	**Flocculating Agent Added**
SW-1-3-25-1	AquaMag® SW	No
SW-1-33-25-F-1	AquaMag® SW	Yes
NW-2-3-25-1	AquaMag® NW 63 slurry	No
NW-2-33-25-F-1	AquaMag® NW 63 slurry	Yes
MA-3-3-25-1	MAGOX®	No
MA-3-33-25-F-1	MAGOX®	Yes
HP-1-3-25-1	FloMag® HP	No
HP-1-33-25-F-1	FloMag® HP	Yes
MHP-2-3-25-1	FloMag® MHP	No
MHP-2-33-25-F-1	FloMag® MHP	Yes
H-3-3-25-1	FloMag® H Slurry	No
H-3-33-25-F-1	FloMag® H Slurry	Yes
TBD	TBD	TBD
TBD	TBD	TBD
TBD	TBD	TBD
TBD	TBD	TBD
Duplicate	TBD	TBD
Duplicate	TBD	TBD
Duplicate	TBD	TBD

5.1.3 Rapid vs. Slow Addition of $Mg(OH)_2$

Slow addition of $Mg(OH)_2$ can affect the particle size distribution of the precipitate because the total population of particles is reduced. Slow addition also may impact the generation of foam. A limited number of tests will investigate whether there is an advantage to slow addition of the $Mg(OH)_2$. Up to three tests will be performed (Table 5) to evaluate this parameter, pending the results of the previous tests. These tests include one using $Mg(OH)_2$ added as a powder, one test with $Mg(OH)_2$ added as a slurry, and one duplicate. Test conditions will follow those used in the previous test series, and the best performing powder and slurry source materials will be used.

Table 5. Effects of $Mg(OH)_2$ Addition Rate - Test Matrix

Test ID	$Mg(OH)_2$ Form
B-25-3-P-1	Powder
B-25-3-S- 1	Slurry
Duplicate	TBD

5.1.4 Addition of Acid Solution to $Mg(OH)_2$ Slurry (Reverse Strike)

If it is determined that $Mg(OH)_2$ addition as a slurry is the preferred method of addition, then tests will be conducted to determine whether there is further beneficial effect by adding acid to the $Mg(OH)_2$ slurry (reverse strike) instead of adding the $Mg(OH)_2$ slurry to the acid. For this testing, the parameters of interest are filtration time and calcined filter cake density. Tests will be conducted using the baseline test conditions, except that the acid solution will be slowly added to the slurry (Table 6). Two tests will be performed with and without flocculating agent. One duplicate will also be performed. The results will be used to make a decision on the preferred neutralization procedure to be used in subsequent tests.

If reverse strike addition enhances filterability and/or improves calcined filter cake density, confirmation tests will need to be performed with actual PFP solutions by staff at PPSL so that PFP staff can consider incorporating the change into the baseline flowsheet.

Table 6. Acid Addition to $Mg(OH)_2$ Slurry - Test Matrix (Reverse Strike)

Test ID	Flocculating Agent Added
S-25-3-R-1	Yes
S-25-3-R-2	No
S-25-3-R-3 (duplicate)	TBD

5.1.5 Baseline Tests - Effects of Acid and Cerium Concentration

The $Mg(OH)_2$ process at PFP is designed to operate with 50 g/L Pu solutions in nitric acid solutions that are no greater than 3 M nitric acid. However, the RFETS process, used as the basis for the PFP process, operated at a maximum of 25 g/L Pu.

A series of tests will be conducted primarily to determine the effect of the initial nitric acid and cerium (plutonium) concentrations on filtration time, filter cake volume, calcined filtrate density and composition, filtrate volume and composition, and volume percent solids in filtrate neutralized to a $pH > 12$ (Table 7). A key goal of these tests will be to determine the maximum initial Pu concentration

Table 7. Baseline Test Matrix

Test ID	Plutonium (Cerium Hydroxide) Concentration, g/L	Initial Nitric Acid Concentration, M
B25-3-1	25 (21.67)	3
B25-3-2	25 (21.67)	3
B25-3-3	25 (21.67)	3
B25-3-1	25 (21.67)	2
B25-3-2	25 (21.67)	2
B25-3-3	25 (21.67)	2
B25-1-1	25 (21.67)	1
B25-1-2	25 (21.67)	1
B25-1-3	25 (21.67)	1
B37.5-3-1	37.5(32.5)	3
B37.5-3-2	37.5(32.5)	3
B37.5-2-1	37.5(32.5)	2
B37.5-2-2	37.5(32.5)	2
B37.5-1-1	37.5(32.5)	1
B37.5-1-2	37.5(32.5)	1
B50-3-1	50(43.33)	3
B50-3-2	50(43.33)	3
B50-2-1	50(43.33)	2
B50-2-2	50(43.33)	2
B50-1-1	50(43.33)	1
B50-1-2	50(43.33)	1
TBD	TBD	TBD
TBD	TBD	TBD
TBD	TBD	TBD
TBD	TBD	TBD
TBD	TBD	TBD
TBD	TBD	TBD

that can be used in the process. Each test will follow the baseline test conditions and procedures, except that acid and cerium concentrations will be adjusted to selected values.

Based on discussions with PFP staff, solutions with cerium concentrations equivalent to Pu concentrations ranging from 25 g/L to 50 g/L will be tested at nitric acid concentrations ranging from 1 M to 3 M. Tests will initially evaluate cerium concentrations equivalent to Pu concentrations of 25 g/L, 37.5 g/L, and 50 g/L and at acid concentrations of 1 M, 2 M, and 3 M nitric acid. All tests using 37.5 g/L Pu equivalency will be performed in triplicate, while all other combinations will be conducted in duplicate to ascertain the expected scatter of the data. After completion of the initial tests (1 x 3 x 3 + 2 x 3 x 2 = 21), up to six additional tests will be conducted to further evaluate intermediate conditions of interest based on the initial results.

5.1.6 Flocculation Tests

To reduce the overall solids separation time, RFETS typically added 1 to 2 g of BetzDearborn Polyfloc AP1110 (formerly Betz Polymer 1110) per 10 to 12 liter batch of acid solution. The AP1110, a solid, was added to the $Mg(OH)_2$ powder, and then vacuum transferred to the neutralization/precipitator vessel. The AP1110 was selected because of its successful use in another RFETS process. In the $Mg(OH)_2$ process, the AP1110 resulted in a precipitate that settled and filtered at faster rates. In the process at RFETS, after neutralization, the precipitate was allowed to settle for approximately 30 min before filtration. For the implementation of the process at PFP, it is planned to eliminate this settling period. Therefore, the AP1110 polymer may not be the best choice or added at the optimum concentration or time within the process. BetzDearborn technical staff recommended evaluation of four other flocculating agents with the same composition as the AP1110 but different average molecular weights. Generally, higher molecular weights improve floc formation but may result in a more turbid supernatant. BetzDearborn also recommended a Buchner funnel filtration test be conducted instead of a standard jar test to evaluate the flocculating agents, since PFP is primarily concerned with the filtration rate rather than the settling rate.

Flocculation tests will be conducted to screen the set of five flocculating agents recommended for testing by BetzDearborn, Inc. (Table 8). Initially, AP1110 will be tested at 0.1 g/L 0.01 g/L and 0.001 g/L to determine the appropriate dosage. RFETS used a dosage of about 0.1 g/L, but the literature suggests dosage levels on the order of 1 mg/L may be optimum. Once the preferred dosage range is determined, each flocculating agent will be tested at five dosage levels. Two tests will be conducted to determine whether adding the flocculating agent with the $Mg(OH)_2$ affects its performance. Two duplicate tests will be performed as necessary to check the optimum combination of type and dose rate. The test conditions described in Table 8 are tentative, pending initial investigation into the recommended dose range. From the results of these tests, a decision will be made regarding the preferred flocculating agent and dosage for subsequent tests.

5.1.7 Excess Neutralizing Reagent Addition

In industrial applications, $Mg(OH)_2$ is sometimes added to the acid solution in excess of that required by stoichiometry to improve the neutralization rate as the solution approaches a neutral pH where both the solubility and concentration of $Mg(OH)_2$ are very low. [RFETS also added excess $Mg(OH)_2$ to improve the filtration properties (i.e., as a filter aid)]. However, excess $Mg(OH)_2$ will not dissolve. Instead, it will report to the precipitate, thereby diluting the plutonium hydrous oxide concentration in the filter cake. As an alternative strategy, it may be desirable to add NaOH to provide an immediate source of hydroxide ion after the pH has reached about 5 [using $Mg(OH)_2$] to quickly achieve the desired pH. This latter method, which reduces reaction time and would reduce the need for excess $Mg(OH)_2$, is sometimes practiced in industry.

Tests will be conducted to quantify the effect of adding excess neutralizing agent [$Mg(OH)_2$ or NaOH] on the reaction time, the final pH, the filtration properties of the mixed solution, and on the calcined filter cake composition and density (Table 9). Tests will be conducted using the baseline test conditions (3 M nitric acid, Ce equivalent to 25 g Pu/L), using the preferred $Mg(OH)_2$ form and the addition method. One duplicate test is planned for each reagent.

Table 8. Flocculation Test Matrix

Test ID	Flocculating Agent	Concentration
F-25-3-ap-1110-100	Polyfloc AP1110	100 mg/L
F-25-3-ap-1100-10	Polyfloc AP1110	10 mg/L
F-25-3-ap-1100-0.1	Polyfloc AP1110	1.0 mg/L
F-25-3-ap-1110-0.5	Polyfloc AP1110	0.5 mg/L
F-25-3-ap-1110-1.5	Polyfloc AP1110	1.5 mg/L
F-25-3-ap-1110-.2.0	Polyfloc AP1110	2.0 mg/L
F-25-3-ap-1110-3.0	Polyfloc AP1110	3.0 mg/L
Test with AP1110 flocculent added in $Mg(OH)_2$ addition step	Polyfloc AP1110	TBD
Test with optimum flocculent added in $Mg(OH)_2$ addition step	TBD	TBD
F-25-3-ap-1100-0.5	Polyfloc AP1100	0.5 mg/L
F-25-3-ap-1100-1.0	Polyfloc AP1100	1.0 mg/L
F-25-3-ap-1100-1.5	Polyfloc AP1100	1.5 mg/L
F-25-3-ap-1100-2.0	Polyfloc AP1100	2.0 mg/L
F-25-3-ap-1100-3.0	Polyfloc AP1100	3.0 mg/L
F-25-3-ap-1120-0.5	Polyfloc AP1120	0.5 mg/L
F-25-3-ap-1120-1.0	Polyfloc AP1120	1.0 mg/L
F-25-3-ap-1120-1.5	Polyfloc AP1120	1.5 mg/L
F-25-3-ap-1120-.2.0	Polyfloc AP1120	2.0 mg/L
F-25-3-ap-1120-3.0	Polyfloc AP1120	3.0 mg/L
F-25-3-ap-1138-.05	Polyfloc AP1138	0.5 mg/L
F-25-3-ap-1138-1.0	Polyfloc AP1138	1.0 mg/L
F-25-3-ap-1138-1.5	Polyfloc AP1138	1.5 mg/L
F-25-3-ap-1138-.2.0	Polyfloc AP1138	2.0 mg/L
F-25-3-ap-1138-3.0	Polyfloc AP1138	3.0 mg/L
F-25-3-ap-1142-.05	Polyfloc AP1142	0.5 mg/L
F-25-3-ap-1142-1.0	Polyfloc AP1142	1.0 mg/L
F-25-3-ap-1142-1.5	Polyfloc AP1142	1.5 mg/L
F-25-3-ap-1142-.2.0	Polyfloc AP1142	2.0 mg/L
F-25-3-ap-1142-3.0	Polyfloc AP1142	3.0 mg/L
Test with optimum flocculent added in $Mg(OH)_2$ addition step	TBD	TBD
Duplicate – TBD	TBD	TBD
Duplicate – TBD	TBD	TBD
Duplicate – TBD	TBD	TBD

Table 9. Effects of Excess Neutralizing Agent - Test Matrix

Test ID	Reagent	% Excess
Emg-25-3-0-1	$Mg(OH)_2$	0
Emg-25-3-5-1	$Mg(OH)_2$	5
Emg-25-3-10-1	$Mg(OH)_2$	10
Emg-25-3-15-1	$Mg(OH)_2$	15
Ena-25-3-2.5-1	NaOH	2.5
Ena-25-3-5-1	NaOH	5
EM-25-3-TBD-2	$Mg(OH)_2$	TBD
Ena-25-3-TBD-2	NaOH	TBD

5.1.8 Effect of Rinsing

There is a significant quantity of magnesium, as soluble $Mg(NO_3)_2$, in the interstitial liquid of the filter cake caused by the neutralization of 3 M nitric acid. This magnesium will contribute to the total inventory of MgO in the calcined precipitate, which is believed to be a major cause of the low density calcined material. Since the nitrate salt is soluble, it may be possible to rinse this material from the filter cake. In addition, rinsing can reduce other soluble salts in the interstitial liquid such as potassium, which will adsorb water after calcining. Potential problems with rinsing are that the solids could become disperse by peptization and the flocculating agent in the filter cake could become diluted, adversely affecting the behavior of the filter cake. One solution to this problem is to add flocculating agent to the rinse water.

A series of tests will be conducted to investigate the effect of filter cake rinsing on the total rinsing time, and the composition, density, and moisture adsorption properties of calcined filter cake (Table 10). Tests will be conducted using the baseline test conditions (3 M nitric acid, Ce equivalent to 25 g Pu/L), using the preferred $Mg(OH)_2$ form and the addition method. Three methods of rinsing will be investigated: 1) a single rinse using a volume of water equal to the volume of the filter cake; 2) a single rinse using a volume of water equal to four times the filter cake volume; and 3) four consecutive rinses each using a volume of water equal to the volume of the filter cake. Each rinsing method will be evaluated with and without the addition of the flocculating agent to the rinse water. Two additional tests are planned based on the results of the first set of rinsing tests to further optimize the rinsing procedure. Two duplicate tests are also planned.

5.1.9 Effects of Drying and Calcining Protocol

The bulk density of the calcined filter cake depends on its pore structure. Part of the porosity is due to the micropore structure and is reflected in the internal surface area of the solids. These surfaces also contribute to adsorption of moisture. This pore structure will decrease if sufficiently high calcining temperatures are achieved to cause sintering. For $Mg(OH)_2$, this mechanism begins to become significant at calcining temperatures above about 700°C and is essentially complete at temperatures above 1500°C (Mellor 1946). As more sintering takes place, the internal surface area decreases and the bulk density increase.

Large pores are formed as microparticles coagulate and flocculate. These pores are largely responsible for the filtering properties of the filter cake. As filter cake is calcined, the bridges between particles forming the large pores become stronger so that these pores are maintained in the calcined product.

Table 10. Effect of Rinsing - Test Matrix

Test ID	Flocculating Agent Added with Rinse	Filter Cake Volumes of Rinse Water Added
B-25-3-1X-1	No	1X
B-25-3-1XF-1	Yes	1X
B-25-3-4X-1	No	4X
B-25-3-4XF-1	Yes	4X
B-25-3-10X-1	No	1X four times
B-25-3-10XF-1	Yes	1X four times
TBD	TBD	TBD
TBD	TBD	TBD
Duplicate	TBD	TBD
Duplicate	TBD	TBD

Previous experience with tank sludge suggests that very slow drying can significantly reduce the volume of filtered sludge. Presumably, this is due to unbound water wicking to the filter cake surface and evaporating rather than boiling off in the interior of the filter cake.

Tests will be conducted to investigate the quantification of the drying and calcining protocols on the bulk density of the calcined filter cake (Table 11). One set of tests will examine the merits of a staged drying process to first remove moisture at low temperatures (below the boiling point) followed by a subsequent higher drying temperature (nominally 250-500°C). Dried filter cake will then be calcined at a temperature of 950°C for 2 hours. The results of these tests will be used to examine the trade-offs between increased drying times and calcined density.

The second set of experiments will involve calcining filter cake at higher temperatures and for longer periods of time. These tests will use filter cakes dried under the best drying schedule determined from the previous tests. The results of these tests will be used to correlate the relationship of the calcining temperature to the calcine density and deliquescence.

5.1.10 Effects of Additional Cations

A series of tests will be conducted as needed in which other species present in some PFP solutions, such as U, K, Mn, Fe, Ni, Cr, Al, Gd, Cd, B, and TBP (and degradation products), are added to determine how these species will affect the filtration rate, filtrate composition, and calcined filter cake density and composition. These tests will be primarily directed towards identifying any significant adverse effects to processing rates and calcined filter cake density. The specific tests and test conditions will be determined as more PFP solution compositional data are obtained. However, it is expected that six solution groups will be tested: solutions previously treated with $KMnO_4$, solutions containing U, solutions contaminated with stainless steel corrosion products, solutions contaminated with TBP and its degradation products, solutions containing aluminum, and solutions containing combinations of boron, gadolinium, and cadmium. It is expected that four test conditions will be evaluated for each group. A test matrix for this testing series will be developed as data on the cation compositions in the PFP solutions become available.

Table 11. Effects of Drying and Calcining Protocols - Test Matrix

Test ID	First Stage Drying Time and Temperature	Second Stage Drying Time and Temperature	Calcining Time and Temperature
B25-3-D-1	1 hr at 100°C	2 Hr At 250°C	2 Hr At 950°C
B25-3-D-2	2 hr at 100°C	2 Hr At 250°C	2 Hr At 950°C
B25-3-D-3	2hr At 100°C	2 Hr At 500°C	2 Hr At 950°C
B25-3-D-4	1 hr at 80°C	2 Hr At 250°C	2 Hr At 950°C
B25-3-D-5	2 Hr At 80°C	2 Hr At 250°C	2 Hr At 950°C
B25-3-D-6	2 Hr At 80°C	2 Hr At 500°C	2 Hr At 950°C
B25-3-D-7	TBD	TBD	2 Hr At 900°C
B25-3-D-8	TBD	TBD	2 Hr At 1000°C
B25-3-D-9	TBD	TBD	2 Hr At 1100°C
B25-3-D-10	TBD	TBD	2 Hr At 1200°C
B25-3-D-11	TBD	TBD	2 Hr At 1500°C
B25-3-D-12	TBD	TBD	2 Hr At 950°C
B25-3-D-13	TBD	TBD	2 Hr At 950°C

5.1.11 Alternative Neutralizing Methods

A significant fraction of the $Mg(OH)_2$ added to the process is used to neutralize 3 M nitric acid to form soluble $Mg(NO_3)_2$ salt. Magnesium in the filter cake contributes to the low bulk density of the calcined filter cake. Magnesium in the filtrate forms solids when neutralized to meet DST waste acceptance criteria. The amount of $Mg(OH)_2$ required to neutralize the acid solutions can be reduced by using soluble neutralizing reagents, such as NaOH, KOH, or NH_4OH, to reduce the nitric acid concentration from about 3 M to 1 M (Table 12). However, if alternative reagents are used, it will be necessary to thoroughly rinse the filter cake to remove the soluble cations (e.g., Na, K) to avoid forming a deliquescent calcine product.

Table 12. Alternative Neutralization Methods – Test Matrix

Test ID	Neutralizing Agent
N-3-25-Na-1	NaOH
N-3-25-K-1	KOH
N-3-25-NH-1	NH_4OH
Duplicate	TBD

If the results of the previous test series are found to be inadequate for managing the magnesium inventory in the filter cake and filtrate, a series of tests will be conducted to investigate the feasibility of using alternative methods for reducing the quantity of $Mg(OH)_2$ to be added within the process. Tests using soluble hydroxides will be performed under the baseline conditions to reduce the nitric acid concentration from 3 M to 1 M. Next, the neutralization/precipitation will be finished using $Mg(OH)_2$. The effectiveness of rinsing on the residual levels of the cations from the filter cake will be investigated. The rinsing procedure used will be based on the results obtained from rinsing test series.

Alternatively, to reduce the quantity of $Mg(OH)_2$ added within the process, the nitric acid concentration can be reduced by adding a reducing agent (e.g., sugar) to denitrate the solution or by distilling nitric acid from the solution. A matrix will be developed to investigate distillation and reductant addition if it is decided to pursue reduction or removal of nitric acid.

5.2 Tests with Actual PFP Process Solutions and Large-Scale Testing

The results of the tests with the simulated PFP process solutions will be used to design a more limited set of tests using actual PFP process solutions. The latter tests will confirm or modify the results for those parameters identified as important in the simulant testing phase. The tests with the actual solutions will provide data to prepare the full-scale process for operation. The testing then will be extended to full-scale process experiments to finalize the derived process operations and parameters. Detailed planning of the tests with actual PFP solutions will begin as soon as initial results are obtained from the testing with simulants.

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Appendix

Summary of RFETS Experience with Magnesium Hydroxide Treatment of Plutonium-Bearing Nitric Acid Solutions

Summary of RFETS Experience with Magnesium Hydroxide Treatment of Plutonium-Bearing Nitric Acid Solutions

LA-13039 – Precipitation Flow Sheet Development for RFETS Solution Stabilization

This report examined hydroxide precipitation using NaOH and $Mg(OH)_2$ as a primary treatment process, as well as a two-step process involving oxalate precipitation followed by $Mg(OH)_2$ precipitation. The latter process is not of particular interest because the hydroxide step treated filtrate that contained low (mg/L) plutonium concentrations. Simulants were used to test the first process. Conditions for tests using $Mg(OH)_2$ as the neutralizing reagent process are summarized in Table A1. Trace quantities of other heavy metals and silicon also were present in the simulant solutions with a combined total of dissolved solids ranging from 0 mg/L (test 1-1a) to 1650 mg/L (test 1-2b). Solutions were gently sparged with air during the slow addition of $Mg(OH)_2$ reagent addition. Solutions were mixed for a total of 30 minutes after reagent addition. However, if the pH was less than 6 after 15 minutes of mixing, an additional 10 g of $Mg(OH)_2$ was added. The filtration procedure involved settling the solids and decanting to remove standing solution over the precipitate. The precipitate was transferred to a filter boat and vacuum-filtered to remove any remaining standing solution. The precipitate was then rinsed twice with a total of 1.0 L of water. The rinsed precipitate was heated to 600°C and held there for 4 hours.

Table A.1. Test Conditions and Results for Magnesium Hydroxide Precipitation Tests on Simulated RFETS Pu Solutions

Test	Feed Volume, L	Filtrate Volume, L	Feed Concentration				Filtration Time, min	Oxide Comp., Wt%	
			[Pu], g/L	U, g/L	H^+, M	Cl^-, M		Pu	Mg
1-1a - 10	2	2.5	7.4	-	3.7	1.94	6	71	4.5
1-1b - 11	2	2.5	7.4	-	3.7	1.94	8	71	4.5
1-1b - 13	2	2.5	7.4	-	3.7	1.94	10	71	4.5
1-2b - 15	1.5	3.8	0.03	31.7	7.0	-	10	0.2	19.0
1-3 - 12	2	2.5	5.3	3.9	5	1.43	70	33.0	14.0
1-3 - 14	2	2.5	5.3	3.9	5	1.43	90	33.0	14.0
1-4 - 16	1.5	2.0	-	61.5	5.0	-	15	NA	NA

The test results provide little useful information that can be compared to the conditions at PFP in terms of filtering time, except to suggest that the filtration times were all fairly short. Only those solutions from test batch 1-3 took significantly longer to filter. The unique feature of this solution was its approximately equal Pu and U concentrations. More important is the amount of magnesium in the calcined product following two rinsings.

LA-13126 – Precipitation Flow Sheet Optimization and Demonstration for RFETS Liquid Stabilization

This report focuses on the two-step treatment process for Pu-bearing solutions at RFETS. The two steps were Pu(III) oxalate precipitation followed by precipitation of the oxalate filtrates with magnesium hydroxide. This report discusses the dilution of high nitric acid concentration feed by blending with 0.35 M nitric acid to achieve a feed concentration of 2.5 M nitrate. Solutions first were pre-reduced so that only Pu(III) was in solution. One set of experiments examined several variables in a matrix of experiments based on a 12-run Plackett-Burman R_{III} screening design. Variables investigated were Pu and H^+ concentration (due to 10X dilution), stirring speed (slow, fast), reagent addition rate (dump, 3.3%/min), reagent addition order (direct or reverse), excess oxalate ion, cationic impurities, digestion time (30 min, 4 hr) and excess sodium ion. The two parameters measured were settling time (qualitative observation) and filtration time (5 mL through a 0.45-µm filter syringe). The analyses of the variance (ANOVA) of the results were inconclusive, likely from inconsistency in the methods of measuring settling time and filtration rate; filtration times varied from 3 to 23 minutes and settling times varied from 1 to 10 on a scale of 10. The limited number of experiments and the fact that no duplicate runs were done to determine reproducibility of the results make it impossible to glean any useful data from these tests. More useful was the vendor literature basis for using a minimum 30 minutes for digestion following the addition of reagents. The RFETS parameters they considered may also be applicable to PFP solutions treatment.

This report also provides some information on calcined magnesium hydroxide precipitates prepared from the oxalate precipitation filtrate. The calcined material had densities ranging from 0.31 g/mL to 0.45 g/mL. However, it must be noted that these precipitates were produced from solutions containing 100 mg/L or less plutonium concentrations and molar magnesium concentrations.

RFP-5000 Mock-up Testing of the Caustic Waste Treatment System Phases I & II

This report investigated the pilot-scale use of KOH and $Mg(OH)_2$ as precipitation reagents for neutralizing solutions nominally containing 1 M nitric acid, 1 g Ce /L and 0.5 g Fe /L. The process of interest was the one used in Phase II. In this phase, tests were performed using either reagent. The system operated with NaOH neutralized the solution to a pH between 10 and 12.5. The system operated with $Mg(OH)_2$ used 105% of the stoichiometric amount to neutralize the acid and precipitate the waste. The primary data recorded were settling time and filtrate composition for a total of 12 successful runs (six of each). Table 3 of the report combines the summary results of each set of tests. It was found that while the settling time was much shorter for the $Mg(OH)_2$ process (8 min vs. 40 min), the filtration time was nearly the same [22 min for $Mg(OH)_2$ vs. 28 min for NaOH]. The filtered precipitate was dried on a hotplate for 150 minutes and 75 minutes for the NaOH and $Mg(OH)_2$ tests, respectively. The dried precipitate densities were 288 g/L and 168.6 g/L respectively. While these densities are not for calcined material, they do provide an indication of what the ultimate bulk density would be. No compositional data were provided for the precipitates.

Memorandum dated 4/15/99 from Thurman Cooper to Caroline Sutter – Trip Report for Evaluating Caustic Treatment Facility at RFP

This memorandum was a summary of discussions with RFETS personnel regarding the operation of their operating magnesium hydroxide precipitation process. Some key points made regarding the process are summarized below:

- The process adds 15% excess magnesium hydroxide to the solution to achieve complete precipitation and improved filterability. The latter reason is important because filtering times ranged from 30 minutes to several hours, depending on the precipitate characteristics. The purpose of adding excess magnesium hydroxide to facilitate reaching the desired pH is to increase the kinetics of magnesium hydroxide dissolution. If it is assumed that magnesium hydroxide is used to neutralize 3 M nitric acid and 25 g Pu/L, then the stoichiometric amount of magnesium hydroxide is 1.7 M, which corresponds to 99 g of $Mg(OH)_2$. A 15% excess of magnesium hydroxide (which presumably would remain undissolved) will add about 15 g of magnesium hydroxide to the precipitated solids containing 32 g of $Pu(OH)_4$. Thus, the total solids would be approximately 32% magnesium hydroxide. With the assumption that magnesium hydroxide particles are larger than plutonium hydroxide particles, the precipitate will filter more readily, and the calcined product would contain approximately 26% magnesium oxide. The soluble magnesium nitrate in the interstitial liquid of the precipitate will increase the magnesium oxide fraction of the calcined product to an even greater value, thereby significantly decreasing the density of the calcined product.

- If RFETS cannot achieve complete precipitation by excess magnesium hydroxide, sodium and potassium hydroxide are added to increase the hydroxide concentration. The most likely impact of adding the alkali hydroxides would be to cause precipitation of magnesium hydroxide, which, in turn, should carry Pu to the precipitate, because magnesium hydroxide is a good adsorbent in neutral to alkaline solutions. An alternative solution might be to add the alkali hydroxides in lieu of excess magnesium hydroxide both to achieve the target pH and, if necessary, precipitate out some of the dissolved magnesium. This approach can reduce the amount of magnesium inventory in the precipitate as a solid at the expense of introducing a soluble alkali cation to the interstitial liquid. The practice of adding alkali or lime (CaO) to reach higher pH as a final step in magnesium hydroxide precipitation is known in industrial practice.

- The memo states that MD accepts calcined product with 10 wt% or less magnesium. This limit may be based on limits imposed by ceramic the waste forms zirconolite, pyrochlore, and perovskite, all of which have a 1:1 Pu:Ca molar ratio. The 10% limit for magnesium may therefore be based on substituting Mg for Ca and using the ratio of these elements respective molecular weights (240:24). On an oxide basis this limiting ratio PuO_2: MgO would be 272/40, which would correspond to a calcined product containing 87 wt% PuO_2 and 13 wt % MgO. While RFETS stated that their magnesium in the solids ranged from 5 to 30 wt% with typical values ranging from 5 to 9 wt%, the corresponding Pu content was not stated, and other impurities may have been present in the precipitate.

- The memo states that RFETS precipitates had problems meeting the LOI criterion of 0.5%. This problem may result from both the fact that hydroxides tend to be hygroscopic and the fact that the calcined solids will have a relatively large surface area. Information on a Martin Marietta website, indicates that when magnesium carbonate is calcined at temperatures ranging from 700°C to 1000°C it produces a "light burned" magnesium oxide that has a specific surface area of 1.0 to 250 m^2/g. When the carbonate is calcined at temperatures ranging from 1000°C to 1500°C, the specific surface area ranges from 0.1 to 1.0 m^2/g. The specific surface continues to be reduced as the temperature is further increased. This information suggests that calcining at higher temperatures or perhaps increasing the calcining time at 950°C could reduce the surface area of the calcined precipitate and thereby reduce its ability to adsorb significant quantities of moisture.

- The memo states that RFETS produced calcined product densities ranging from 0.5 to 0.8 g/mL. These densities are consistent with predicted densities based on the density of magnesium oxide and the expected concentration of magnesium oxide in the calcined product.

Phone Conversation with Larry Martella at Rocky Flats – January 25, 2000

Mark Gerber (PNNL) discussed the RFETS magnesium hydroxide process with Larry Martella of Rocky Flats. The questions and responses are summarized.

- How was the acid stream neutralized 0.5 M nitric acid. Was magnesium hydroxide or a different hydroxide used?

Magnesium hydroxide was used to neutralize the nitric acid from its initial concentration, which was no greater than 3 M.

- Was magnesium hydroxide slurry ever used?

Slurried magnesium hydroxide was not used because the system was not designed to use slurry. LANL apparently tried it at one time and it worked okay.

- What were typical maximum, nominal, and minimum Pu concentrations?

Maximum Pu concentration was 25 g/L, but ranged as low as 0.01 g/L.

- Were problems encountered adding the hydroxide as a powder? How much time was required to add the powder?

RFETS did not experience any problems adding the hydroxide as a powder. Vacuum was applied to the top of the mixing vessel and the powder from its holding vessel into the mixing vessel by a 0.25-inch (best recollection) Tygon tube. Occasionally, the vacuum hose sucked up a portion of the hydroxide because no baffle was present to separate the vessel top from the vacuum hose. About 30 seconds were required to add the powder. During powder addition, the air sparge valve was cracked just enough to provide mixing to wet the powder. If any greater flow was used, foaming occurred. Once the powder was in solution, air sparging was increased to achieve very gentle mixing. The magnesium hydroxide powder was obtained from Strem Chemical Company. This also was the source of powder for the LANL experiments. Granular material was also tested by found not to work very well (too slow).

- How long were the precipitates heated on the hot plate? What LOI was achieved?

The precipitate was heated for about 1 hour on the hot plate. A thermocouple in the middle of the filter cake but nearer to the bottom read a little less than 500°C. The hotplate temperature was 500°C. The filter cake was mixed while drying.

- How dense was the calcined precipitate? What was the calcination temperature? What was the typical Pu, Mg composition?

The dried precipitate was very fluffy after drying. Grinding after calcining might improve the powder density (this was not tested). A typical calcined precipitate was about 60% Pu and the balance magnesium oxide.

- How much excess hydroxide was used; what was the basis?

Per standard procedure, 15% excess magnesium hydroxide was used.

- Why was a flocculating agent used? How was the flocculating agent selected?

The flocculent (BetzDearborn Polyfloc AP1110) was the same as used on another hydroxide process at RFETS. About 1 to 2 g per 18-L batch (estimate) was used. The flocculent helped both settling and filtration rates. The number distribution precipitate particle size when 25 g

Pu/L solutions were processed had the majority greater than 25 μm (to about 50 μm). Lower Pu concentrations produced a finer particulate. The flocculent was premixed with the magnesium hydroxide powder.

- Were 0.5-μm filters considered for use as the first filter?

  Based on Mr. Martella's experience in filtering hydroxide solutions, he expected that use of 0.5-μm filters as primary filters would be much slower. Downstream bag filters were used, but solids build-up was not observed. If higher tolerances for Pu in the filtrate were available at Hanford than at RFETS, a 10-μm filter might be successful and the polishing filter omitted.

- Could a copy of the memorandum from LANL (NMT-2:FY95-178, January 26, 1995) that discusses the justification for using cerium as a surrogate for plutonium be supplied to PNNL?

  Though the memo may be found in Mr. Martella's files, it was suggested to ask Dave Bruce. Dave Bruce was present on most visits from Hanford and he was provided many papers including, most likely, the memo of interest.

There were two other items mentioned by Mr. Martella. First, he thought that it might be possible to increase the density of the calcined particles by grinding them. Jeffery Stevenson in our materials group also suggested his approach. Grinding helps break bridges between microparticles in the calcined material and thus helps packing. The other item mentioned was that RFETS filtered their neutralized solution in two steps. First the precipitate was allowed to settle in the mixing vessel and then the sludge was drained to a filter where it was dewatered. The dewatered sludge was scraped from the filter paper and transferred to another vessel. The clarified solution remaining in the mixing vessel was then drained onto the scraped filter and filtered. The latter filtered more quickly than it would have if the filter cake was still on the filter.

Appendix B

Laboratory- and Bench-Scale Testing of Cerium/Nitric Acid Solution Treatment by $Mg(OH)_2$ Precipitation

Appendix B

Laboratory- and Bench-Scale Testing of Cerium/Nitric Acid Solution Treatment by $Mg(OH)_2$ Precipitation

Laboratory- and bench-scale prototype testing of the $Mg(OH)_2$ process for precipitating plutonium from PFP plutonium solutions was carried out using cerium(IV) as a surrogate for plutonium. Cerium was chosen for these tests to reduce cost, because it is chemically similar to plutonium but nonradioactive. This allowed for more process parameters and a greater range of process conditions to be evaluated in a systematic manner to identify preferred operating conditions for subsequent tests using actual plutonium solutions. The materials, equipment, and general procedures used in the testing are described here.

Overall Test Strategy

The precipitation test program strategy was to conduct sequential test series, building on the results of prior test series to identify conditions for subsequent series. Because of the interdependency of the process parameters and the inability to accurately predict test outcomes, some supplemental tests were added to optimize the experimental process.

The test series were performed in the following order:

- Shakedown tests
- $Mg(OH)_2$ source tests
- Neutralization rate tests
- Baseline tests
- Rinsing tests
- Prototype tests.

The first five test series were conducted with 200 ml of solution in a 400-mL beaker and used a magnetic stirrer to mix the reagents and suspend the slurry. The magnetic stirring was accompanied by air sparge mixing in the shakedown and $Mg(OH)_2$ source testing. The sixth (prototype) test series was conducted primarily in the prototype reactor, a 1.8-L, 3-inch-diameter, tubular vessel of proportions similar to, but about 1/10 of the scale, the vessel planned to be used in actual plant operations. Like the plant process vessel, the mixing and slurry suspension in the prototype tests was accomplished using an air sparge. The prototype tests were performed using 1000 ml of test solution.

Shakedown Tests

Two shakedown tests were performed to establish operating procedures and to investigate the effects on foaming and filtration rate of using a flocculating agent. The flocculating agent was used at the design dosage of 0.1 g/L based on Rocky Flats Environmental Technology Site (RFETS) experience. The shakedown tests, which were performed at 0.209 M Ce in 3 M HNO_3, indicated that the flocculating agent had no effect on foaming or filtration rate. Because of the lack of effect, most of the subsequent tests were performed without adding flocculating agent.

$Mg(OH)_2$ Source Tests

The $Mg(OH)_2$ source test series was conducted to compare the effects of different sources of $Mg(OH)_2$ on several key process variables: neutralization rate, filtration rate, calcined filtercake weight gain, and product solids density. The commercially available $Mg(OH)_2$ sources included three $Mg(OH)_2$ powders, two $Mg(OH)_2$ aqueous slurries, and two MgO powders. The MgO hydrolyzes to $Mg(OH)_2$ when contacted with water. All tests were conducted at the nominal test conditions of 0.157 M Ce in 3 M HNO_3. Based on its favorable process properties, Fluka BioChemika $Mg(OH)_2$ (Fluka Chemie, AG) powder was selected as the $Mg(OH)_2$ source to be used in all subsequent tests.

Neutralization Rate Tests

The effects of neutralization rate on the filtration rate, wet filtercake properties, and calcined filtercake volume were investigated. The test results showed that a neutralization time of 1 to 5 minutes over the pH 2 to pH 4 interval produced the more satisfactory results. These tests also illustrated the effects of excess $Mg(OH)_2$ on neutralization rates and provided the basis for continuing with 8% excess $Mg(OH)_2$ in subsequent tests.

Baseline Test Series

The baseline test series was conducted to provide process and product data for the range of composition conditions expected in PFP's "pure" plutonium solutions (i.e., those solutions in which plutonium is the only metal present to a significant degree). These tests identified the effects of solution acidity, cerium concentrations, and operating parameters on filtercake properties. The results provided preliminary guidelines in selecting optimal operating conditions, acidity, cerium concentration, and neutralization rate. The data also provided a basis to evaluate the prototype precipitation system and rinsing test series.

Rinsing Tests

The rinsing test series provided information on the effects of different rinsing strategies on the filtration rate, wet filtercake volume, and calcined filtercake densities and weight gains. These data identified the effects of rinsing and combining filtercakes from different precipitation runs on a single filter.

Prototype Tests

The prototype test series was conducted to determine the effects of scaling and mixing in a prototype precipitation vessel in comparison with the results found in the beaker tests. The effects of air sparge rate on the neutralization rate and of flocculating agent on processing (particularly on foam formation) also were investigated. Additional beaker tests were conducted to aid in comparing scaling effects. The prototype test results provided some guidance on the amount of excess $Mg(OH)_2$ required to obtain optimal neutralization rates for solutions containing high acid and low cerium concentrations.

Preparation of Chemical Solutions

Reagent-grade cerium(IV) nitrate [$H_2Ce(NO_3)_6$] and nitric acid (HNO_3), with distilled and deionized (DI) water, were the reagents used to prepare the test solutions. The cerium(IV) nitrate (~1.5 M in cerium with 5% "excess" HNO_3) and nitric acid (69.0-71.0 wt%) reagents both were obtained from GFS

Chemicals, Inc. A 3 M HNO_3 stock solution was prepared from the HNO_3 reagent and DI water. The reagent cerium nitrate and 3 M HNO_3 solutions were measured gravimetrically and brought to volume in volumetric glassware. To prepare the test solutions, the 3 M HNO_3 was first diluted using about 95% of the required DI water prior to adding the 1.5 ceric nitrate solution. This addition sequence helped to prevent the formation of polymeric ceric hydroxide. The balance of the water then was added and quickly mixed to make the final 200-mL (beaker tests) or 1000-mL (prototype mixer tests) volume.

During the shakedown, $Mg(OH)_2$ source, and the neutralization rate test series, the solution preparations were based on the nominal (label) nitric acid and cerium assays. However, during the neutralization rate tests, a small but significant bias became apparent in the $Mg(OH)_2$ demand for the solutions using stoichiometry, based on the nominal HNO_3 and Ce(IV) nitrate reagent concentrations and the actual $Mg(OH)_2$ required. Because all tests used the same solution recipes and the test results to that point were comparative, the error was not critical to the test outcomes other than to determine how much excess $Mg(OH)_2$ was actually used.

The HNO_3 stock solution was titrated using reagent grade 1.010 N NaOH (Aldrich Chemicals) to determine its true acidity. The NaOH normality was standardized by pH titration using dried Baker Analyzed reagent potassium hydrogen phthalate as the primary standard. The total acidity of the ceric nitrate stock solution also was determined by titration. Then, using the supplier's assayed concentration of Ce(IV) in the stock solution, and knowing that each mole of Ce(IV) requires four equivalents NaOH, the concentration of "free" HNO_3 could be determined by difference. These results showed that the prepared solutions were about 2.2% higher in total acidity [i.e., "free" HNO_3 plus four times the Ce(IV) concentration]. All later tests (baseline, rinsing, prototype test series) were performed using solution recipes that were based on concentrations derived from solution acid-base titration.

Table B.1 shows recipes to prepare various test solutions for one of the two cerium lots used in the tests (the other lot had slightly a different cerium assay).

The only other chemical solutions prepared for the tests were the flocculating agent and a 50 wt% NaOH solution used to neutralize the filtrate to pH 13 in the baseline tests. The flocculating agent added as a solution in selected tests was BetzDearborn Polyfloc AP 1110 (BetzDearborn Inc.), the same flocculating agent used at RFETS. This flocculating agent was prepared as a stock solution by dissolving a measured quantity into a known quantity of DI water and stirring for about 30 minutes. The stock solutions were prepared fresh for each test. In two of the prototype tests, a measured quantity of flocculating agent was mixed with the $Mg(OH)_2$ powder before adding it to the precipitation vessel.

Beaker Tests

All tests, except those in the prototype reactor test series, were performed by using 200 mL of solution containing the desired nitric acid and $Ce(NO_3)_4$ equivalent concentration in a 500-mL beaker. The experimental apparatus used for these tests is diagrammed in Figure B.1. The air sparge was used in the shakedown and $Mg(OH)_2$ source tests to evaluate possible foaming during neutralization. The air sparge was not used in the subsequent neutralization rate, baseline, and rinsing test series.

In a typical test, a single aliquot of $Mg(OH)_2$ of specified amount was added rapidly to 200 mL of well-stirred solution in a 400-mL beaker. A pH probe, calibrated before each run using Fisher Brand pH 4.01 and 7.00 pH buffers, and a thermocouple, both with digital readouts, were present in each test. A

Table B.1. Solution Recipes Used in the Test Program

Target Composition, M		Mass, 1-L Basis, grams			Mass, 200-mL Basis, grams		
[Ce(IV)][a]	[HNO_3]	Ce(IV)	3.00 M HNO_3	Fluka $Mg(OH)_2$, at 108% stoich.	Ce(IV)	3.00 M HNO_3	Fluka $Mg(OH)_2$, at 108% stoich.
0.052	0.50	56.218	119.631	22.558	11.244	23.926	4.512
0.052	1.00	56.218	302.481	38.463	11.244	60.496	7.693
0.052	1.50	56.218	485.331	54.368	11.244	97.066	10.874
0.052	2.00	56.218	668.181	70.274	11.244	133.636	14.055
0.052	2.50	56.218	851.031	86.179	11.244	170.206	17.236
0.052	3.00	56.218	1033.881	102.084	11.244	206.776	20.417
0.105	0.50	112.436	56.412	29.210	22.487	11.282	5.842
0.105	1.00	112.436	239.262	45.115	22.487	47.852	9.023
0.105	1.50	112.436	422.112	61.021	22.487	84.422	12.204
0.105	2.00	112.436	604.962	76.926	22.487	120.992	15.385
0.105	2.50	112.436	787.812	92.831	22.487	157.562	18.566
0.105	3.00	112.436	970.662	108.737	22.487	194.132	21.747
0.157	0.50	168.655	-6.807	35.862	33.731	-1.361	7.172
0.157	1.00	168.655	176.043	51.767	33.731	35.209	10.353
0.157	1.50	168.655	358.893	67.673	33.731	71.779	13.535
0.157	2.00	168.655	541.743	83.578	33.731	108.349	16.716
0.157	2.50	168.655	724.593	99.483	33.731	144.919	19.897
0.157	3.00	168.655	907.443	115.389	33.731	181.489	23.078
0.209	0.69	224.873	0.000	48.605	44.975	0.000	9.721
0.209	1.00	224.873	112.824	58.420	44.975	22.565	11.684
0.209	1.50	224.873	295.674	74.325	44.975	59.135	14.865
0.209	2.00	224.873	478.524	90.230	44.975	95.705	18.046
0.209	2.50	224.873	661.374	106.136	44.975	132.275	21.227
0.209	3.00	224.873	844.224	122.041	44.975	168.845	24.408

[a] Lot assay: 1.46 M Ce(IV); 5.0% "excess" nitric acid; 1.57 g/mL density; "free" acid concentration determined by titration to be 3.075 meq/g.

stopwatch marked the time of addition. A 1-inch stir bar on a Corning magnetic stirrer set at 8 accomplished the mixing. This rate was just sufficient to pull the vortex near, but not to, the spinning stir bar. Time, temperature, and pH readings were taken periodically, more frequently at the beginning of each test. Visual observations of the evolving slurry were also recorded. The reaction was allowed to continue for a specified time period or until the solution pH reached 7.00, whichever was the greater time period.

At the conclusion of the neutralization period, the aqueous slurry, containing the excess $Mg(OH)_2$, Ce(IV) hydrous oxide solids, and dissolved $Mg(NO_3)_2$, was immediately filtered through a Whatman 41 paper filter (nominal 25-µm pore-size filter) supported on a 70-mm-diameter Büchner funnel. The times when the surface of the filtercake was first uncovered and when the filtration rate became less than

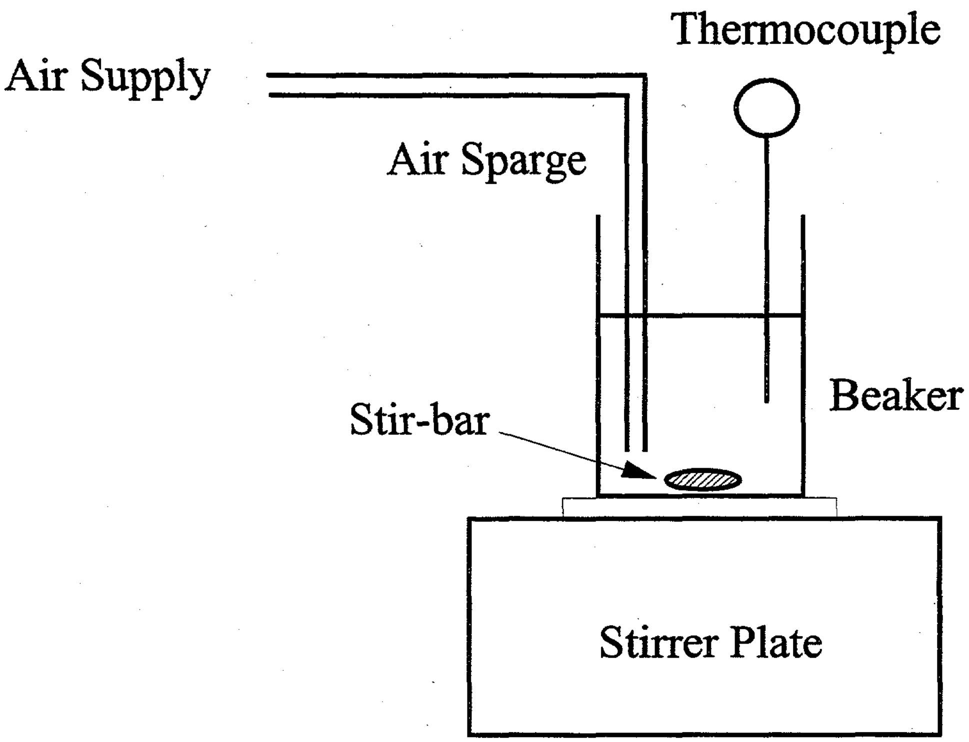

Figure B.1. Apparatus for Beaker Tests

1 drip/minute also were recorded, and the filtercake collected and weighed. The filtercake volume was determined by packing the wet filtercake into a volume-calibrated, 30-mL beaker. The filtercake was dried at 500°C for 2 hours followed by calcination at 950°C for 2 more hours. The calcined cakes were cooled in a desiccator, weighed, and then left on the laboratory bench exposed to air and reweighed at 1 and 24 hours to determine the amount of weight gain due to moisture and CO_2 absorption from the air. The bulk and tapped densities of the calcined filtercake were determined by measuring the weights and respective volumes of ground and sieved (to pass a 20-mesh screen) powders in a 10-mL graduated cylinder having 0.1-mL graduations.

In the shakedown tests and the $Mg(OH)_2$ source and neutralization rate test series, the $Mg(OH)_2$ was added at 10% excess based on the nominal assays of the stock solutions and the $Mg(OH)_2$ sources. Subsequent titrations of the test solutions showed that the true amount of $Mg(OH)_2$ was added at about 7.8% excess in these tests. All remaining beaker-scale tests were conducted at 8% excess $Mg(OH)_2$ [based on the titrated acidities of the stock solutions and the assayed values of the $Mg(OH)_2$ source]. The specified neutralization time was 30 minutes in the shakedown tests and the $Mg(OH)_2$ source and neutralization test series; in all subsequent tests, the neutralization time was decreased to 20 minutes.

The test procedure was varied from this procedure in some of the neutralization rate tests to determine the effects of adding the $Mg(OH)_2$ in two or more aliquots to control the neutralization rate. Deviations from the filtration procedure occurred in the rinsing test series to study the effects of adding a rinse step and of filtering two or more slurries through the same filter paper before removing the filtercake. These deviations from the general procedures are discussed in more detail in Appendices D and F.

Prototype Reactor Tests

All tests using the prototype reactor were performed by using 1 L of solution containing the desired HNO_3 acid and $Ce(NO_3)_4$ concentrations in a 1/10-scale, 1.8-L precipitation vessel. A schematic diagram of the prototype system is shown in Figure B.2. The precipitation vessel was a right circular glass cylinder 3 inches in diameter with a fused conical bottom, tapered at 60° to a 3/8-inch-diameter outlet. The vessel height from the outlet was 20.25 inches (18-inch cylindrical height). The precipitation vessel to be used at PFP has a 6-inch-diameter tapering at 60° to a ¾-inch outlet and has a 43-inch cylindrical height (approximately 47.5-inch total height).

A bleed valve on the vacuum hose was used to establish a nominal 2.5-inch Hg vacuum on the top of the vessel. A needle valve was placed at the air inlet to control the air flow rate to the bottom of the vessel. A ball valve was used to isolate the solution in the reactor when the air was not flowing and to allow the three-way valve to be reset to drain the vessel. A thermocouple was inserted through the vessel cap to monitor temperature and a temperature-compensated Hanna Piccolo Plus stick pH meter was suspended from the cap to monitor pH. During a limited number of tests, an Humonics Optiflow 650 digital flowmeter (electronic bubble meter) and a downstream moisture trap (to capture soap from the bubble meter) was attached to the air inlet to monitor the air sparge rate.

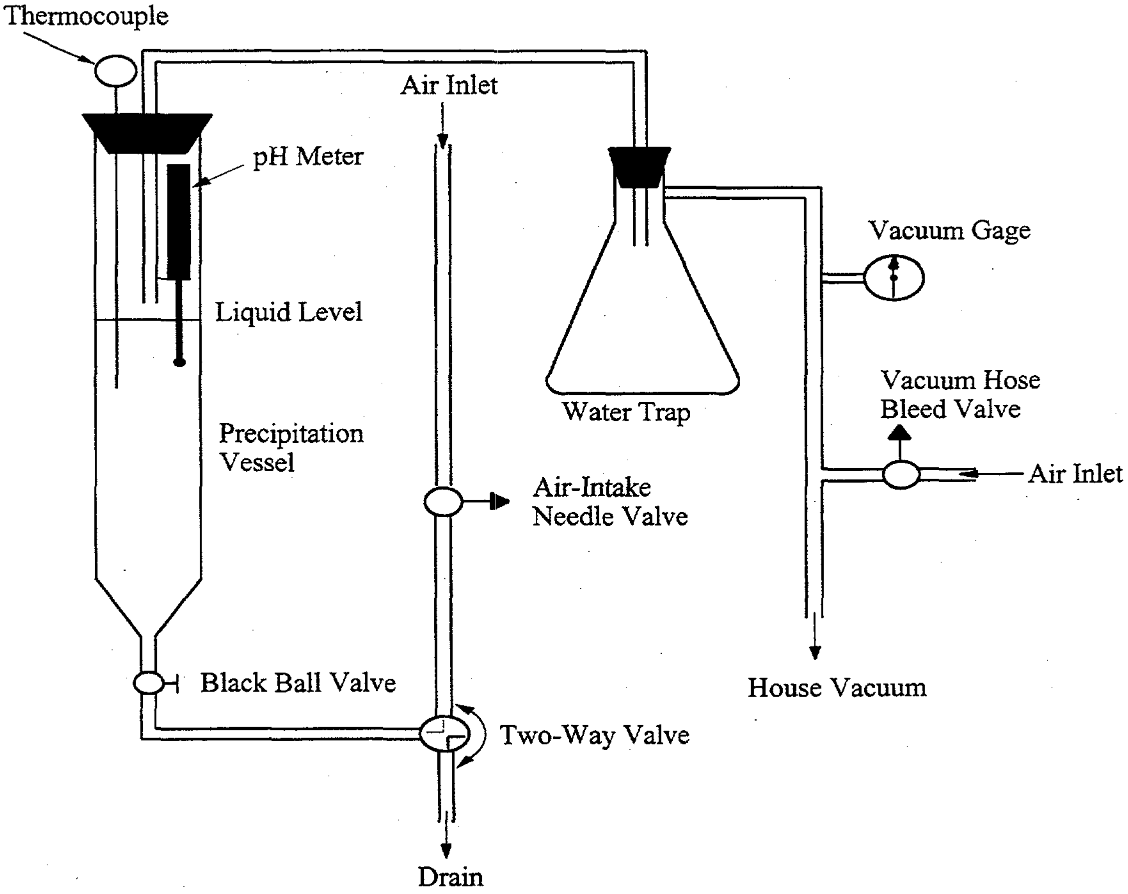

Figure B.2. Prototype Precipitation System

In a typical test with the prototype reactor, 1 L of solution was added to the reactor and the vacuum established at about 2.5 inches Hg. The ball valve was opened and the air flowrate was adjusted using the needle valve. The ball valve then was closed, and the vessel cap assembly containing the thermocouple and pH meter was lifted from the vessel. A specified quantity of $Mg(OH)_2$ was added to the vessel and allowed to sink to the bottom of the vessel, which provided enough open surface to insert the pH meter into the solution without plugging the meter with unreacted $Mg(OH)_2$. The cap assembly was returned to the top of the vessel to reestablish the vacuum. The ball valve was opened to initiate the sparging, and the solution pH, temperature, flowrate, and physical appearance were monitored for 20 minutes or until the pH reached 7.0, whichever was longer.

The neutralization time was measured from when the $Mg(OH)_2$ was added, but the time was noted when the air sparge was established. At the conclusion of the neutralization period, the slurry was drained from the precipitation vessel into a beaker and transferred to a Whatman 41 paper filter supported by a 90-mm-diameter Büchner funnel. The operation and data recording procedures for filtering, drying, and calcining the filtercake in the prototype tests were the same as in the beaker tests, except that a larger beaker was used to estimate the filtercake volume.

Appendix C

$Mg(OH)_2$ Source Tests

Appendix C

$Mg(OH)_2$ Source Tests

The $Mg(OH)_2$ source test series was conducted to determine the preferred source and physical/chemical form of magnesium hydroxide to use in subsequent experiments and in the PFP process. The $Mg(OH)_2$ process design at PFP calls for the addition of $Mg(OH)_2$ as a powder. Accordingly, tests were performed with $Mg(OH)_2$ powder. However, other tests were performed with $Mg(OH)_2$ added as a slurry and added as magnesium oxide (MgO) powder to determine whether either of the latter two forms had superior performance over the $Mg(OH)_2$ powders. Magnesium oxide converts to $Mg(OH)_2$ when exposed to water. Table C.1 lists the sources and compositions of the magnesium hydroxide used in this test series. The $Mg(OH)_2$ powder manufactured by Strem Chemicals was used in the RFETS process.

Table C.1. Magnesium Hydroxide and Magnesium Oxide Composition and Properties

Manufacturer	**Martin Marietta, Magnesium Specialties Inc., FloMag®**			**Premier Chemicals**	**Fluka BioChemika**		**Strem Chemicals**
Product Name	MHP	H	HP	AquaMag® NW 63	$Mg(OH)_2$	MgO	$Mg(OH)_2$
Material	$Mg(OH)_2$ powder	$Mg(OH)_2$ aq. slurry	MgO powder	$Mg(OH)_2$ aq. slurry	$Mg(OH)_2$ powder	MgO powder	$Mg(OH)_2$ powder
Purity, wt%	98.6	98.6 (62.0 % solids)	98.0	93 (63 % solids)	≥99	≥98	95%
Ca, wt%	--	0.7 CaO	--	4.4 CaO	≤0.5 Ca	≤0.02 Ca	--
Surface Area, m^2/g	10	--	30	--	--	--	--
Particle Size, μm	--	2.0-4.0	5	--	--	--	--
Wet screen, % past 325 mesh	99.6	99.8	99	--	--	--	--
Viscosity, cps	--	250	--	500	--	--	--

Procedure

All experiments were performed using 0.157 M Ce(IV) in 3 M HNO_3 as the test solution with the magnesium hydroxide source added to satisfy 110% of the stoichiometric requirement to reach the design endpoint pH of 6.8, based on the chemical specifications of the feed solution and magnesium hydroxide sources. Subsequent titration of the cerium nitrate and nitric acid stock solutions showed that the total acid concentration was about 2.2% higher than the target. Hence, the tests actually were conducted at 107.8% stoichiometry (i.e., 7.8% excess).

Tests were conducted by adding the measured amounts of the magnesium hydroxide source material to 200 mL of cerium/nitric acid solution in a single aliquot. The solution was stirred magnetically at a rate sufficient to move the vortex just above the rotating 1-inch, Teflon-coated magnetic stir bar. Air sparging also was used to agitate the suspension. Temperature and pH were monitored during the neutralization reaction. Except where noted, all tests were conducted for a 30-minute period (measured from the time of addition) regardless of the actual time it took to reach a pH of 6.8. After 30 minutes, the magnesium nitrate solution slurry of excess $Mg(OH)_2$ and ceric hydrous oxide precipitate was filtered through a Whatman 41 paper filter (25-µm nominal pore size), and the filtration time was recorded. The filtercake was collected and weighed. The filtercake volume was estimated by pressing the wet filtercake into a volume-calibrated 30-mL beaker. The filtercake was transferred to a Coors ceramic crucible and dried at 500°C for 2 hours, and then calcined at 950°C for 2 more hours. The calcined filtercake was weighed, and the bulk and tapped densities of the ground and sieved (to –20 mesh) product powder were determined using a 10-mL graduated cylinder with 0.1-mL graduations.

Results

All of the magnesium hydroxide source materials initially formed curd-like clumps in the acid solution. The clumps then dispersed to smaller agglomerates. Because the tests were run at 7.8% excess magnesium hydroxide, a portion of the $Mg(OH)_2$ did not dissolve. As the pH increased above about 1.8 to 2.0, Ce(IV) hydrous oxide began to precipitate. The yellow cerium precipitate then coated and encapsulated the remaining white $Mg(OH)_2$ solids. This coating was demonstrated by the appearance of a white smear when the yellow-brown pinhead-sized curds were crushed against the beaker wall. The curds required aggressive agitation, particularly when they were larger at the beginning of the experimental runs, to keep them in suspension, expose them to the acid solution, and thus maximize the neutralization rate. A key operational parameter during these tests, therefore, was to maintain a good suspension of the magnesium hydroxide solids. Rotation and movement of the beaker around the stir plate surface allowed the stir bar to reach all areas in the bottom of the beaker and maintain agitation. Some tests in this series clearly had inferior mixing; those test results were not used.

Results for the $Mg(OH)_2$ source tests (Table 2) show key parameters used to compare the performances of the different sources of material. All but two of the magnesium slurries and powders had acceptably low times (less than 20 minutes) to attain pH 6.8. The two with unacceptable times were the magnesium oxide powder from Fluka BioChemika, which required more than the target 30 minutes to reach pH 6.8, and the Aquamag 63 $Mg(OH)_2$ slurry, which reached pH 6.8 in less than 30 minutes but longer than 20 minutes. All of the magnesium hydroxide sources produced slurries having acceptable filtration times, although the precipitates generated by the Strem and FlowMag $Mg(OH)_2$ powders had filtration times that were significantly longer than the others. The Fluka MgO product had the shortest filtration time.

The Strem $Mg(OH)_2$ powder and the Aquamag 63 $Mg(OH)_2$ slurry products also produced poorer (lower) calcined filtercake tapped densities compared with the other test materials, with tapped densities 12% and 14% below the average densities of the samples in Table C.2. The Fluka MgO product had a tapped density 22% higher than the seven-test average. The other four tests had tapped densities within 2% of the average.

The magnesium hydroxide sources differed in their handling behaviors. The MgO powders were less dense than the $Mg(OH)_2$ powders and, thus, were more difficult to wet and enter the solution. The amount of dry MgO that had to be scraped from the sides of the beaker and into the solution using a spatula was greater than that of the $Mg(OH)_2$. However, once in the liquid, the MgO powders suspended in a manner comparable to the $Mg(OH)_2$ powders. The MgO powders also were more prone to dusting (and falling outside the beaker) during addition than the $Mg(OH)_2$ powders. The MgO powder initially floating on the solution surface also became airborne where the air-sparge bubbles broke through the solution.

Though the $Mg(OH)_2$ powders dusted to some extent during addition, the dusting was not as pronounced as with the MgO powders. The $Mg(OH)_2$ powders also did not cake as badly as the MgO on the moist sides of the beaker, but scraping with a spatula still was required to push the $Mg(OH)_2$ into the suspension. The reaction of the magnesium hydroxide sources with the test solution is exothermic and is manifested as a temperature rise upon reaction. The temperature increases produced by the MgO powders were about 18°C greater (to ~81°C) than those produced by the $Mg(OH)_2$ powders or slurries (to ~63°C).

As would be expected, the two $Mg(OH)_2$ slurries did not dust or cake on the sides of the beaker. These slurries were easily directed to the solution vortex at the center of the beaker. The Aquamag 63 appeared to be less viscous than the FlowMag H slurry. Perhaps because of its lower viscosity, the Aquamag 63 formed smaller curds less prone to settling than were found for the other materials. The Aquamag 63 was added as a steady stream from a small beaker. The FlowMag H slurry was gravity fed through a 6-mm hole at the bottom of a 50-mL syringe body. As a result, the FlowMag H stream added to the stirring solution was thicker than the Aquamag 63 stream and settled more rapidly to the beaker bottom. The stir bar had to be moved around the edge of the beaker to create a suspension of the settled material. The FlowMag H has an additive to maintain a stable suspension so that only daily agitation is needed to maintain a uniform mixture. The additive may have contributed to the behavior of the slurry when it was gravity fed from the syringe tube. The Aquamag 63 slurry is not stabilized and needed to be well agitated just prior to aliquoting to obtain a uniform suspension. The difficulty of maintaining a uniform suspension in the Aquamag 63 perhaps contributed to the fact that that the Aquamag 63 supplied by the vendor had a lower concentration of magnesium hydroxide than was specified.

The test results showed that any of the $Mg(OH)_2$ powders would be acceptable for use in the process with the least desirable being the Strem material. The Fluka $Mg(OH)_2$ powder is recommended over the other two because it had the best combination of neutralization time, filtration time, calcined filtercake weight, and tapped density. The slurries that were tested did not demonstrate superior neutralization time, filtration time, calcined filtercake weight, or tapped density but were easier to handle. The MgO powders did not handle as well as the $Mg(OH)_2$ powders. However, the Fluka MgO had superior filtration time, calcined filtercake weight, and tapped density compared with all materials tested.

The benefits of handling slurries (to defeat dusting and eliminate the need for scraping moist powders from the vessel walls) while preserving the benefits of powders [i.e., the ability to deliver a known quantity of MgO or $Mg(OH)_2$] may be attained by pre-slurrying weighed powder portions. However, tests must be performed to determine if the presence of the slurrying water unduly affects the process outcomes.

Table C.2. Summary of Source Test Results

Test No.	$Mg(OH)_2$ Source	Time, min				Filtercake		Calcined Powder		
		pH 2	pH 4	pH 6.8	Filtration	Weight, g	Volume, mL	Weight, g	Bulk Density, g/L	Tapped Density, g/L
FLKAOH-2-3-25-1	Fluka $Mg(OH)_2$ - $Mg(OH)_2$	5.6	7.5	13.3	6	24.96	18	6.91	1.57	2.02
STRM-1-3-25-1	STREM - $Mg(OH)_2$	4.6	6.7	13.5	12	25.69	18	7.64	1.41	1.73
MHP-2-3-25-1	FlowMag MHP - $Mg(OH)_2$	3.3	6.5	18.5	9	28.09	20	7.32	1.54	2.01
H-3-3-25-1	FlowMag H - $Mg(OH)_2$ slurry	5.6	7.6	15	7	21.93	15	6.63	1.62	1.93
NW-2-3-25-2	Aquamag 63 - $Mg(OH)_2$ slurry	1.8	8.1	24.7	7	24.61	18	7.59	1.17	1.70
FLKAO-3-3-25-1	Fluka MgO - MgO	5.6	10.2	35.5	4.5	22.76	18	6.13	2.01	2.42
HP-1-3-25-2	FlowMag HP - MgO	3.7	6.4	20	6	26.27	20	7.29	1.45	2.01

Appendix D

Effect of Neutralization Rate on the $Mg(OH)_2$ Process

Appendix D

Effect of Neutralization Rate on the $Mg(OH)_2$ Process

During the $Mg(OH)_2$ source test series, while the mixing protocol still was being developed, it became apparent that the neutralization rate significantly affected both the wet filtercake volume and the filtration time. The variable conditions required that several of the $Mg(OH)_2$ tests be repeated. However, it appeared that for the same source of $Mg(OH)_2$, very slow neutralization times produced slurries with faster filtration times and lower wet filtercake weights. However, it was not obvious whether the favorable qualities occurred because of extended time over the entire neutralization period or just that period where the majority of the neutralization took place. Several tests were conducted using the Fluka $Mg(OH)_2$ powder to investigate further the effects of neutralization time on the filtration rate, the wet filtercake weight, and the properties of the calcined material.

Procedure

The neutralization rate tests generally were conducted in the same manner as used in the source test series. The beaker test apparatus (Figure B.1, Appendix B) was used with air sparging; 10% stoichiometric excess (later determined to be 7.8% excess) Fluka BioChemika $Mg(OH)_2$ was added to 0.157 M Ce(IV) in 3 M HNO_3. The primary difference between the source test series and the neutralization rate test series was in the rate used to add the $Mg(OH)_2$ to the test solution. In the $Mg(OH)_2$ source test series, the $Mg(OH)_2$ was added in a single aliquot; in the neutralization rate test series, the $Mg(OH)_2$ was added in two or more batches so that initially there much less than 8% excess $Mg(OH)_2$ available for neutralization. In some cases, the $Mg(OH)_2$ was added in only two or three batches; in others, it was added in as many as six separate batches. To take full advantage of the test information, data from the source tests series for the Fluka BioChemika $Mg(OH)_2$ were included in the analysis of the results from the neutralization rate test series.

Results

To evaluate the effect of neutralization rate on the filtercake properties, particular attention was paid to the elapsed time between pH 2 and pH 4. The ceric hydrous oxide precipitate first forms around pH 2; above about pH 4, the precipitate begins to coagulate, and the precipitation color changes from yellow to light brown. As shown in Figure D.1, a decreasing neutralization rate, measured as the time elapsed between pH 2 and pH 4, decreases both the wet filtercake weight and the filtration time. The sensitivity to neutralization rate is most pronounced for intervals less than 3.5 minutes (i.e., increasing the neutralization time between pH 2 and pH 4 above about 3.5 minutes has little marginal effect on improving filtercake properties).

Figure D.2 shows the effect of neutralization time, in the interval pH 2 to pH 4, on the calcined filtercake volume and density. A constant minimum calcined filtercake volume occurs for neutralization times between about 1 and 3 minutes, and is reflected in the relatively constant tapped density in this range. As shown in Figure D.1, the wet filtercake weight decreases over this time interval and should reduce the calcined weight of the filtercake because the inventory of entrained $Mg(NO_3)_2$ is decreased. The calcined filtercake volume increase as the time interval increases above 3 minutes is mirrored by a decrease in the tapped density. The wet filtercake weight remains relatively constant over this time interval.

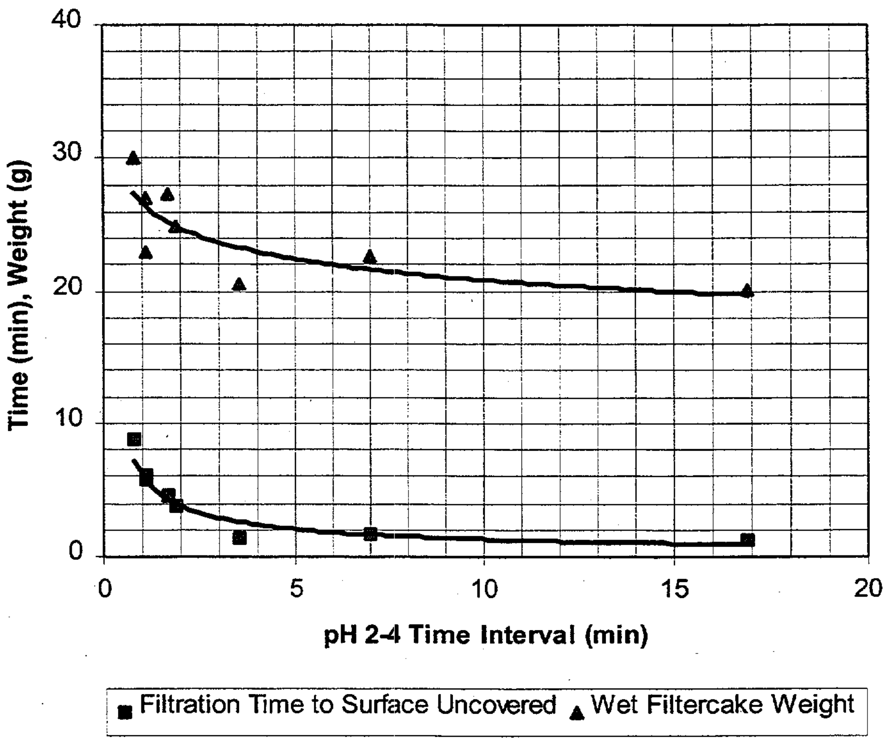

Figure D.1. Effect of Neutralization Time (pH 2-4) on the Filtration Rate and Wet Filtercake Weight

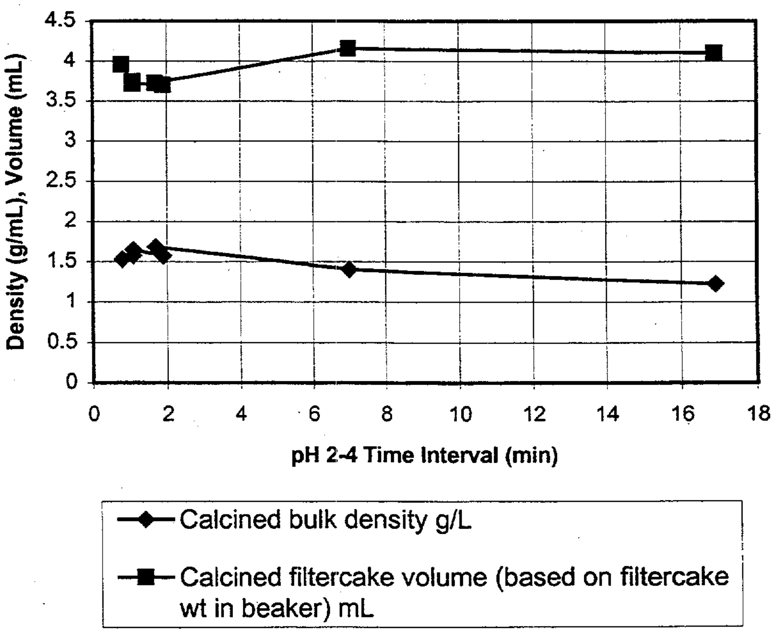

Figure D.2. Effect of Neutralization Time (pH 2-4) on the Calcined Filtercake Density and Volume

Figure D.3 shows the effect of the pH 2-4 neutralization time on the 1-hour and 24-hour calcined filtercake weight gains caused by water and CO_2 absorption from the air. The weight gains decrease sharply as neutralization times increase to 4 minutes. This trend matches the corresponding wet filtercake weight decrease [and parallel decrease in entrained $Mg(NO_3)_2$] over the same interval. The MgO produced by calcining the entrained $Mg(NO_3)_2$ is hygroscopic and also can collect CO_2 from the air to produce $Mg(OH)_2$ and $MgCO_3$, respectively. The absorption of the H_2O and CO_2 to form these compounds is manifested in the observed solids weight gains.

The best combination of low filtration time, high product density, and low retained interstitial liquid [and thus low entrained $Mg(NO_3)_2$ salt] is with a pH 2-4 time of about 3 minutes. Greater times decrease calcined solids density, whereas shorter times increase the hygroscopicity of the solids and slow the filtration.

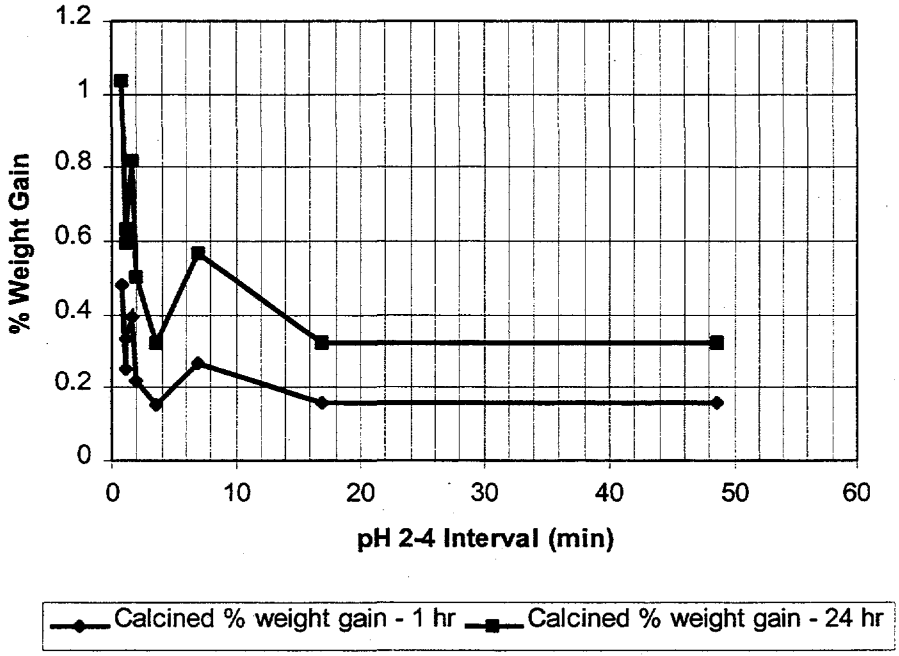

Figure D.3. Effect of Neutralization Time (pH 2-4) on Calcined Solids Weight Gain by Absorption

Appendix E

Discussion of Baseline Tests

Appendix E

Discussion of Baseline Tests

The baseline test series was conducted to examine a range of solution acidities and cerium(IV) concentrations (at three levels each) to simulate the range of pure plutonium nitrate/nitric acid solutions available for processing at the PFP. "Pure" plutonium nitrate solutions are considered to be those without significant concentrations of other metal ions such as Fe^{3+}, UO_2^{2+}, Na^+, and Al^{3+}.

Table E.1 lists the conditions evaluated in the baseline test series. The tests examined neutralization time, filtration time, wet filtercake volume and weight, and dried/calcined filtercake weight, volume, density, and weight gain by absorption after calcination. Each condition was tested in triplicate to ascertain the scatter of the data. In addition to the original test matrix, tests were conducted using 0.157 M Ce at intermediate 1.5 M and 2.5 M HNO_3 concentrations to better define the observed trends. Tests at 0.209 M Ce in 0.69 M HNO_3 also were conducted to extend the high Ce(IV) concentration series to the lowest acid concentration possible with the stock ceric nitrate solution.

To complete the baseline test series, reverse strike (acid added to base) treatment of $Mg(NO_3)_2$ filtrates over a range of concentrations was performed to determine the volume percent of settled and centrifuged solids. The filtrates were adjusted to pH 13 (0.1 M NaOH) using 50 wt% NaOH solution (i.e., under the conditions that would be used to dispose of the filtrates to the Hanford underground waste storage tanks).

Table E.1. Test Matrix

[Ce(IV)], M (Pu Equivalent)	1 M HNO_3	2 M HNO_3	3 M HNO_3
0.109 (25 g/L)	X	X	X
0.157 (37.5 g/L)	X	X	X
0.209 (50 g/L)	X	X	X

Experimental Procedures

In each of the Ce(IV) precipitation baseline tests, a single aliquot of Fluka $Mg(OH)_2$ powder at 8% stoichiometric excess was added to 200 mL of test solution in a 400-mL beaker. Agitation was accomplished using a 1-inch stir bar on a Corning magnetic stirrer set at 8. Neutralization time was either 20 minutes or until the solution reached a pH of 7.00, whichever was the greater time. Only one test (0.209 M Ce/1 M HNO_3) required longer than 20 minutes (23.8 minutes) to complete.

The product mixture of excess $Mg(OH)_2$ and ceric hydrous oxide ($CeO_2 \cdot xH_2O$) slurry was immediately filtered through a Whatman 41 paper filter (nominally a <25 μm filter), and the filtration time was recorded. The filtercake was collected and weighed. The filtercake volume was measured by packing the filtercake into a volume-calibrated 30-mL beaker. The filtercake was transferred to a crucible where it was dried at 500°C for 2 hours and then calcined at 950°C for 2 more hours. The calcined samples were cooled in a desiccator, removed and weighed, and then left on the laboratory bench exposed to the room air and reweighed at 1 and 24 hours to determine the amount of weight gain due to moisture and CO_2 absorption from the air. The calcined product was then ground and sieved to pass a 20-mesh screen. The bulk and tapped densities of the calcined filtercake were determined using the whole sample and a 10-mL graduated cylinder with 0.1-mL graduations.

Filtrate was collected from one test at each of the nine compositions (Table E.1) and made alkaline to determine the volume of $Mg(OH)_2$ solids produced. [Materials disposed to the mild steel Hanford waste storage tank system must be made alkaline before being discharged.] The filtrates, which are essentially $Mg(NO_3)_2$ solution, were treated with 50% NaOH by reverse strike (filtrate added to NaOH) to reach pH 13 (0.1 M NaOH). The NaOH treatment immediately produced slimy gel-like $Mg(OH)_2$ precipitates. Four additional lower-concentration slurries were prepared by diluting several of the NaOH-treated filtrates with 0.1 M NaOH (as perhaps would be necessary to meet the <5 vol% solids criterion for tank farms disposal). The slurries were settled for 12-13 days, and the settled solids volumes determined periodically. The slurries then were resuspended by shaking, and the slurries centrifuged at 3200 G (18-cm radius rotor at 4000 RPM) for 20 and 40 minutes in volume-calibrated cones. The settled solids volumes were measured and recorded after the 20- and 40-minute centrifugation periods.

Operational Results

Several operational phenomena noted in the baseline tests as discussed below. These include the formation of gel during neutralization and variations in the neutralization rate, filtration time, and filtercake properties.

Gel Formation

A sequence of visible changes occur during the treatment of acidic Ce(IV) solution with the $Mg(OH)_2$. The initial Ce(IV) solution is bright yellow-orange in color and pure $Mg(OH)_2$ is white. As described in Appendix B, the $Mg(OH)_2$ powder forms clumps when added to the well-stirred Ce(IV) solution. The solution's yellow-orange color weakens in intensity as the $Mg(OH)_2$ dissolves and the pH increases from the initial negative values noted in the starting Ce(IV) solution. The solution also becomes more turbid as the $Mg(OH)_2$ clumps are dispersed. At pH 1.8 to 2.3, an abrupt increase in turbidity occurs with the suspension taking on a milky lemon-yellow appearance. The brightness of the yellow color fades as the pH continues to increase. At about pH 2.3 to 2.7, the more concentrated suspensions rapidly form gel such that under the most extreme conditions, the agitation may not propagate past the immediate volume swept by the stir bar. Despite the lack of agitation, the pH continues to rise, the gel color deepens from a yellow to light tan to brown. The suspended solids become visibly grainy with a mixture of white $Mg(OH)_2$ particles and purplish brown particles presumably the hydrous ceric oxide. (The purplish brown color likely is an optical effect. It persists in calcined filtercake, but individual particles under a microscope appear more yellowish brown.) If the dark particles are crushed by a spatula, the inside is white. By about pH 5, the gel is brown and begins to break up, as shown by the suspension beginning to stir throughout the entire volume with ultimate formation of a vortex.

Evaluations of the severity of gel formation for the different test conditions are given in Table E.2. At 0.105 M Ce(IV), though gel formed, it did not stop the suspension from mixing through its entire volume. The lesser effect at the lower cerium concentrations no doubt is a manifestation of lower solids loading. At 0.157 M Ce(IV), gel formation was moderate in both the 1 and the 3 M HNO_3 solutions but was not apparent in the 2 M HNO_3 solution. Gel formation was significant in the 0.209 M Ce(IV) solutions at 1 and 3 M HNO_3 but only moderate in the 2 M HNO_3 solutions. Where gel formation was severe, it was not possible to agitate the gel with the stir bar except in its immediate vicinity. One result of gelation is

Table E.2. Severity of Intermediate Gel Formation for Various Operating Conditions

Solution	**1 M HNO_3**	**2 M HNO_3**	**3 M HNO_3**
0.209 M Ce	Severe	Slight	Severe
0.157 M Ce	Slight	None	Slight
0.105 M Ce	None	None	None

the formation of pH gradients in the suspension. The pH increase lags in regions of lower agitation with the result that longer neutralization times are required. The retardation of pH by gelation could be especially crucial for solutions of low initial acid concentration that already have long neutralization times.

Neutralization Time

The time to reach pH of 6.8 for each test decreased with increasing acidity, even though more acid required neutralization. Data for this trend, shown in Figure E.1, are scattered likely because of variations in the way that the $Mg(OH)_2$ solids were stirred into solution. For example, it was necessary in all experiments to move the magnetic stir bar around the bottom of the beaker to break up solids that rested on the bottom. Differences in this agitation would contribute to the variability in neutralization rates. Prior test results showed that the neutralization rate decreased if solids were allowed to accumulate without agitation on the bottom.

The time interval required for the pH to increase from 2 to 4 (the pH 2-4 interval) was evaluated to compare the behaviors of systems having different starting acidities. The pH 2-4 interval was chosen because it spans the pH range where most of the ceric hydrous oxide precipitation occurs. The pH 2-4 interval decreased with increasing HNO_3 concentration (Figure E.2). This trend might be explained by

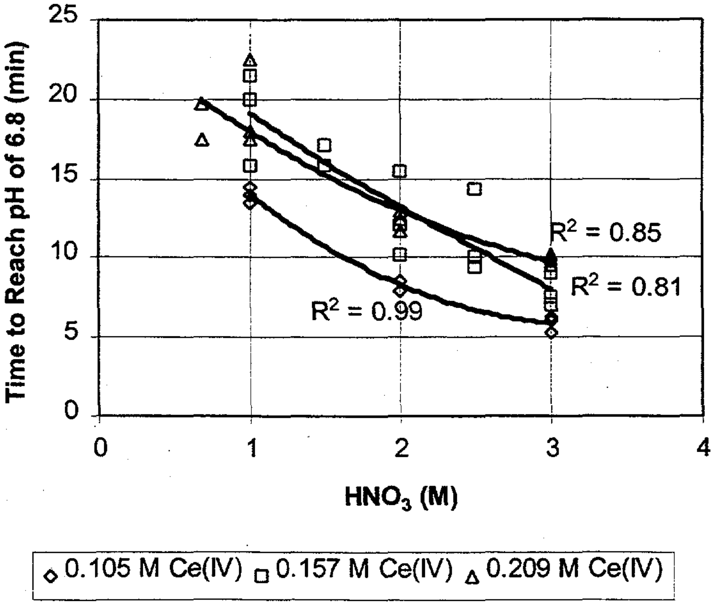

Figure E.1. Effect of Solution Initial Acidity on the Neutralization Time to pH 6.8

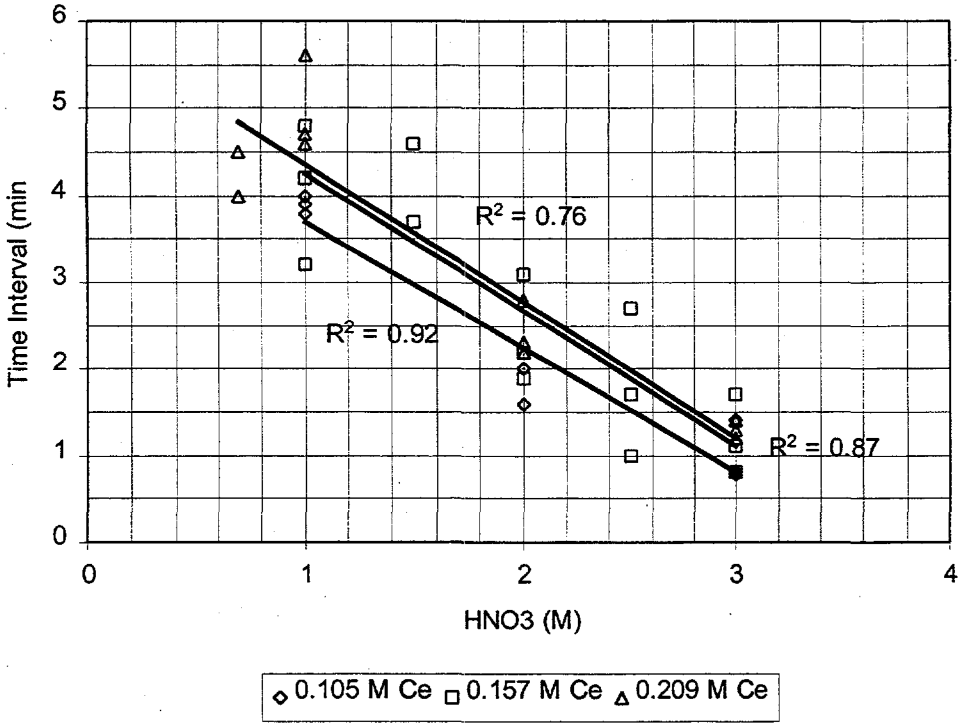

Figure E.2. Effect of Initial Solution Acidity on the Neutralization Time between pH 2 and pH 4

the fact that at higher acidities there is a corresponding increase in the amount of excess $Mg(OH)_2$ in the solution. For example, once each solution has reached 1 M HNO_3, solutions with the higher initial acidity will have a greater concentration of unreacted excess $Mg(OH)_2$ present for the remainder of the neutralization.

Temperature also could affect the neutralization rate because solutions with higher initial acidities produced higher temperatures by the heat of neutralization. In opposition to this effect, the lower $Mg(OH)_2$ solubility in water at higher temperatures (Linke 1965) would reduce the neutralization rate.

Data from the baseline tests were evaluated to investigate the effect of excess $Mg(OH)_2$ on the neutralization rate. While all baseline tests used 8% stoichiometric excess $Mg(OH)_2$, different combinations of cerium and acid concentrations produced different stoichiometric requirements, on a molar concentration basis, and required, in turn, different molar excess $Mg(OH)_2$.

As shown in Figure E.3, the pH 2-4 time interval decreases with excess $Mg(OH)_2$ as might be expected. Above about 0.09 M excess $Mg(OH)_2$ the pH 2-4 time interval was less than 2 minutes.

The inverse of the pH 2-4 time interval is a measure of the neutralization rate over the critical pH range in which the cerium precipitates. Calculation shows that the neutralization rate is correlated to the excess $Mg(OH)_2$ with a linear trend-line R^2 value of 0.63 using Microsoft Excel 2000 software. Including either initial acid concentration or the inverse of the cerium concentration significantly improved the correlation by the same amount (R^2 of 0.71 and 0.72, respectively), but including both parameters only marginally

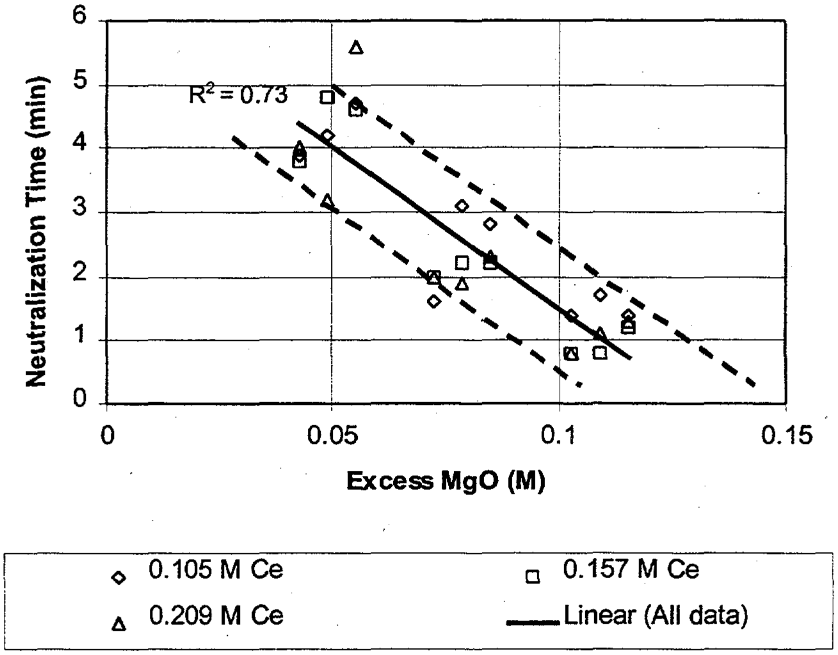

Figure E.3. Effect of Excess $Mg(OH)_2$ on the pH 2-4 Neutralization Rate

improved the correlation. One experiment was performed neutralizing 3 M HNO_3 with 8% excess $Mg(OH)_2$ as an extreme case. Using the data point in the above calculations produced a very poor R^2 value when only nitric acid was included with the $Mg(OH)_2$. On the other hand, the correlation including the $Mg(OH)_2$ and cerium terms significantly improved the R^2 value. The best empirical correlation including these two terms was :

$$\frac{1}{(\text{pH 2 - 4 time interval})} \propto \frac{[\text{excess Mg(OH)}_2]^{1.2}}{(0.05-[\text{Ce}])} \qquad (1)$$

This correlation is shown in Figure E.4. The factor in the denominator of the correlation includes a constant (0.05) to account for the limiting rate for neutralization of pure nitric acid and is based on the single experiment neutralizing 3 M HNO_3 with 8% excess $Mg(OH)_2$. If the nitric acid-only data point is included in the set, a correlation with slightly different constants produces an R^2 of 0.87 with the y-intercept set to zero (Figure E.5).

The inverse relationship of the neutralization rate with the cerium concentration may be due to buffering caused by ripening and recrystallization of the cerium hydrous oxide precipitates in this pH range. During the ripening process, acidity present as occluded HNO_3 or incompletely hydrolyzed Ce(IV) is released for exposure to the increasingly alkaline solution. Diffusion of reagents through the slurry and encapsulation of the $Mg(OH)_2$ by the precipitating Ce(IV) hydrous oxide also increase with increasing Ce(IV) concentration and could cause lower neutralization rates.

While the correlation agrees well with the data (Figures E.4 and E.5), scatter still exists. The scatter may be attributed to mixing variations in the individual experiments. Even though the stir rate was constant, size variations were observed in the $Mg(OH)_2$ solid agglomerate sizes and wetting behavior of the solids

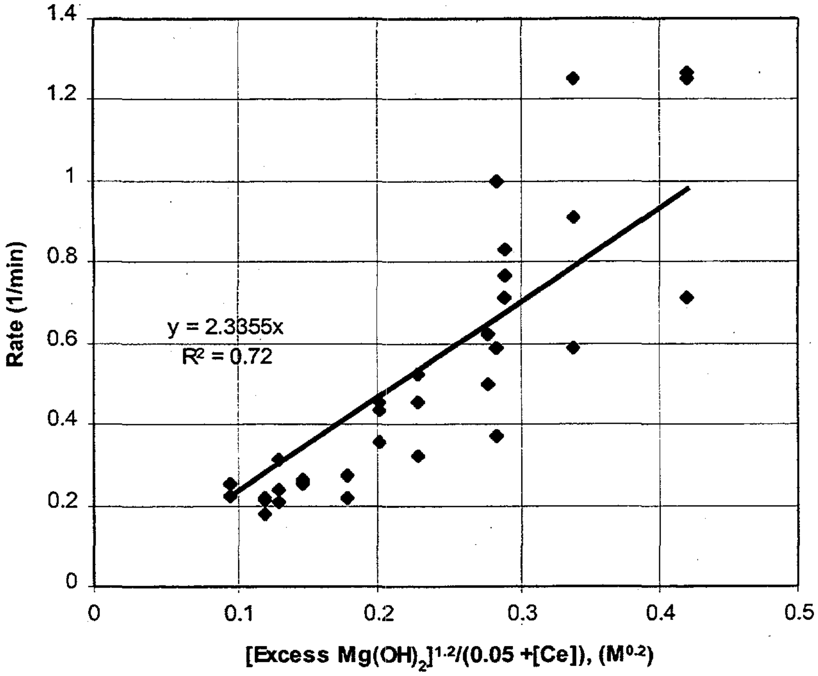

Figure E.4. Effect of Excess $Mg(OH)_2$ and HNO_3 and Cerium Concentrations on the pH 2-4 Neutralization Rate

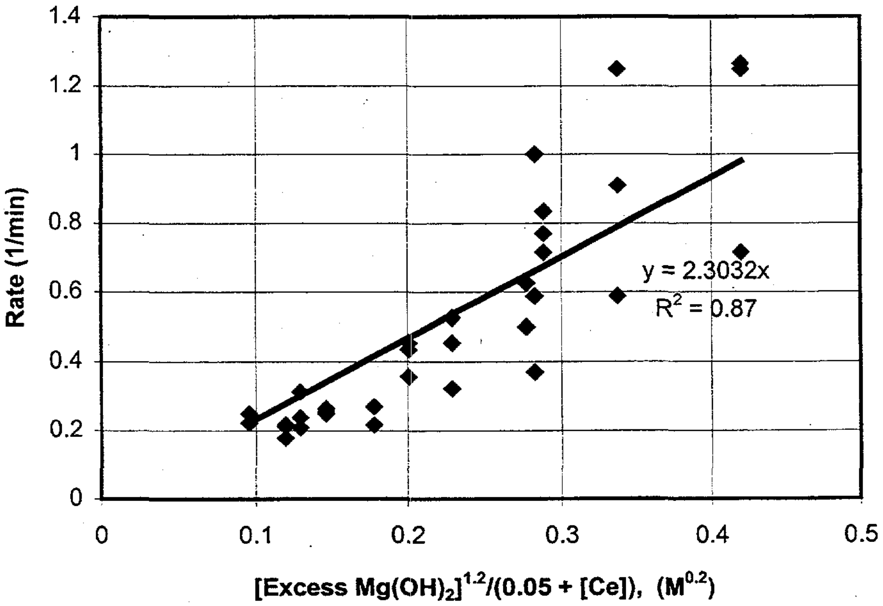

Figure E.5. Effect of Excess $Mg(OH)_2$ and Cerium on the pH 2-4 Neutralization Rate, Extrapolated to Neutralization of 3 M HNO_3 Not Containing Cerium surfaces after addition to the beaker. For plant application, the relationship given in Equation 1 may be helpful to estimate changes in the amount of excess $Mg(OH)_2$ required once the pH 2-4 time interval has been measured for one batch of solution at a specific sparge rate. The correlation of the Ce(IV) observations with plutonium and with the mixing behaviors in the large-scale process reactor may first have to be verified.

Filtercake Volume

The wet filtercake volume is an important product quality for process design because it limits the number of batches that can be held in a single filter before scraping or unloading the filter. The volume also may limit the solids mass that can be processed by a single drying/calcining boat filled with wet filtercake. The correlations between filtercake volume and filtration time, calcined filtercake volume, and loss-on-ignition (LOI) were investigated with respect to various process parameters.

Precipitation of Ce(IV) hydrous oxide is quantitative and thus, for a given initial Ce(IV) concentration and constant volume of the feed solution, the amount of precipitating Ce(IV) likewise is constant. Despite the constant Ce(IV) quantities, differences in filtercake volume and weight were noted. As shown in Figure E.6, the filtercake volume is lowest between 2.0 and 2.5 M HNO_3 for the three Ce(IV) concentrations tested. The scatter in the data, particularly for 0.157 M Ce, is attributed to the difficulty in accurately measuring the wet filtercake volume. The filtercake weight is more accurately measured, and its dependence on feed acidity (Figure E.7) shows that the filtercake undergoes a significant weight loss due to contraction of the filtercake between 1 and about 2.3 M HNO_3, even though the total $Mg(OH)_2$ inventory and product $Mg(NO_3)_2$ concentration increase in this range. Above 2.3 M HNO_3, the effects of increasing $Mg(OH)_2$ inventory and $Mg(NO_3)_2$ concentration begin to dominate, and the filtercake weight increases.

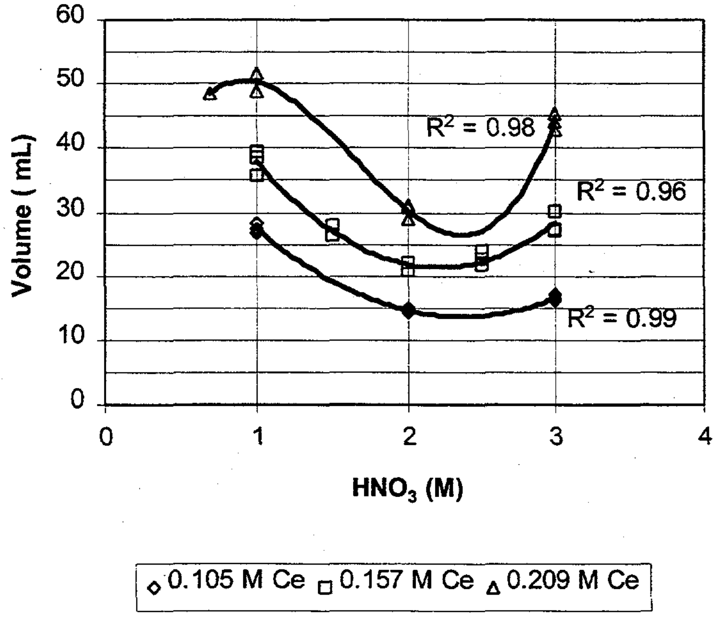

Figure E.6. Effect of Excess HNO_3 Concentration on Wet Filtercake Volume

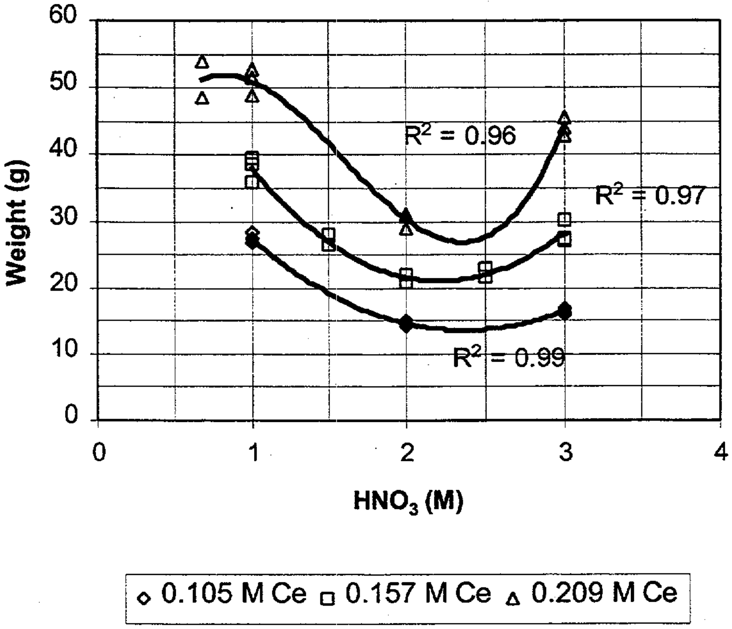

Figure E.7. Effect of Excess HNO_3 Concentration on Wet Filtercake Weight

The filtercake volume decrease from 1 to 2.3 M HNO_3 is accompanied by a change in the wet filtercake texture. At 1 M HNO_3, the wet filtercake has a crystalline texture with tendency to fracture when pulled apart with a spatula; at 2 M HNO_3 the filtercake has a clay-like texture that undergoes plastic deformation when pulled apart with a spatula. The effect of initial solution acidity on the texture and volume of the filtercake may be related to an increase in its ionic strength and the resulting non-ideal behavior of the solution at high molar concentrations. The apparent leveling or slight decrease in the filtercake volume at <1 M HNO_3 (Figures E.6 and E.7) may indicate transition to ideal solution behavior at lower electrolytic strength. Alternatively, the decrease in volume in the range 1 to 2.3 M HNO_3 again may be a manifestation of the complementary increase in temperature (and solid phase ripening).

The filtercake volumes and weights (Figures E.8 and E.9, respectively) also are related to the pH 2-4 interval, particularly for 0.105 and 0.209 M Ce. Minimum filtercake volumes and weights are found at pH 2-4 intervals of about 1.5 to 2.3 minutes. As noted above, these trends may be an artifact of the correlation between the volume, weight, and the solution initial acidity.

Filtration Time

Filtration time depends on several factors, including, but not limited to, the total mass of the solids and liquid in the slurry, the filter area, and the pore structure of the filtercake being formed (filter material and differential pressure being constant). Increasing the mass of slurry liquid should increase the filtration time. Similarly, an increasing solids mass can increase filtration time by thickening the cake and increasing the resistance to flow. Increasing the filter area decreases the filtration time by decreasing the specific filtercake thickness and by decreasing the liquid flux (flow per unit area).

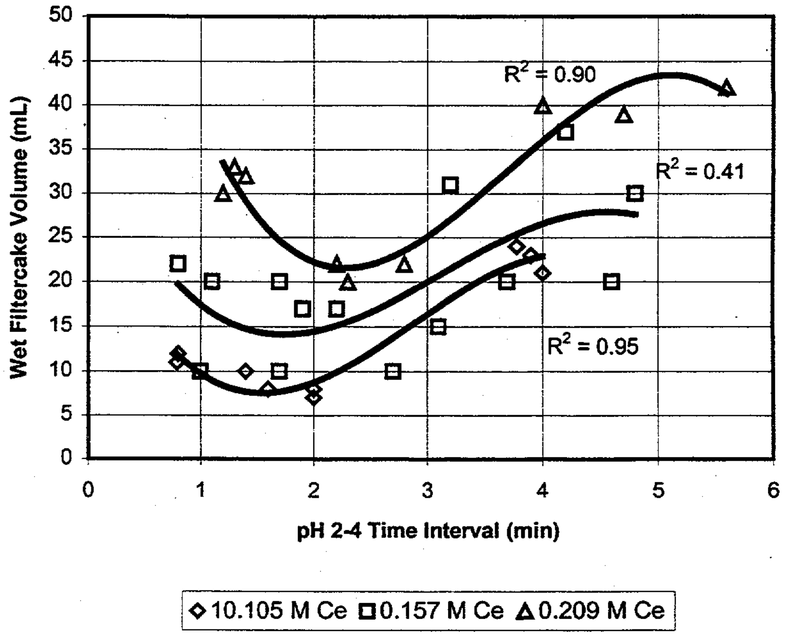

Figure E.8. Relation of pH 2-4 Time Interval to Wet Filtercake Volume

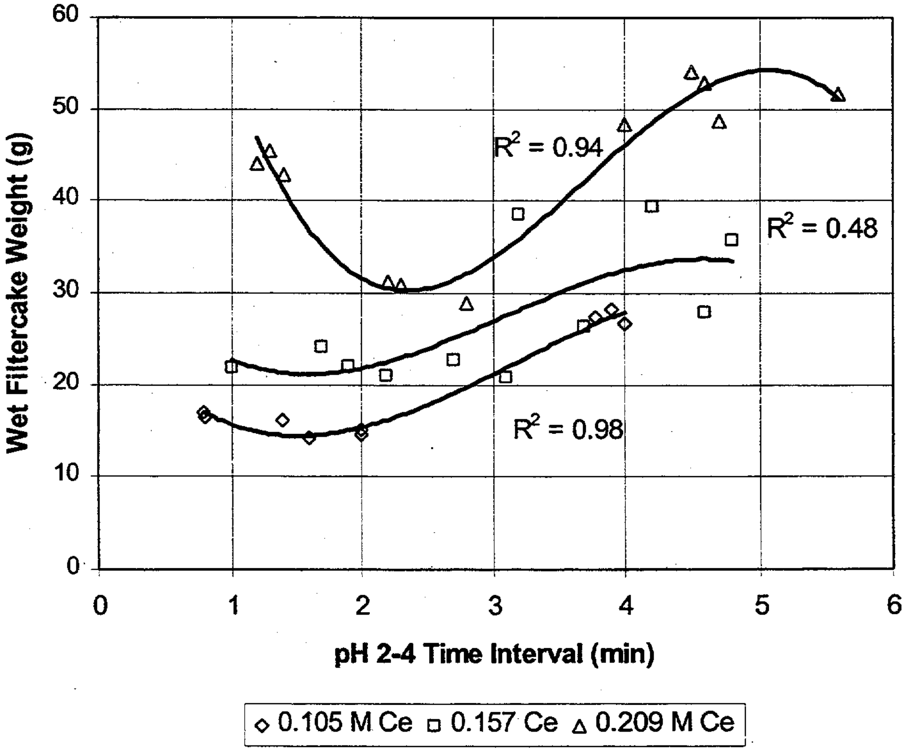

Figure E.9. Relation of pH 2-4 Time Interval to Wet Filtercake Weight

The filtercake pore structure depends on the particle size distribution, particle shape, and surface charge effects. The particle size distribution for the filtercake produced by neutralizing Ce(IV)/nitric acid solutions also may be influenced by the initial $Mg(OH)_2$ particle size distribution, the degree of uniformity of the $Mg(OH)_2$ solids dissolution, and the rate of neutralization. At high neutralization rates, the solution is highly supersaturated with respect to Ce(IV) hydrous oxide solubility and many small crystal nuclei or Ce(IV) hydrous oxides form; at lower rates, the precipitating cerium can add to existing nuclei to grow larger particles. However, at very low neutralization rates while the acidity is just below about 0.5 M HNO_3, highly insoluble polymeric ceric oxide may slowly form. The dissolution of the curd-like $Mg(OH)_2$ is inhibited by the precipitation of Ce(IV) hydrous oxide on the solid-liquid interface. This precipitated Ce(IV) coating presents a diffusion barrier to contact of solution with the $Mg(OH)_2$ solids within the curd. The surface coating can be overcome somewhat by high shear mixing, but the alkaline $Mg(OH)_2$ surface is a natural site for Ce(IV) precipitation, particularly as the pH rises. The darker Ce(IV) hydrous oxide coating on white $Mg(OH)_2$ agglomerates was demonstrated by crushing the pinhead-sized particles against the test beaker wall. The initially darker particles produced white smears when crushed.

Quantitation of the filtration time is subjective depending on the phenomena chosen to mark filtration progress. Arbitrarily, the filtration time for all tests was taken to be the interval between the start of filtering and the time at which the 70-mm-diameter filter passed filtrate at less than 1 drip/minute. In many cases, because of dewatering, the filtercake curled upwards at the edge as the filtercake compressed in the center. The subsequent curling and cracking would decrease the differential pressure and the filter surface in contact with the applied vacuum, and the filtration rate might slow in an inconsistent manner. Therefore, the time required for the surface of the filtercake to be uncovered by supernatant solution (before filtercake compression became significant) was recorded as perhaps a more consistent technique to estimate the effects of various parameters on the slurry filtering properties. For the baseline tests, the total filtration time (to <1 drip/minute) was found to be roughly twice that required to uncover the filtercake surface (Figure E.10).

Data from the baseline test series were evaluated to investigate the effects cerium and acid concentrations exert on the filtration rate. The cerium concentration would be expected to increase the filtration time by increasing the total mass of both $CeO_2 \cdot xH_2O$ and $Mg(OH)_2$ solids to be filtered. Increased acid should increase the total solids and thus the filtration time by increasing the excess $Mg(OH)_2$. Higher acid concentration would increase the concentration (and hence viscosity) and ionic strength of the product $Mg(NO_3)_2$ solution. As shown in earlier in this Appendix, increasing acid concentration also increased the neutralization rate. This, in turn, would be expected to decrease the cerium oxide particle size.

As expected, increase in cerium concentration increases filtration time for the 1 and 3 M HNO_3 solutions (Figure E.11). However, the filtration time does not appear to depend at all on cerium concentration at 2 M HNO_3, although the minimum filtration time for all cerium concentrations occurs at 2 M HNO_3.

The effect of solution acidity on filtration time is shown in Figure E.12. Tests were run at 1.5 and 2.5 M HNO_3 for 0.157 M Ce and at 0.69 M HNO_3 for 0.209 M Ce to improve understanding of the parametric trends. The tests showed a minimum filtration time is found between about 1.6 and 2.2 M HNO_3, with the filtration time minimum shifting to the lower HNO_3 concentrations at lower Ce concentrations. Filtration time also seems to level off or slightly decrease below 1 M HNO_3 for the 0.209 M Ce solutions. Similar behavior was observed with the wet filtercake weight and volume below 1 M HNO_3.

The decrease in filtration time from 1 to 2 M HNO_3 is accompanied by the previously discussed change in the wet filtercake texture from crystalline (easy to fracture when pulled apart with a spatula at 1 M HNO_3)

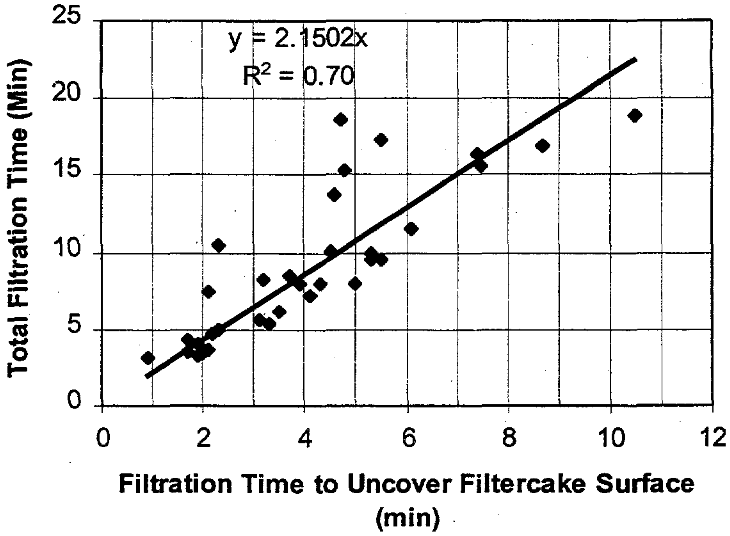

Figure E.10. Correlation of Total Filtration Time to the Time to Uncover the Filtercake Surface

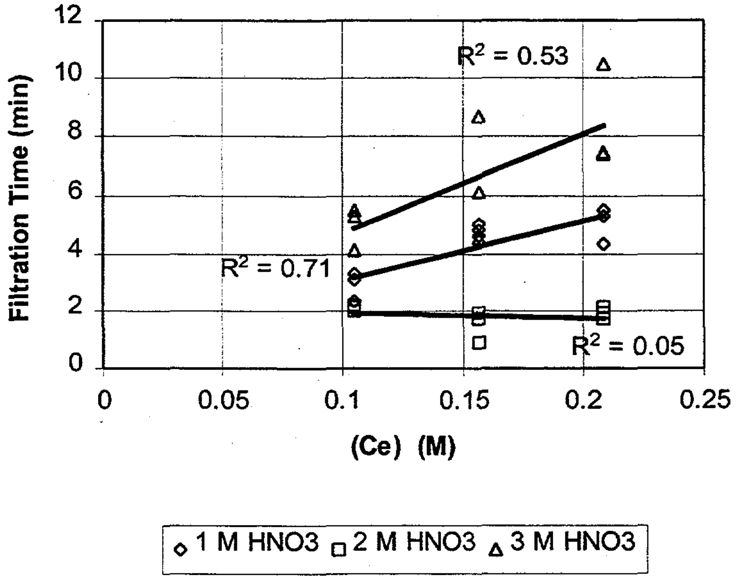

Figure E.11. Effect of Cerium Concentration on Filtration Time

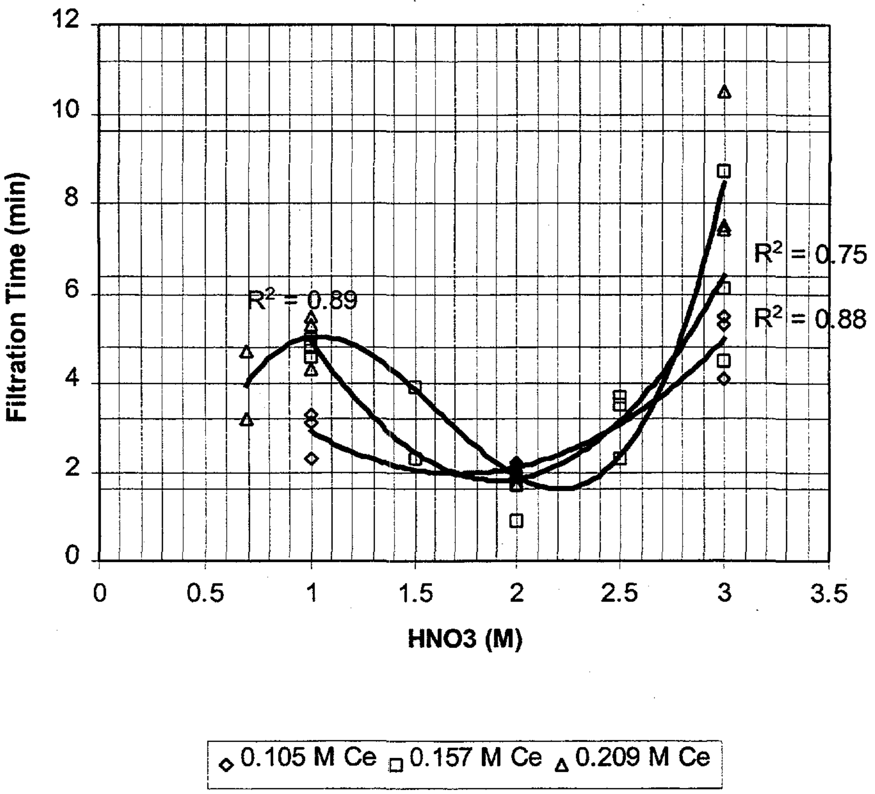

Figure E.12. Effect of Nitric Acid Concentration on Filtration Time (no supernate on cake)

to clay-like (undergoing plastic deformation when pulled apart with a spatula at 2 M HNO_3). Apparently, increased pore flow resistance does not accompany the filtercake volume contraction that was observed. Between 2 and 3 M HNO_3, the filtercake maintains its texture but the filtercake thickness increases to give an increased filtration time. Between 0.69 and 1.0 M HNO_3, the wet filtercake texture also appears to remain unchanged and may account for the increased filtration time in this region.

As seen by comparing Figures E.7 and E.12, the wet filtercake weight and filtration time have similar dependencies on HNO_3 concentration and show minima at intermediate (~2 M) HNO_3 concentration. However, there is little correlation between the filtration time and filtercake volume if all the baseline tests are considered together (Figure E.13). If the data for tests at 1 and 3 M HNO_3 initial solution acidities are considered separately; however, the expected filtration time increase with wet filtercake weight is found (Figure E.14), whereas at 2 M HNO_3, no effect is observed. Comparing the curves for 1 and 3 M HNO_3 initial solution acidity in Figure E.14, it can be seen that there is less resistance to filtration for the filtercake from the 1M HNO_3 solutions than for those of similar weight from the 3 M HNO_3 solutions. This difference can be attributed to the fact that a greater proportion of the filtercake from the 3 M HNO_3 consists of solids, because more excess $Mg(OH)_2$ would be used to neutralize the solution. Presumably, the 1 M HNO_3 solutions produce a filtercake with a more rigid and porous structure that supports a greater inventory of interstitial liquid in order to make a comparable weight of filtercake. The more porous structure would be expected to produce a better filtration rate. The independence of filtration rate with respect to the Ce(IV) concentration (and thus the quantity of cerium hydrous oxide present on the filter) at around 2 M HNO_3 is surprising (also see Figure E.11). The

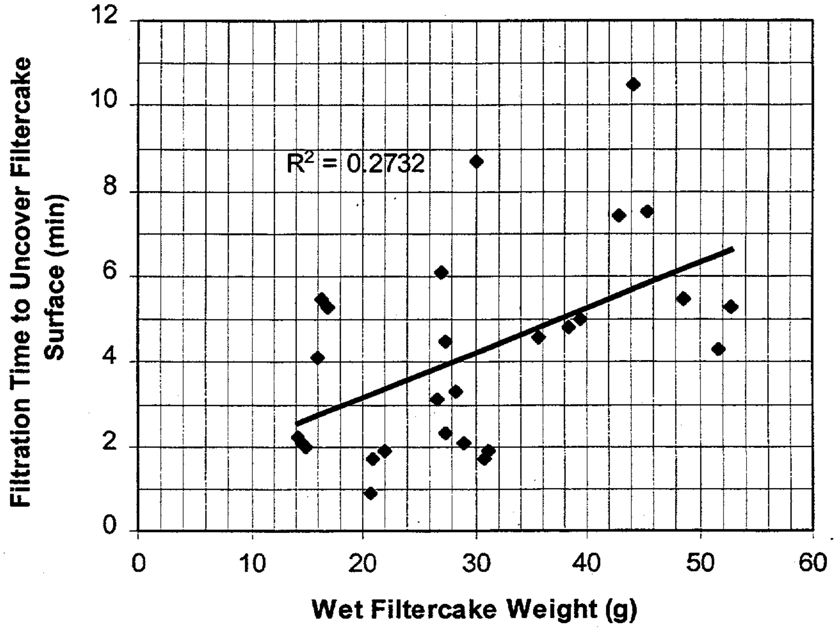

Figure E.13. Effect of Wet Filtercake Weight on Filtration Time (no supernate on cake); All Nitric Acid Concentrations Included

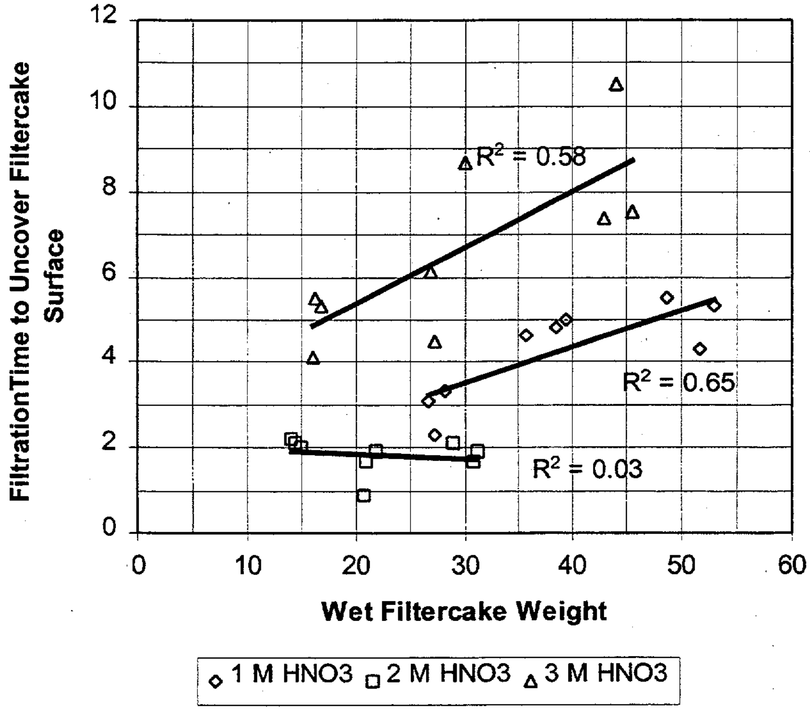

Figure E.14. Effect of Wet Filtercake Weight on Filtration Time (no supernate on cake); Various HNO_3 Concentrations Considered Separately behavior of the filtercake at 2 M HNO_3 cannot be explained at this time other than to suggest that it represents a transient condition between the other two acidities. Based solely on these findings, however, 2 M is the ideal acid concentration with respect to filtration rate.

The neutralization time also appears to affect the filtration time. Thus, as shown in Figure E.15, tests conducted at the same test conditions but with shorter (<2 minute) pH 2-4 neutralization times have significantly higher filtration times. A slight increase in filtration time occurs if the pH 2-4 neutralization time is above about 3 minutes. As noted previously, the lowest filtration times occur at ~2 M HNO_3. The pH 2-4 interval generally decreases with increasing acid concentration (Figure E.13), but the correlation is not strict. The implication of this figure is that the initial acid concentration affects both the neutralization rate and the filtration rate. It is likely that at the shorter pH 2-4 neutralization times, the $CeO_2 \cdot xH_2O$ particles have insufficient time to grow. The resulting smaller particles offer greater resistance to filtration.

Properties of the Calcined Filtercake

Two issues of concern associated with the calcined product from the neutraliztion of plutonium solutions at PFP are volume and hygroscopicity. Limited vault storage space is available at PFP. If the average calcined filtercake density is less than 2 g/cm^3, then vault storage space will not be adequate. The DOE-STD-3013-99 limit for moisture content (or weight loss if using LOI method) of oxide packaged in sealed containers is <0.5%. These two parameters for the cerium oxide used as the plutonium oxide surrogate are considered in light of the baseline testing.

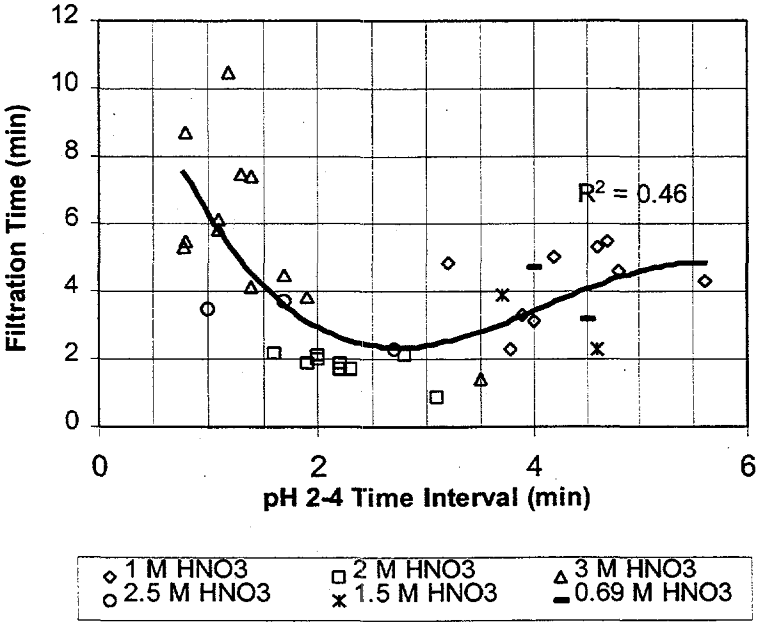

Figure E.15. Effect of Neutralization Time on Filtration Time

Calcined Filtercake Volume

The volume of calcined filtercake depends on both the mass of filtercake and the calcined filtercake density according to the equation:

$$V_{CFC} = (M/\rho)_{CFC} \tag{2}$$

where, V is volume, M is mass, ρ is density, and CFC designates calcined filtercake.

The filtercake mass depends on both the mass of precipitated solids and the mass of dissolved solids accompanying the interstitial liquid present in the wet filtercake. The precipitated solids mass for a specific test solution is fixed by the cerium concentration and the excess $Mg(OH)_2$ added to the solution beyond that required to neutralize the acid and precipitate the cerium. The cerium precipitates quantitatively as $CeO_2 \cdot xH_2O$. The $Mg(OH)_2$ mass increases with increasing cerium and acid concentration in the starting solution because it is based on 8% of the stoichiometric requirements to neutralize the solution to pH 7. As the stoichiometric requirements increase, the quantity of excess $Mg(OH)_2$ correspondingly increases. The dissolved solids mass, in turn, depends on the wet filtercake volume (and its porosity) and the $Mg(NO_3)_2$ concentration dissolved in the interstitial liquid. Upon calcination, the $CeO_2 \cdot xH_2O$ converts to CeO_2, while both the excess $Mg(OH)_2$ and the interstitial $Mg(NO_3)_2$ convert to MgO.

The baseline test conditions significantly influenced the weight, density, and volume of the calcined filtercake. Because transfers of the wet filtercake to the crucible were not quantitative, the total calcined filtercake weight was estimated by multiplying the weight of the calcined material by the wet filtercake weight recovered from the filter divided by the wet filtercake weight transferred to the crucible. Bulk densities of the calcined materials were calculated by measuring the weight and volume of calcined filtercake (ground to <20 mesh) that was added through a funnel to a 10-mL graduated cylinder. The volume was estimated to the nearest 0.05 mL. The tapped density was determined by mechanically vibrating the graduated cylinder until the volume reached a steady value. The densities of the dried and calcined pure Fluka $Mg(OH)_2$ and GFS cerium nitrate reagents also were determined in the same manner.

The effects of the cerium and nitric acid concentrations on the calcined filtercake weights are shown in Figure E.16. The calcined weight consists of the respective weights of calcined cerium oxide, calcined MgO from excess $Mg(OH)_2$, and the calcined MgO from the $Mg(NO_3)_2$ present in the interstitial liquid and produced by neutralizing the cerium nitrate and nitric acid. The calcined weight increases with increasing Ce(IV) concentration. Besides the additional cerium, the increase is due to the increase in the quantity of excess $Mg(OH)_2$ in the wet filtercake and to a lesser extent to an increase in the amount of $Mg(NO_3)_2$ in the interstitial liquid due to the neutralization of the cerium nitrate.

The calcined weight does not increase linearly with the increase in the solution acidity as might be expected. Instead, the calcined weight, as shown in Figure E.17 remains fairly constant between 1 and 2 M HNO_3 for all three cerium concentrations evaluated. Apparently, the wet filtercake volume decrease between 1 and 2 M HNO_3 concentration in the interstitial liquid (shown in Figure E.6) compensates for the $Mg(NO_3)_2$ concentration increase in the interstitial liquid and the increased excess $Mg(OH)_2$. The filtercake mass between 2 and 3 M HNO_3 increases due to an increase in the wet filtercake volume (increasing the interstital liquid inventory), the $Mg(NO_3)_2$ concentration in the interstitial liquid, and an increase in the excess $Mg(OH)_2$.

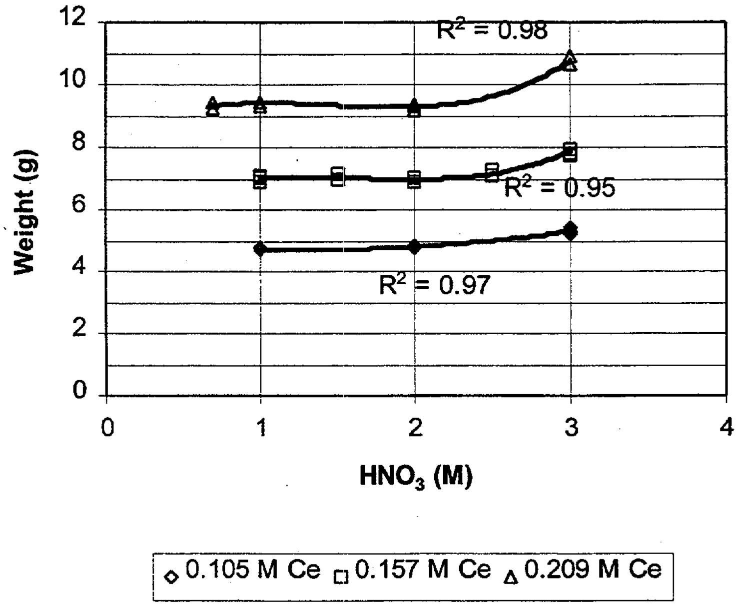

Figure E.16. Effect of Nitric Acid Concentration on Filtercake Weight

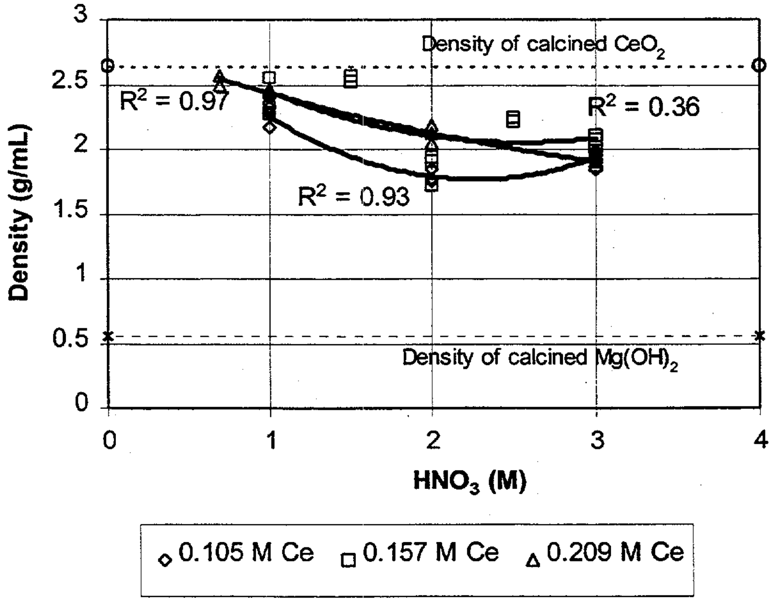

Figure E.17. Effect of Nitric Acid Concentration on Filtercake Tapped Density

Calcined Filtercake Density

The bulk and tapped density of the calcined filtercake provides a lower and upper limit for expected density of samples that are packed for storage. The tapped density was chosen over bulk density to compare the results of the different baseline tests because tapped density is considered to be the more reproducible value. Bulk density values are difficult to reproduce as accurately because the volume of a sample being measured will change significantly with any agitation of the graduated cylinder during handling. The average bulk density for all of the samples in this series was 77% of the tapped density with a maximum and minimum of 85% and 69%, respectively.

The tapped density of the calcined filtercake should follow the expected trend of decreasing density with an increasing fraction of $Mg(OH)_2$ in the sample because pure MgO has a tapped density (0.55 g/mL) that is much less dense than the tapped density of pure CeO_2 (2.65 g/mL). For solutions with the same cerium concentration, the amount of cerium oxide in the calcined filtercake should also be the same. Thus, the density of the calcined filtercake should decrease as the calcined filtercake increases, because the added weight is due to additional MgO. Similarly, the tapped density should decrease as the solution acidity increases for solutions with the same amount of cerium oxide.

The effects of cerium and nitric acid concentrations on the calcined filtercake tapped density are shown in Figure E.17. The data for 0.105 and 0.209 M Ce correlate well (R^2 of 0.79 and 0.97). However, the data for 0.157 M Ce, with additional data collected at the intermediate HNO_3 concentrations (i.e., 1.5 and 2.5 M) are not as well correlated. The data points collected at the intermediate acid concentrations, though scattered in Figure E.17, trend consistently with weight in Figure E.16. The reasons for the unusual values cannot be conclusively explained.[a] However, if the 1.5 and 2.5 M HNO_3 data are ignored, the calcined material densities at all cerium concentrations were significantly lower for materials prepared at 2 M HNO_3 than for materials prepared at 1 M HNO_3. This is true even though the total calcined filtercake weight remained the same or decreased slightly in this interval (Figure E.16). The density then increased with increasing sample weight between 2 and 3 M HNO_3 for tests using 0.105 and 0.157 M Ce. This trend contradicts the expected behavior, because the added weight should have been due to the less dense $Mg(OH)_2$. The cause for the unexpected behavior of the calcined filtercake for the higher cerium and acid concentrations was not evaluated further. However, XRD analysis did not reveal any phases other than CeO_2 and MgO in the calcined filtercake. The only other explanation at this time for these trends is that $Mg(OH)_2$ and $Mg(NO_3)_2$ may interact with the CeO_2 during calcining and not merely combine with CeO_2 as a mixture.

The combined effects of calcined sample weight and density on total sample volume for different Ce(IV) and HNO_3 concentrations are shown in Figure E.18. The calcined filtercake volume increases with increased cerium concentration at all acid concentrations. However, the sensitivity of the calcined filtercake volume to acid concentration changes depends on the cerium concentration, with higher cerium concentrations producing a much greater increase between 2 and 3 M acid concentrations.

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[a] The fact that the data at similar conditions have very similar densities for all of the tests suggests that differences arose in either the calcination procedure or the sample preparation for measuring the density. It is noted that the density measurements of materials prepared at 1.5 and 2.5 M HNO_3 and materials prepared using 0.209 M Ce in 0.69 M HNO_3 were performed after the original baseline tests and rinsing tests described in Appendix D.

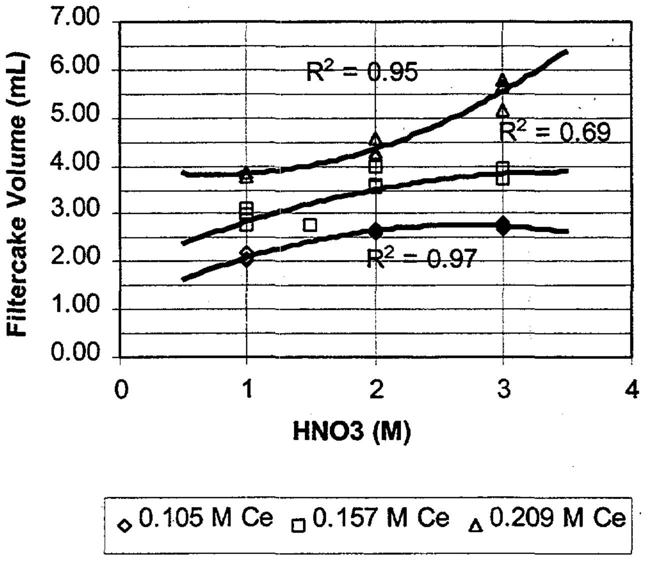


Figure E.18. Effect of HNO_3 and Ce(IV) Concentrations on Filtercake Volume

Loss-On-Ignition

An LOI test is used to estimate the amount of moisture remaining in solid materials before they are sealed into 3013 cans for storage. Moisture content must be kept low (<0.5 wt% LOI) because radiolysis decomposes water into hydrogen and oxygen gases. Gas accumulation increases the internal pressures in sealed cans and may deform them. The estimate of moisture content by the LOI test contains the key assumption that the weight lost by heating to the LOI temperature (950-1000°C) is due to water alone. However, CO_2 can absorb from the air onto the solids to form carbonates; weight loss because of decomposition of the carbonate as well as salt volatilization may increase the LOI value and overstate the water concentration of the starting material.

The LOI test results as applied to the CeO_2/MgO solids generated in the present experiments depend on the calcined material composition, calcination time and temperature, ambient air humidity, the exposure time to the ambient air, and the total mass and manner in which the material is stored during exposure.

The weight increase of calcined samples after exposure to ambient air can be measured to estimate their hygroscopicity. Measurements were taken immediately after calcined samples were removed from a desiccator where they had been allowed to cool, and again at specified periods of time following their removal. A higher weight gain for a given period was taken to indicate that the sample was more likely to fail the LOI test.

Wet filtercakes from the baseline tests were dried at 500°C for 2 hours followed by calcination at 950°C for 2 hours. The calcined filtercakes were cooled in a desiccator, weighed, exposed to ambient air for 1 hour, and reweighed. The sample mass typically ranged from 2 to 7 g, and the calcine appeared as a coarsely divided material or a single monolith in the crucibles. Many of the samples subsequently were weighed after 24 hours of exposure. Some samples were recalcined at 1000°C. Results for samples of

Fluka BioChemika $Mg(OH)_2$ and GFS Chemical $Ce(NO_3)_4$ reagents, dried and calcined by the same methods, were used for comparison.

The calcined filtercake weight gains at 1 and 24 hours for the different test conditions are shown in Figures E.19 and E.20. By comparing Figures E.19 and E.20, it is seen that approximately one half of the weight gain observed at 24 hours occurred within the first hour of exposure. One-hour weight gains of 0.08% and 0.95% observed for pure CeO_2 and MgO, respectively, bracket the 0.19% to 0.49% gains observed in the baseline test calcines at 1-hour exposure. Similarly, the 24-hour weight gains of 0.08% and 2.49% for CeO_2 and MgO, respectively, bracket the 0.37% to 1.12% gains observed for the baseline test calcines. The percent weight gains for tests at the same cerium concentration generally follow the same trends with respect to HNO_3 concentration as the calcined filtercake weight. This similarity suggests that the increased filtercake weight (due to the additional magnesium in the filtercake) is responsible for the greater weight gain. The importance of MgO content on the wet gain is confirmed by the significantly higher weight gains posted by pure MgO compared with pure CeO_2.

The effect of pH 2-4 neutralization time on the percent weight gain is shown in Figure E.21. The data suggest that the moisture and CO_2 uptake (i.e., the calcine weight gain) increases if the pH 2-4 time interval decreases below 3 minutes. Because the neutralization times are closely grouped for tests with the same initial solution acidity, the trend may be an artifact of the solution acidity.

Filtercake from one of the solutions containing 0.157 M Ce in 2.5 M HNO_3 was was first calcined at 950°C for 2 hours, cooled in a descicator, and exposed to ambient air for 1 hour. It was then recalcined at 1000°C for 2 more hours, cooled and exposed to ambient air. The 1-hour weight gain for the sample after calcining at 950°C was 0.3%. After recalcining at 1000°C the 1-hour weight gain was 0.22%, which corresponds to a reduction of 27%. While calcining for an additional 2 hours may have contributed to the lower weight gain, other samples that were recalcined at the same temperature did not show a significant decrease in the 1-hour weight gain.

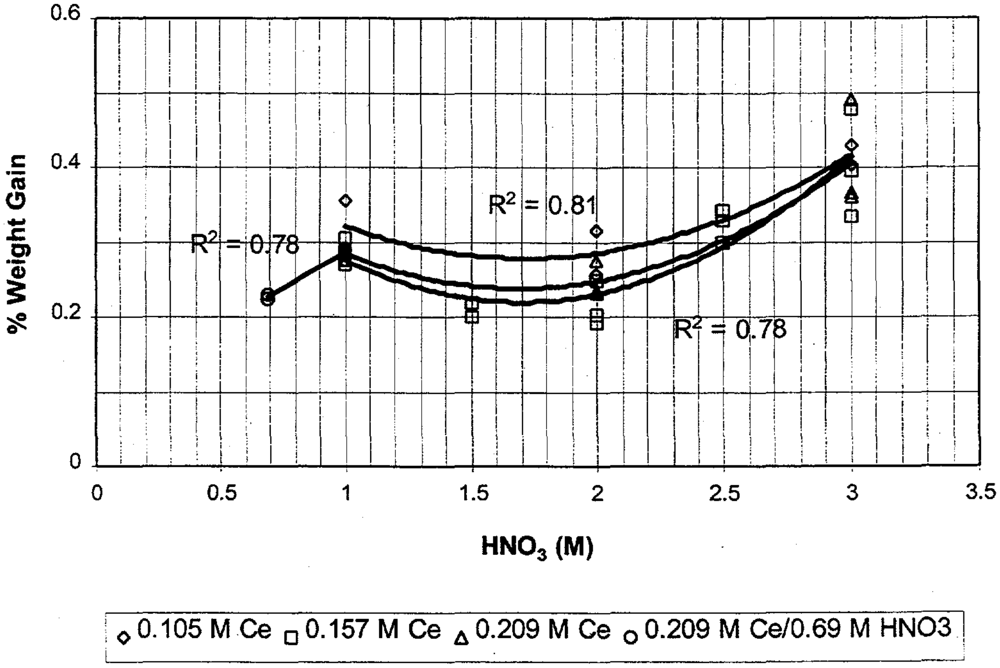


Figure E.19. Effect of 1-Hour Exposure Ambient Atmosphere on Calcined Filtercake Weight

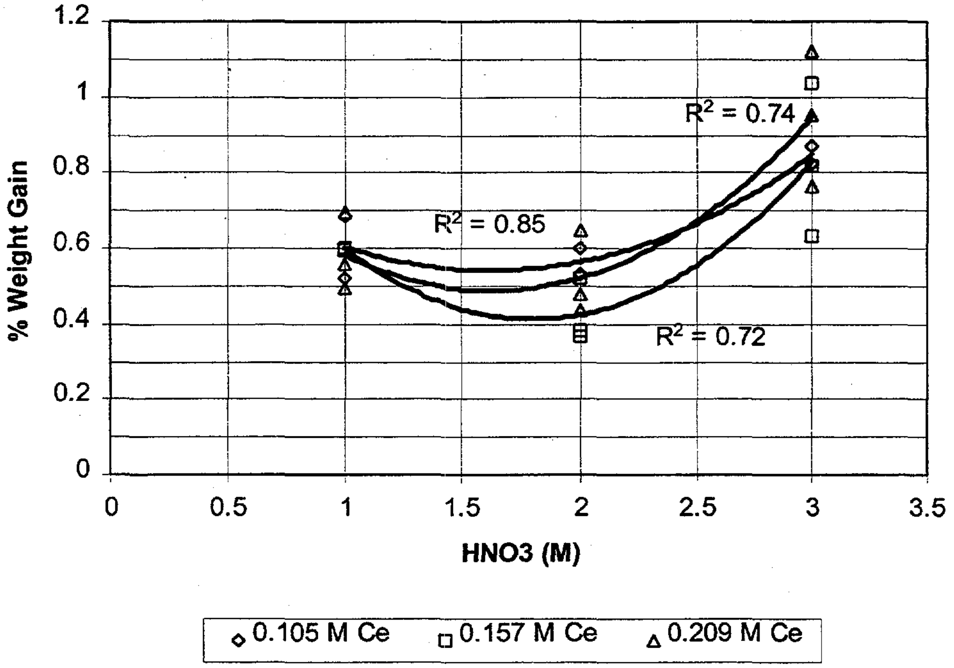


Figure E.20. Effect of 24-Hour Exposure to Ambient Atmosphere on Calcined Filtercake Weight

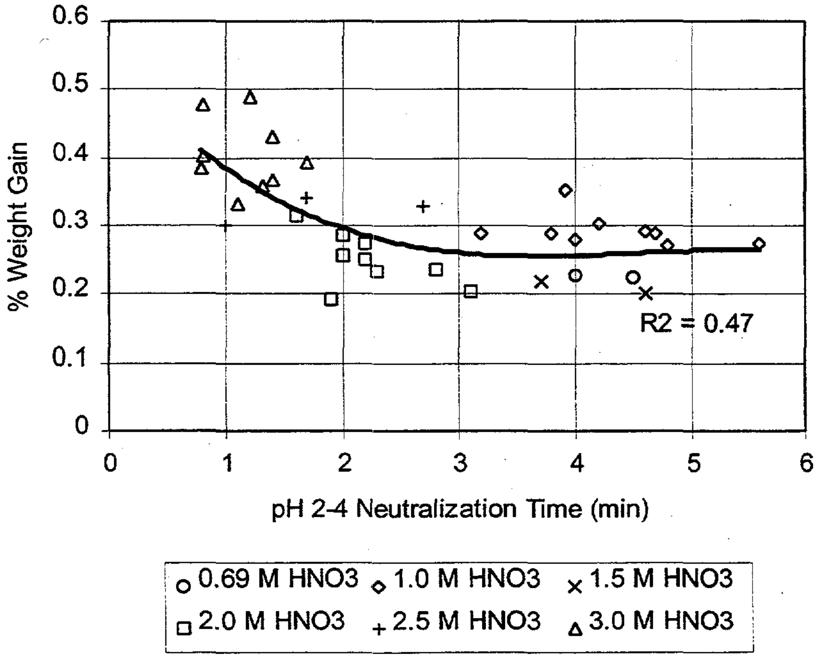


Figure E.21. Effect of pH 2-4 Neutralization Time on the Calcined Filtercake Weight Gain at 1 Hour

Alkaline Treatment of Filtrate

A 5 vol% solids-loading limit exists for disposing liquids from PFP to the underground storage tanks. Tank disposal also demands that the treated effluents be pH 12 or higher (and that the filtrate be lower than 330 mg Pu/L; furthermore, between 1 and 330 mg Pu/L, the filtrate must meet criticality criteria prior to disposal). The filtrate from the precipitation process contains dissolved $Mg(NO_3)_2$ at concentrations proportional to the alkali required to convert the plutonium-bearing acidic feed solution to reach pH 7. Treatment of the filtrate with NaOH to reach the pH >12 criterion will cause the magnesium to precipitate as $Mg(OH)_2$ according to the following reaction:

$$Mg(NO_3)_{2(s)} + 2NaOH_{(aq)} \rightarrow MgO_{(s)} + 2\ NaNO_{3(aq)} \qquad (3)$$

The volume of solids produced by NaOH treatment of $Mg(NO_3)_2$ filtrates were measured to determine the maximum $Mg(NO_3)_2$ concentration that could be tolerated and yet meet the 5 vol% disposal criterion. The starting filtrates also were analyzed for cerium concentration as an indicator by chemical analogy of plutonium concentrations, which might be expected in the process.

Inductively coupled plasma (ICP) analyses of filtrate for the baseline tests were performed to determine whether the solution contained suitably low cerium concentrations. All filtrates analyzed by ICP first were filtered through 0.5-μm polishing filters. All solutions had cerium concentrations at or below the 1 ppb detection limit (corresponding to $\sim 7 \times 10^{-9}$ M Ce). Provided Pu(IV) behaves like Ce(IV) on a molar basis, this concentration corresponds to <0.002 mg Pu/L, well below concern for direct tank farm disposal.

The $Mg(NO_3)_2$ concentrations are expected to range from about 1 to 1.5 M in the process. Filtrates produced from $CeO_2 \cdot xH_2O$ slurry filtration in the baseline tests ranged from 0.71 to 1.91 M $Mg(NO_3)_2$. These $Mg(NO_3)_2$ filtrates were treated with 50% NaOH by reverse strike (filtrate to NaOH) to reach pH 13 (0.1 M NaOH). In each case, neutralization produced slimy to pasty glutinous white $Mg(OH)_2$ slurries. Additional lower concentration slurries subsequently were prepared by diluting several NaOH-treated filtrates with 0.1 M NaOH as would be necessary for tank farms disposal.

The slurries were settled for 12 to 13 days and the settled solids volumes determined periodically. Most settling occurred in the first few days, but the more concentrated slurries were slower to settle. The slurries were then resuspended (shaken), and the slurries were centrifuged at 3200 G (18-cm radius rotor at 4000 RPM) for 20 and 40 minutes.

Results of the settling and centrifugation tests of the neutralized filtrates are shown in Figure E.22. The settling by centrifugation seemed to be complete (and the results linear) at 40 minutes for those tests conducted with feeds at or below 2 M nitrate. It is expected that further centrifugation would bring the three points at around 3 M nitrate in line with the data from the lower concentration tests. For the lower concentration tests, additional centrifugation is expected to have little effect (see the lack of effect between 20 and 40 minutes below 1 M nitrate). Based on the results shown in Figure E.22, filtrates must be diluted to approximately 0.5 M nitrate [0.25 M magnesium in these tests without significant other nitrate salts] to achieve the 5 vol% solids concentration limit. Under the range of baseline test conditions studied, this corresponds to filtrate dilutions ranging from about 14X to 30X.

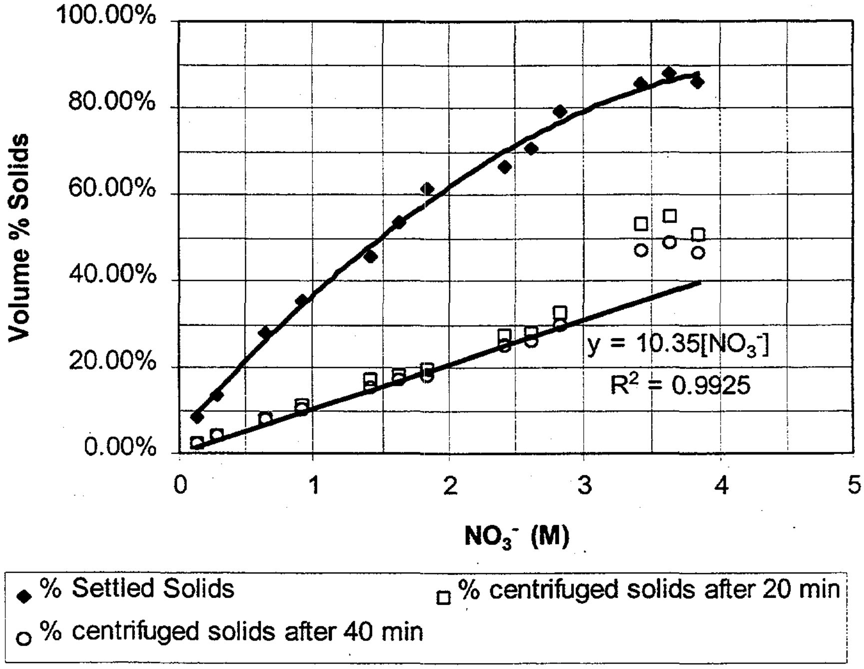


Figure E.22. Settled Centrifuged Solids of Neutralized (pH ~13) Filtrate vs. Initial HNO_3 Concentration

Reference

Linke, W. F. 1965. *Solubilities of Inorganic and Metal-Organic Compounds*, 4th edition. American Chemical Society, Washington, D.C.

Appendix F

Rinsing Test Series

Appendix F
Rinsing Test Series

The rinsing test series was conducted to determine whether filtercake tapped density and hygroscopicity [as measured by weight loss-on-ignition (LOI) after exposure to room air] could be improved by rinsing $Mg(NO_3)_2$ from the filtercake before the latter is dried and calcined. To this end, the effects of rinsing strategies on filtration time and filtercake properties were investigated. The effect of calcination temperature on tapped density and LOI also was investigated in limited tests.

Overview of the Test Procedures and Test Strategy

Rinsing solution can be added in three ways:

1. to the slurry, effectively diluting it
2. to the surface of the filtercake just as it becomes uncovered but not further dewatered
3. after the filtercake has been filtered until most or all of the solution has been removed and the filtercake is compressed and cracked.

Using a spreader to heal the cracks in the compressed and cracked filtercake before adding the rinse water could also prevent the rinse water from bypassing the filtercake and simply draining. Figure F.1 diagrams an uncompressed and a compressed and cracked filtercake.

The slurry from more than one precipitator also may be added to the filter prior to rinsing. In this mode, each slurry would be filtered to some point (e.g., compressed or uncompressed) before adding the next slurry. After two or more slurries were filtered in this manner, the filtercake would be rinsed.

Tests were performed with solutions having low-Ce/high-acid (0.105 M Ce in 3 M HNO_3) and high-Ce/low-acid (0.209 M Ce in 1 M HNO_3) concentrations. These concentrations are consistent with the PFP plutonium solution compositions thought most likely to be processed. The 0.105 and 0.209 M Ce molar concentrations correspond to 25 and 50 g Pu/L, respectively.

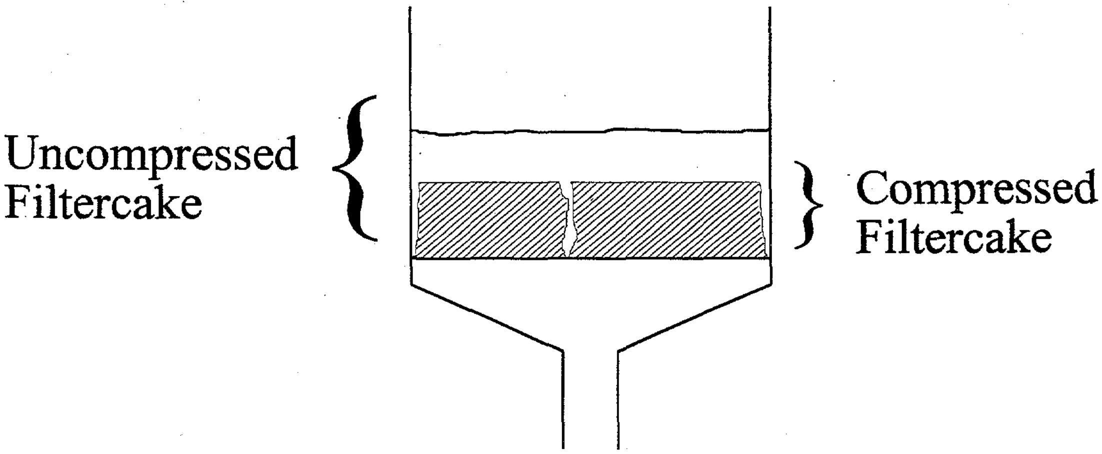


Figure F.1. Sketch of Uncompressed and Compressed Filtercake

Slurries for the rinsing tests were prepared using the same methods described for the baseline tests (Appendix E). When two or more slurries were filtered on the same filter paper, the slurries were prepared concurrently but with a delay between batches to decrease the time between the second slurry batch reaching neutralization (nominally 20 minutes or pH 7, whichever was later) and its addition to the filter.

The filtercakes were rinsed with deionized water. The water volume used, except where specifically noted, was based on the volume of the compressed filtercake produced from comparable solutions in the baseline tests and filtered to less than 1 drip/minute filtration rates. This rinse water volume, described as 1 filtercake volume, corresponds to 40 mL (for 0.209 M Ce/1 M HNO_3) or 11 mL (for 0.105 M Ce/3 M HNO_3) based on a 200-mL initial solution volume. Unless otherwise specified, rinse water was added when the filtercake was first uncovered but not compressed.

The time was recorded when the following events occurred:

- uncovering the filtercake surface
- filtercake surface cracking and/or filtering to less than 1 drip/min
- adding a second (and third) slurry to the filter
- adding rinse water.

Brief descriptions of the 0.209 M Ce/1 M HNO_3 and the 0.105 M Ce/3 M HNO_3 slurry rinsing tests are given in Table F.1.

The first four tests for each solution (Table F.1) assess rinsing of uncompressed filtercakes having no cracks. The next two tests (5 and 6) investigate the effects of filtercake cracking before rinsing. For cracked filtercakes, rinse water would be expected to flow primarily through the cracks and be less effective in removing interstitial salts. The seventh and eighth tests for 0.105 M Ce/3 M HNO_3 investigate the effects of partial dilution of the rinse water with supernate in rinsing strategies designed to ensure that the surface would not become cracked. The last two tests in both series investigate rinsing of two or three stacked filtercakes. Only two filtercakes were evaluated for the 0.209 M Ce/1 M HNO_3 solution, because the PFP full-scale filter has insufficient capacity to hold a third slurry. Three filtercakes from the less concentrated 0.105 M Ce/3 M HNO_3 solution could be accommodated in the PFP filter. The last test of both series was conducted to determine whether the second slurry would effectively heal the cracked filtercake it was layered on.

The baseline test results come from the average of three baseline tests. Most of the other one-filtercake test results are averages of two tests. However, one test result arose from a single 1 filtercake volume rinse of an uncompressed filtercake produced from 0.209 M Ce in 1 M HNO_3 solution. Only single tests were conducted for those experiments involving two or more filtercakes

Discussion of the Test Results

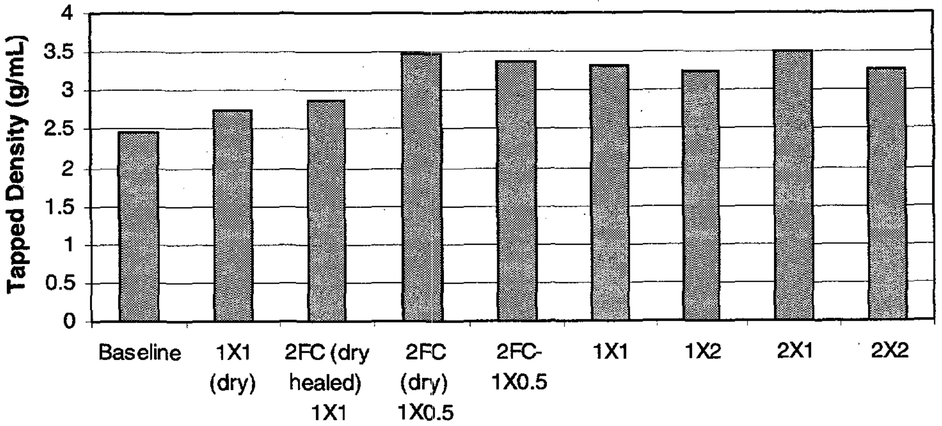
Three parameters of interest in the rinsing tests are the calcined filtercake density, the calcined filtercake weight gain when exposed to ambient air, and the filtration time. The effects of calcination temperature on calcined filtercake density and weight uptake upon exposure to air also were evaluated for filtercakes from two of the tests.

Table F.1. Slurry Rinsing Tests and Conditions

Test	Parameter	
0.209 M Ce / 1 M HNO_3	**Rinse Volume (filtercakes)**	**Filtercake Amount and Condition**
1a	1 volume	One, uncompressed
2a	Two rinses, 1 volume each	One, uncompressed
3a	One rinse, 2 volumes	One, uncompressed
4a	Two rinses, 2 volumes each	One, uncompressed
5a	1 volume	One, compressed and cracked, but soaked unmixed for 5 minutes prior to resuming vacuum filtering
6a	1 volume	One, compressed and cracked, but the surface mechanically mixed to heal the cracks prior to rinsing
7a	1 volume	Two, uncompressed
8a	1 volume	Two, lower layer cracked and compressed, upper layer uncompressed
0.105 M Ce / 3 M HNO_3	**Rinse Volume (filtercakes)**	**Filtercake Amount and Condition**
1b	1 volume	One, uncompressed
2b	Two rinses, 1 volume each	One, uncompressed
3b	One rinse, 2 volumes	One, uncompressed
4b	Two rinses, 2 volumes each	One, uncompressed
5b	1 volume	One, compressed and cracked, but soaked unmixed for 5 minutes prior to resuming vacuum filtering
6b	1 volume	One, compressed and cracked, but the surface mechanically mixed to heal the cracks prior to rinsing
7b	One rinse, 40 mL each (~3.6 filtercake vol)	One, still having ~10 mL supernate on top before adding rinsewater
8b	Two rinses, 40 mL each (~3.6 filtercake vol)	One, still having ~10 mL supernate on top before adding each rinsewater volume
9b	3 single-filtercake volumes	Two, uncompressed
10b	3 single-filtercake volumes	Two, compressed and cracked, and one, uncompressed, on top

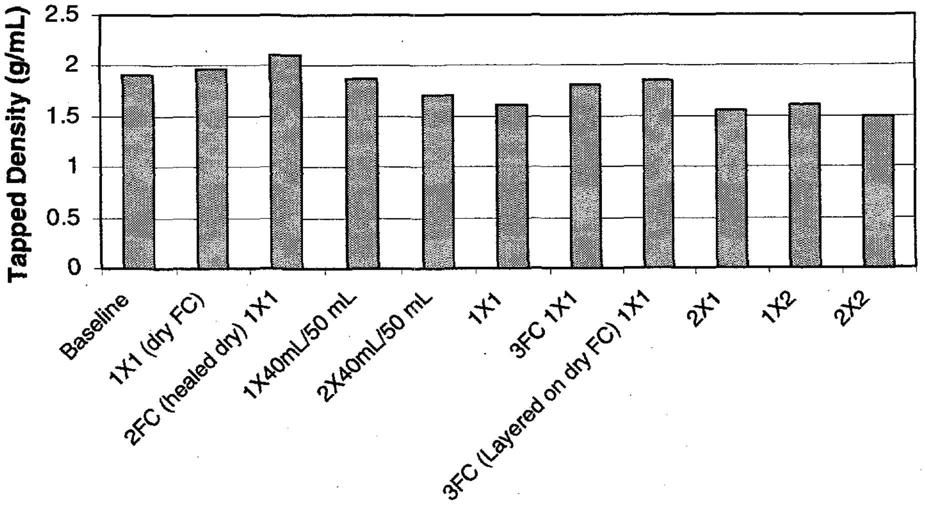
Calcined Filtercake Tapped Density

The effects of the various filtering strategies on the tapped density of the calcined filtercake prepared from 0.209 M Ce in 1 M HNO_3 and 0.105 M Ce in 3 M HNO_3 solutions, are shown in Figures F.2 and F.3, respectively. For 0.209 M Ce in 1 M HNO_3 (Figure F.2), about a 35% increase in tapped density occurs if 1 filtercake volume or more of DI water is used to rinse uncompressed filtercake. Only about half that improvement accrues if the rinsing takes place on a single filtercake that was allowed to compress and crack before rinsing.



AXB = (A rinses) X (B filtercake volumes per rinse).
Dry = rinsing on a filtercake that has been filtered to the point of cracking.
Healed = mechanically spreading a cracked filtercake to remove cracks prior to rinsing.

Figure F.2. Effects of Rinsing on Tapped Density of Calcined Solids from Precipitating 0.209 M Ce/1 M HNO_3



AXB = (A rinses) X (B filtercake volumes per rinse).
Dry = rinsing on a filtercake that has been filtered to the point of cracking.
Healed = mechanically spreading a cracked filtercake to remove cracks prior to rinsing.

Figure F.3. Effects of Rinsing on Tapped Density of Calcined Solids from Precipitating 0.105 M Ce/3 M HNO_3

In contrast, for 0.105 M Ce/3 M HNO_3 (Figure F.3), tapped density decreases about 12% by rinsing a single uncompressed filtercake with 1 or more filtercake volumes. However, filtering a compressed filtercake or mixing rinse water with a small quantity of the supernate above the surface of an uncompressed filtercake did not have a pronounced effect on the density. The observations for the 0.105 M Ce/3 M HNO_3 tests suggest that at least for this composition, residual $Mg(NO_3)_2$ quantities may not have decreased the calcined material density.

Significantly, rinsed calcined filtercakes from 0.209 M Ce in 1 M HNO_3 generally are denser than solids produced by directly calcining 1.5 N ceric nitrate solution. The CeO_2 produced by calcining ceric nitrate has a density of 2.65 g/mL. The compositions and predicted and measured densities of rinsed and unrinsed filtercakes from 0.209 M Ce in 1 M HNO_3 are compared in Table F.2. The predicted densities are based on the calcined sample weights, the amounts of cerium in the original solution, and the densities of the individual ceric and magnesium oxides.[a] The measured densities are higher than the predicted densities, possibly because calcined ceric nitrate produces ceric oxide of lower density than that produced from ceric hydroxide. Plutonium shows a similar trend; plutonium oxide derived by calcining plutonium hydroxide has higher bulk density than oxide derived by calcining plutonium nitrate (Table F.3).

The origin of the magnesium oxide (MgO) in the calcined product also may affect the calcined product density. The unrinsed filtercake from the 0.209 M Ce/1 M HNO_3 solution and the rinsed filtercake from the 0.105 M Ce/3 M HNO_3 solution have nearly identical compositions in terms of contained CeO_2 and MgO. The two filtercakes are significantly different in that the unrinsed filtercake contains both $Mg(OH)_2$ and $Mg(NO_3)_2$ [which, when calcined, both produce MgO, whereas the rinsed sample contains only $Mg(OH)_2$]. The unrinsed filtercake (from the 0.209 M Ce/1 M HNO_3 solution) has a much higher density. Higher product densities also occurred with calcined filtercakes from the baseline tests having higher ratios of $Mg(NO_3)_2$ in the wet filtercake.

Calcined Filtercake Weight Gain

The various filtering and rinsing strategies also affected the weight gain observed when the cooled calcined samples were exposed to ambient air for 1 hour. Beside the weight gain due to water

Table F.2. Comparison of Measured and Predicted Tapped Densities

Solution Composition	Rinsing Conditions	Concentration in Calcined Filtercake, wt%		Tapped Density, g/mL	
		CeO_2[a]	MgO[b]	Predicted	Measured
0.209 M Ce / 1 M HNO_3	None	76	24	2.09	2.44
	1 filtercake volume	88	12	2.33	3.33
0.105 M Ce / 3 M HNO_3	None	68	32	1.98	1.91
	1 filtercake volume	77	23	2.16	1.62

(a) Based on cerium weight in original solution.
(b) Based on difference between calcined filtercake weight and initial cerium weight in solution.

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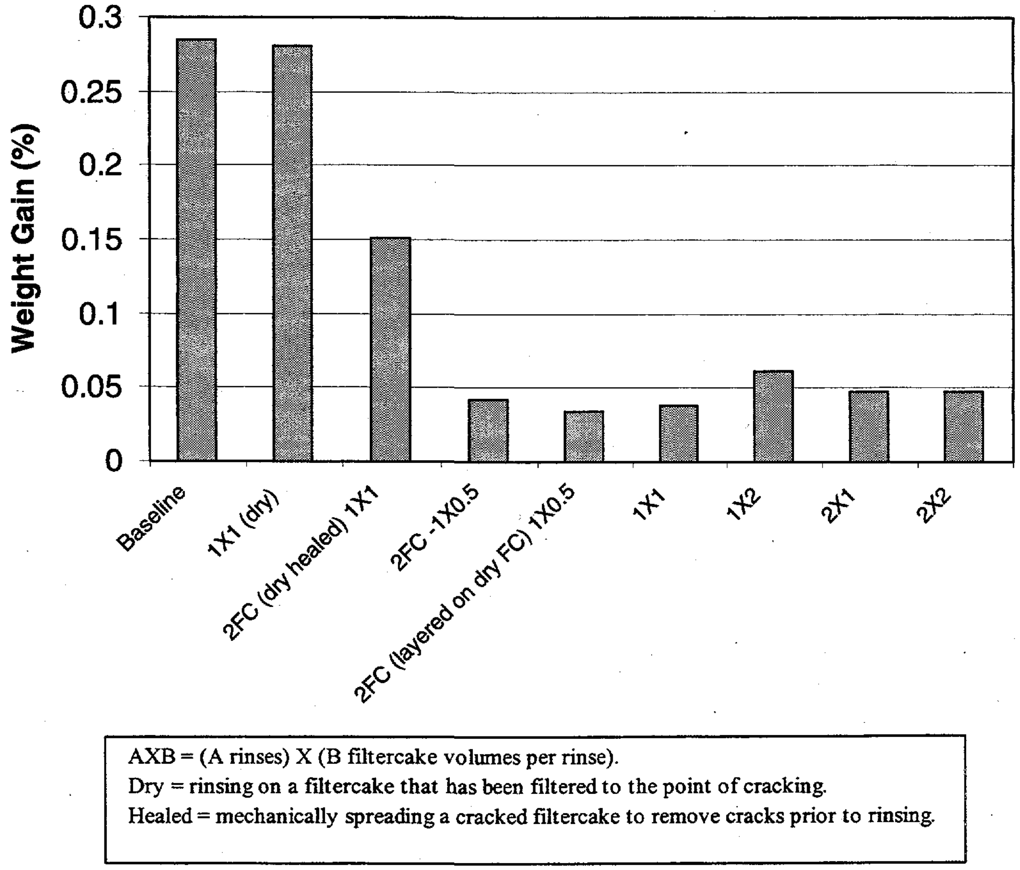
[a] Analytical data on the composition of the calcined samples were not considered at this time because of difficulties measuring cerium oxide in the samples.

Table F.3. Bulk and Tap Densities of Plutonium Oxide Prepared from Different Starting Materials[(a)]

Starting Material	Decomposition Temperature, °C	Density, g PuO_2/mL	
		Bulk	Tap
Pu Nitrate	240	1.7	2.1
	400	1.9	2.4
	600	1.7	1.8
	800	2.9	3.6
	1000	- -	- -
Pu Peroxide	240	3.5	4.1
	400	3.8	4.3
	600	3.9	4.4
	800	4.5	4.8
	1000	4.9	5.8
Pu(IV) Oxalate	240	1.0	1.4
	400	1.1	1.5
	600	1.2	1.5
	800	1.4	1.7
	1000	1.7	2.3
Pu Hydroxide	240 *	2.9	3.2
	400 *	3.7	4.2
	600 *	3.5	4.0
	800	3.2	3.7
	1000	3.8	4.2
Pu Metal	Unknown	4.8	5.3
* Average of two or more measurements. Other data are single measurements. RFP-503, "Properties of Plutonium Dioxide," I. D. Moseley and R. O. Wing.			
Pu (IV) Oxalate	-475°C **	2.0	2.5
** Maximum values for eight measurements, tapped to constant density. From letter, R. D. Fox to G. W. Upington, ARHCO, August 30, 1972.			
(a) Table taken from ARC-600. 1980. Atlantic Richfield Hanford Company, Richland, Washington.			

uptake (hygroscopicity), weight gain also may be caused by some reaction of atmospheric CO_2 with MgO. The results are presented in Figures F.4 and F.5 for calcined filtercakes prepared from 0.209 M Ce in 1 M HNO_3 and 0.105 M Ce in 3 M HNO_3, respectively. For filtercake from 0.209 M Ce in 1 M HNO_3 (Figure F.4), about a seven-fold decrease in weight gain is obtained if rinsing is performed with 1 filtercake volume or more of DI water through uncompressed filtercake. These data suggest that if the filtercake is not allowed to compress and crack, 1 filtercake volume of rinse water, passing through the filtercake uniformly in a plug flow, is sufficient to remove most of the $Mg(NO_3)_2$ present in the interstitial liquid. This conclusion is supported by the decreased hygroscopicity observed if the cracks in compressed and cracked filtercakes are healed prior to rinsing.

Rinsing with 1 filtercake volume or diluting the supernate in the filter achieves a 16% to 37% reduction in the 1-hour weight gain for both compressed and uncompressed filtercakes from precipitating 0.105 M Ce/3 M HNO_3 regardless of whether one or more filtercakes are present (Figure F.5). However, it also appears that rinsing beyond this amount negates the improvement and may even produce a greater weight gain. The reasons for the unexpected results from additional rinsing are unknown, except to note



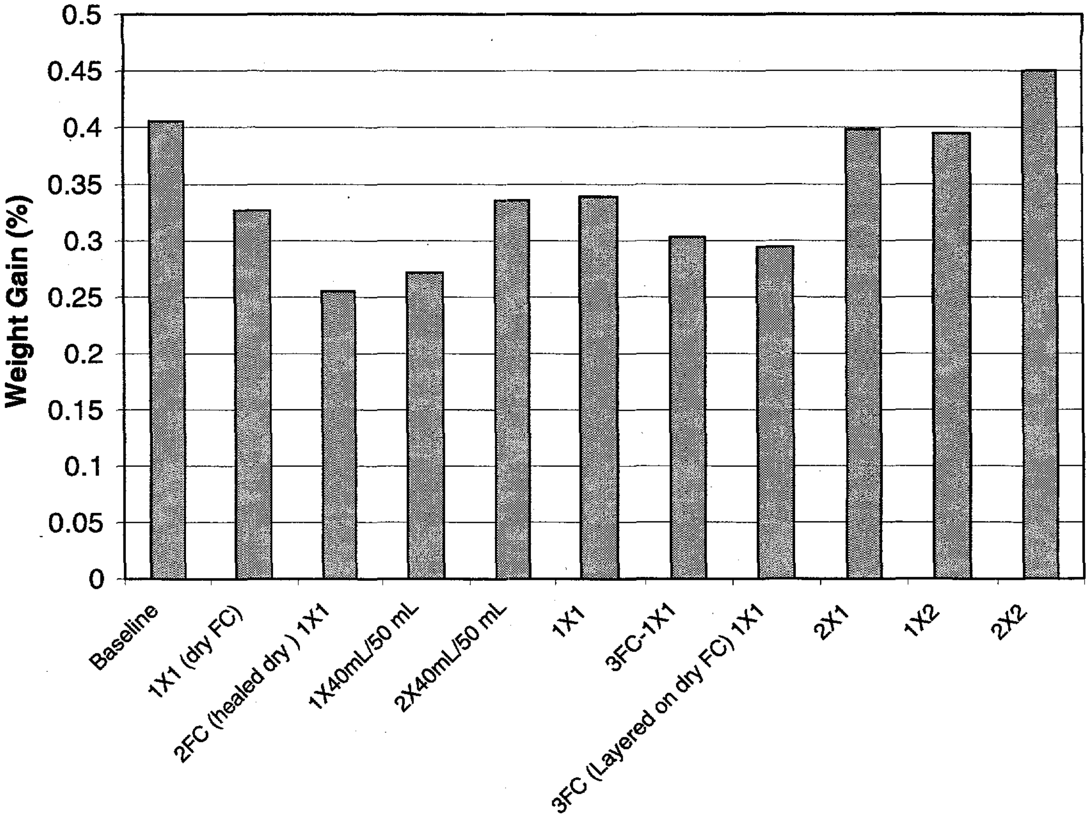
AXB = (A rinses) X (B filtercake volumes per rinse).
Dry = rinsing on a filtercake that has been filtered to the point of cracking.
Healed = mechanically spreading a cracked filtercake to remove cracks prior to rinsing.

Figure F.4. Effects of Rinsing on Hygroscopicity of Calcined Solids from Precipitating 0.209 M Ce/1 M HNO_3

that the density and the hygroscopicity of these calcined filtercakes are inversely correlated and depend on the presence or absence of $Mg(NO_3)_2$-derived MgO in the calcined material.

Effects of Drying Method and Calcining Temperature on Calcined Filtercake Density and Weight Gain

The effects of the drying method and the calcination temperature on the tapped density and weight gain of the calcined filtercake were investigated using samples from two of the 0.209 M Ce/1 M HNO_3 tests. The first sample was the filtercake from two slurries layered on top of one another and rinsed with 1 filtercake volume (test 7a, Table F.1). This filtercake was first calcined at 950°C for 2 hours, cooled in a desiccator, and then exposed to ambient air for 1 hour. The powder than was recalcined at 1000°C for 2 additional hours, cooled, and exposed to ambient air.



AXB = (A rinses) X (B filtercake volumes per rinse).
40 mL/50 mL = 40 mL of rinsate added to 10 mLof supernate to make 50 mL solution above filtercake surface.
Dry = rinsing on a filtercake that has been filtered to the point of cracking.
Healed = mechanically spreading a cracked filtercake to remove cracks prior to rinsing.

Figure F.5. Effects of Rinsing on Hygroscopicity of Calcined Solids from Precipitating 0.105 M Ce/3 M HNO_3

The second sample was single filtercake that was rinsed with 1 filtercake volume (test 1a, Table F.1). The rinsed filtercake then was split into two subsamples. One subsample underwent the standard procedure for drying and calcining. The other subsample was dried in a crucible on a hot plate at its highest setting for 2 hours. The filtercake was stirred and crushed with a spatula as it dried. The solids formed fairly small particles (much of the material did not require grinding to pass a 20-mesh sieve). The solids temperature near (not on) the crucible bottom was 450°C as measured by thermocouple. The samples then were calcined at 950°C for 2 hours. Results for all tests are given in Table F.4.

Increasing the calcination temperature by 50°C decreased the 1-hour weight gain by about 36% (relative) and the 24-hour weight gain by about 48%. The density increased about 4%. Drying on a hot plate and stirring the sample while drying decreased the 1-hour weight gain by about 41% and the 24-hour weight gain by about 36%. The density decreased about 4%. These results suggest that drying filtercake by the current plan on a hot plate is preferred, although tests to confirm this trend for other solutions are needed.

Table F.4. Effects of Drying Conditions and Calcination Temperature on 0.209 M Ce/1 M HNO_3 Calcined Filtercake Properties

Test Conditions	Drying Conditions	Calcining Conditions	Weight Gain, wt%		Tapped Density, g/mL
			1-hr	24-hr	
Two filtercakes rinsed once with 1 filtercake volume DI water	500°C for 2 hr	950°C/2 hr	0.22	0.42	2.71
		1000°C/2 hr	0.14	0.22	2.82
One filtercake rinsed once with 1 filtercake volume DI water	500°C for 2 hr	950°C/2 hr	0.15	0.28	2.87
	Hotplate drying at highest setting (~450°C)	950°C/2 hr	0.089	0.18	2.75

Filtration and Rinsing Times

The filtration and rinsing times for tests involving more than one filtercake are shown in Table F.5 and Figures F.6 and F.7. To compare the data consistently, the filtration time was taken as the interval from the start of filtration until no standing liquid was visible on the filtercake (i.e., the time to compact and crack the filtercake was not included). Judging the compaction time was arbitrary; a fairly compact filtercake could form but not necessarily filter to <1 drip/min. However, the rinsing time was taken to be the point that the filtration rate was <1 drip/min.

Several important trends are revealed in Table F.5 and Figures F.6 and F.7. First, the slurry layered on top of an uncompressed filtercake takes three times as long to filter as the initial (underlying) slurry. Similarly, the slurry overlying a compressed filtercake requires approximately twice as much time to filter as the slurry overlying an uncompressed filtercake. For slurry from the 0.105 M Ce in 3 M HNO_3 solution, filtration of the third filtercake takes approximately 1.9 times as long as filtration of the second filtercake, either uncompressed or compressed.

The number of filtercakes also impacts the rinsing time. In the case of slurry from the 0.105 M Ce/3 M HNO_3 solution, rinsing time increased by a factor of 6 for both uncompressed and compressed filtercakes. For the slurry from the 0.209 M Ce/1 M HNO_3 solution, the average rinse time increased 2.4 times for both sets of filtercakes.

With the data from Figures F.6 and F.7, the filtration and rinse times for processing the filtercakes either singly or in layers may be compared. Filtering and rinsing three batches of slurry produced by precipitating 0.105 M Ce/3 M HNO_3 solution in single batches requires 3x10=30 minutes (Figure F.6), not counting the setup time between filtrations. If the three filtercakes are stacked, between 75 minutes and 120 minutes are required to filter and rinse. The difference, between 45 and 90 minutes, may be sufficient to perform the two additional setup operations (scrape/exchange the filter) necessary if the batches are processed individually. The time required to filter and rinse two slurries from the

Table F.5. Filtration and Rinsing Times

Solution Composition	Filtering Strategy, Test(a)	Filtercake Filtration Time, min(b)			Rinse Time (<1 drip/min), min(b)
		1st	2nd	3rd	
0.105 M Ce/ 3 M HNO_3	1 filtercake single rinse, 1b	5.3	--	--	4.6
	3 filtercakes (layered on uncompressed filtercake), 9b	5	15	27.7	28.5
	3 filtercakes (layered on compressed filtercake), 10b	6.5	28	56	27
0.209 M Ce/ 1 M HNO_3	1 Filtercake, single rinse, 1a	5.7	--	--	14.4
	2 filtercakes (layered on uncompressed filtercake), 7a	6.5	19.5	--	39.7
	2 filtercakes (layered on compressed filtercake), 8a	8.8	43.2	--	30.4

(a) Test numbers from Table F.1.

(b) Filtration time includes time required to add slurry and to filter until the surface is uncovered but not compressed. Additional time used to compact the filtercake not included.

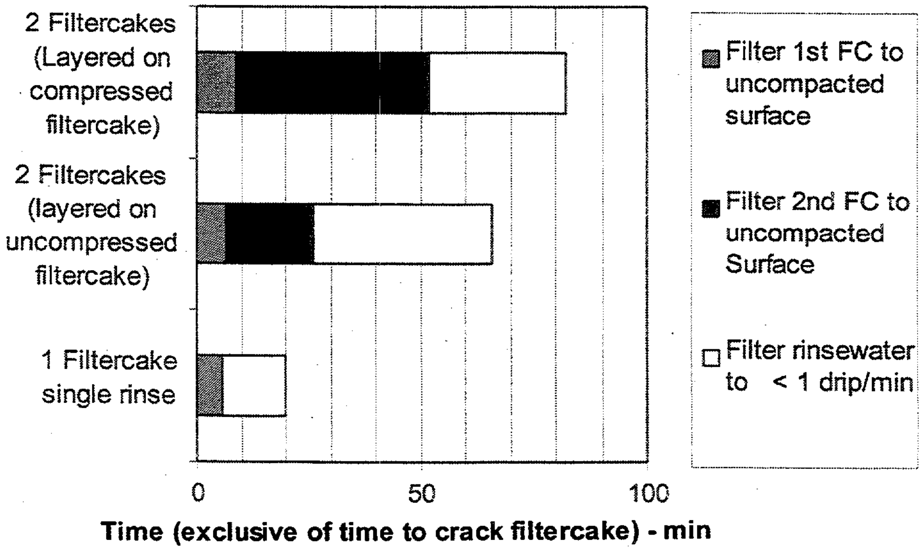


Figure F.6. Effect of Filtercake Layering on Filtration and Rinse Times for Slurries from 0.209 M Ce / 1 M HNO_3 Solution

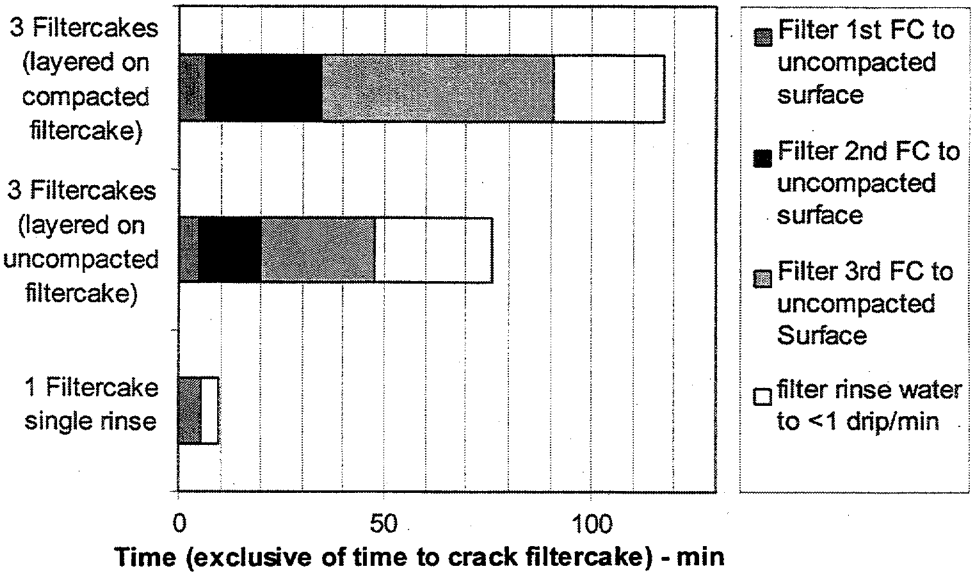


Figure F.7. Effect of Filtercake Layering on Filtration and Rinse Times for Slurries from 0.105 M Ce/3 M HNO_3 Solution

0.209 M Ce/1 M HNO_3 solution individually, not counting set-up time, is 40 minutes; between 65 and 80 minutes are required to process the two slurry batches if stacked. The time difference, 25 to 40 minutes, may be sufficient to perform the setup operations between filtrations if the slurries are processed in single batches.

The uncompressed filtercake volume from processing 0.209 M Ce/1 M HNO_3 solution may be too large to allow stacking more than two slurry batches. As determined using a calibrated Büchner funnel, the uncompressed filtercake volume for these solutions was about 70% greater than the compressed volume at the conclusion of filtration (to <1 drip/min). The uncompressed filtercake volume is 35% of the original slurry volume. Thus, a 12-L solution batch neutralized in the full-scale precipitation vessel would produce 4.2 L of uncompressed filtercake. The volume of the 9.5-cm-deep, 43-cm-diameter filter in the full-scale system is 13.8 L. Therefore addition of the third slurry batch would be impractical because of the limited freeboard.(a) Additional metals in the precipitates (for example, from iron, aluminum, or uranium salts) or higher acid concentrations also would increase the filtercake volume and further compound the problem of insufficient filter space.

(a) As each additional slurry batch is added to a single filter, more operator time is required to keep adding slurry to the filter until all of it is added. With the present filter design, there is insufficient capacity to add a third slurry to the filter, even in very small increments, because the volume of uncompressed filtercake from three slurries is near the capacity of the filter.

Appendix G

Prototype Precipitation Test Series

Appendix G
Prototype Precipitation Test Series

A prototype precipitation system was constructed and tested to model more closely the full-scale precipitation system being constructed at PFP. The prototype configuration, similar to that of the full-scale apparatus, was used to test mixing and other operational attributes and to measure precipitate product quality. An identical prototype system also was constructed and delivered to the PFP Plutonium Processing Support Laboratory for precipitation testing of plant solutions. A schematic diagram of the prototype system and valve arrangement is shown in Figure G.1. A more complete description of the prototype system and its operation is provided in Appendix B.

The vessel design is essentially a 1/10 volume model of the full-scale system. The vessel diameter (2.75 in. ID) was 45% of the full-scale vessel diameter; the outlet diameter (3/8 cm) was 50% of that in the full-scale system; and the height of the vessel was about 42% of the full-scale system. The 1-L depth is 11.5 inches above the vessel outlet for a solution height/diameter aspect ratio 4.2:1 versus approximately 4.9:1 in the full-scale system. The vertical portion of the outlet tube adds 6.5 inches to the solution depth.

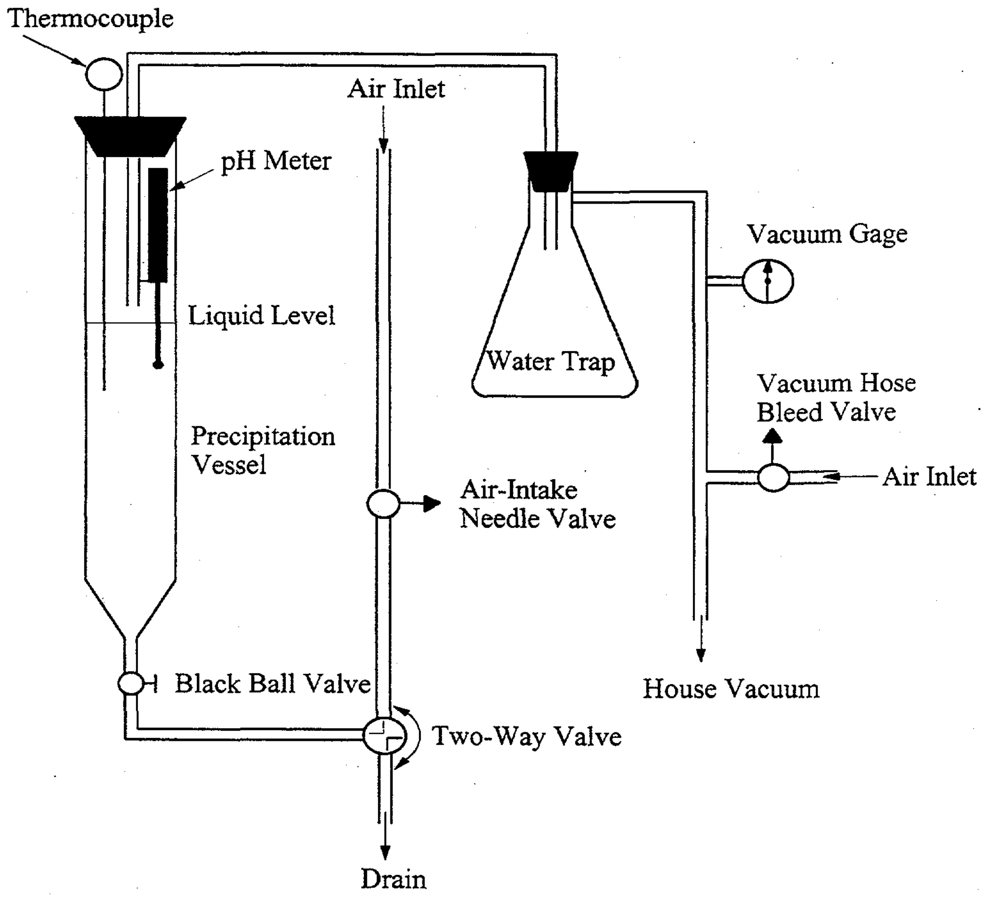


Figure G.1. Prototype Precipitation System

At the time the vessel was constructed, PNNL was directed to conduct a limited number of precipitation tests using a solution containing 0.052 M Ce, 0.1 M KNO_3, and 3 M HNO_3. This solution simulated the expected composition of the first solutions to be processed by the full-scale system at PFP. The same solution composition also was evaluated in the beaker system to provide a basis for comparing data from the prototype and beaker systems. These tests also were used shake down the system and to gain operational experience prior to the glovebox installation of an identical prototype system at the PPSL for testing with actual solutions. A flocculating agent was added in some tests to determine whether the flocculent would support foaming during air sparging.

PNNL also was directed to conduct tests in the prototype system using 0.209 M Ce in 1 M HNO_3 solutions to determine whether the gel intermediate identified in the baseline beaker tests affected mixing in the prototype system. A total of four shakedown tests with this simulant were conducted, with and without flocculating agent, to develop procedures to establish the air flow for mixing (sparging) and for adding the $Mg(OH)_2$ solids. The airflow rate was only monitored qualitatively during these tests. One test using this simulant was conducted in a beaker for comparison.

Four additional tests were conducted using 0.052 M Ce in 3 M HNO_3 but without KNO_3. The air sparge flow rate was monitored in these experiments using an electronic flow meter. One test was conducted in a beaker for comparison. Two additional tests were conducted using a 0.209 M Ce in 1 M HNO_3 solution to evaluate the gel phenomenon. The air sparge flowrate was monitored in these tests using an electronic flow meter. Baseline test results were used for comparison.

Procedure

In a typical prototype reactor test, 1 L of solution was added to the vessel, and the vessel cap assembly containing the thermocouple and pH meter was placed on top. The vacuum was established at about 2.5 inches Hg, and the airflow rate was adjusted before the $Mg(OH)_2$ solids were added. The ball valve used to isolate the system from the drain and air source then was closed, and the vessel cap assembly was lifted from the vessel. The $Mg(OH)_2$ (108% of stoichiometric requirements) was added to the vessel, and was allowed to sink to the bottom of the vessel until the surface was clear enough that the pH probe could be inserted into the solution and not be plugged with floating, unreacted $Mg(OH)_2$. If flocculating agent was to be used, it was added with the $Mg(OH)_2$ solids.

The cap assembly was placed on the vessel to reestablish the vacuum. The ball valve was reopened, and the solution pH and temperature, the air sparge rate (if measured), and physical appearance of the slurry were monitored and recorded for 20 minutes or until the pH reached 7.0, whichever came later. The neutralization time was measured from when the $Mg(OH)_2$ was added; however, the time that airflow was established also was noted. At the conclusion of neutralization, the slurry was drained from the precipitation vessel into a beaker and transferred to a 90-mm Büchner funnel containing a Whatman 41 paper filter. The operation and data recording procedures for filtering, drying, and calcining were the same as used in the beaker tests, except a larger beaker was used to estimate the wet filtercake volume. The supplementary beaker tests were conducted at the selected simulant compositions using the procedures described in Appendix E for the baseline tests.

Operational Results

Five operational characteristics were evaluated in the prototype testing:

- foaming
- solids addition
- airflow rate control; mixing
- filtration rate
- vessel plugging.

Foaming

Two shakedown tests were conducted with added flocculating agent [as a solid with the $Mg(OH)_2$] at a 100 mg/L dose rate to determine if the flocculent caused excessive foaming during air-sparge mixing. These tests used the 0.052 M Ce/0.1 M KNO_3/3 M HNO_3 simulant. The flocculent apparently increased foaming slightly. However, the foam did not grow to more than about 1 inch above the solution surface. Some bubbles clung to the pH meter support above the solution and remained throughout the test. In addition, the moist unreacted $Mg(OH)_2$ solids adhering to the vessel wall above the solution surface at the test conclusion contained significant polymer flocculent.

Solids Addition

A problem in managing $Mg(OH)_2$ solids addition was identified because small, but significant, quantities of solids do not reach the solution to participate in the neutralization reaction. Solids were added through a plastic funnel with a 1.25-inch-diameter extension tube. The tube ended about 3 inches above the solution surface. Even with the extension tube, dusting occurred that backed out of the funnel unless the reactor cylinder and funnel top were covered. About 0.2 g of $Mg(OH)_2$ remained on the funnel by static charge, while about 0.7 g collected on the vessel wall just above the solution surface and remained there throughout the test. The amount retained on the vessel wall was weighed after the test by spatula and rinse water removal. The $Mg(OH)_2$ not reaching the solution was about 12% of the excess $Mg(OH)_2$ used in the tests.

Tests also showed that the solids, which initially float on the solution surface, must be allowed to wet and sink to the reactor bottom before replacing the vessel cap and reestablishing airflow. If the solids are not allowed to sink, the pH meter probe first must penetrate the floating solids upon entering the solution. The solids coat the glass bulb of the pH electrode and produce falsely high pH readings. The time period between solids addition and reestablishment of airflow typically was 1 to 2 minutes. Because an installed pH probe will not be used in the full-scale system, the interval to allow the solids to sink will not occur in plant operations. However, the interval affects interpretation of the total neutralization time in the present prototype tests.

Air Flow Control

Once air flow (sparging) was established, good solution agitation was achieved despite the collection of $Mg(OH)_2$ clumps initially in the conical lower section of the vessel and the vessel outlet tube. The shakedown tests showed that qualitative measurement of the air sparge rate by observing bubbles rising in the vessel was inadequate. Therefore, an electronic flow meter was added to the system to measure airflow.

Neutralization rates as a function of air flow rate for tests with 0.052 M Ce/0.1 M KNO_3/3 M HNO_3 are shown in Figure G.2. A flow rate of at least 80 mL/min is required to adequately suspend the solids in the prototype system and achieve rapid neutralization rates. At 50 mL/min, unreacted $Mg(OH)_2$ solids appeared to stick on the tapered walls at the vessel bottom and collect in the lower section of the outlet tube. At the 50-mL/min air-sparge rate, neutralization from pH 2 to 4 occurred in 1.7 minutes. This rapid rate suggests that less excess $Mg(OH)_2$ and a higher sparge rate should be used. A flow rate of 600 mL/min is an upper practical limit to avoid excessive splashing at the solution surface, although higher flow rates are achievable and may not be a problem if foaming does not occur. In the prototype system, the higher flow rates caused solution to splash on the main body of the pH meter and damaging it.

At airflow rates greater than 80 mL/min, the time through the pH 2-4 range is equal to or less than observed in the beaker tests with the same solution. The displacement of the neutralization in the prototype vessel tests to times longer than observed in the beaker tests is attributed to the time lag between the $Mg(OH)_2$ addition and establishment of air flow in the prototype vessel. Because of the $Mg(OH)_2$ losses described earlier, the prototype tests actually used only about 7% excess $Mg(OH)_2$. Thus, it appears that an even lower amount of excess $Mg(OH)_2$ may be adequate to achieve a 2-minute pH 2-4 neutralization time at the higher air sparge. More tests using less excess $Mg(OH)_2$ are needed to determine the optimum level of $Mg(OH)_2$ at the higher mixing rates.

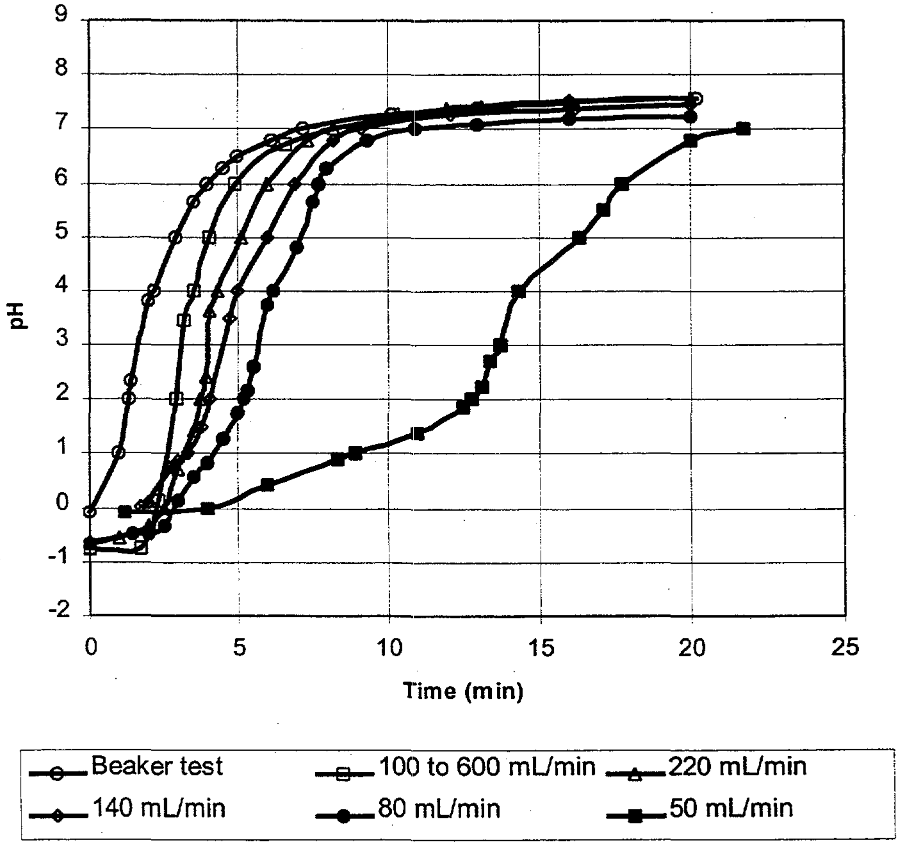


Figure G.2. Effect of Air Sparge Rate on Neutralization Rate for 0.052 M Ce/0.1 M KNO_3/3 M HNO_3

Neutralization rates as a function of air flow rate for tests with 0.209 M Ce/1 M HNO_3 are shown in Figure G.3. Also shown is the neutralization profile of one of the baseline (beaker) tests with the same solution.

In these tests, approximately half as much $Mg(OH)_2$ is required than in the tests with 0.052 M Ce/0.1 M KNO_3/3 M HNO_3. As a result, the relatively constant $Mg(OH)_2$ mass lost to the transfer funnel and wetting the vessel wall above the solution represents a higher fraction (about 25%) of the excess $Mg(OH)_2$, and thus should have a greater effect on neutralization rate. Despite this, an airflow rate of 300 mL/min is sufficient to achieve comparable pH 2-4 neutralization times for the two solutions, although a significant decrease in the neutralization rate occurs between pH 4 and 5. It is also in this pH 4-5 range that the gel intermediate is most developed.

The test conducted at 120-mL/min air flow experienced blockage during the period of gel formation (at ~pH 4.36). Operator intervention (squeezing the Tygon tubing connecting sleeve in the drain line) was required to loosen the blockage. A gradual color change from yellow to tan typically began at about this pH. Once the slurry turned tan, it no longer behaved as a gel but as a fine precipitate interspersed with a few larger particles of unreacted $Mg(OH)_2$ and purple or maroon material (presumably ceric hydrous oxide, which appeared to be amber under a microscope).

The neutralization rate decrease after pH 4 in the prototype tests triples the total neutralization time to pH 7 compared with that achieved in the beaker test. The rate decrease is more pronounced than would be expected from the decrease in the actual amount of excess $Mg(OH)_2$ delivered to the reactor and

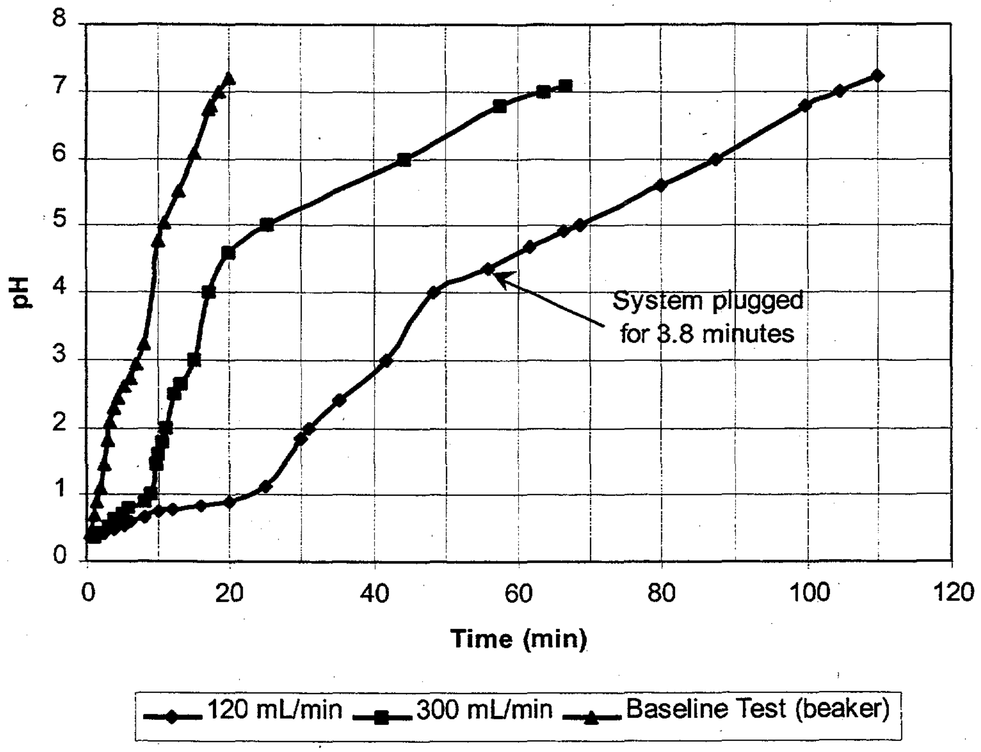


Figure G.3. Effect of Air Sparge Rate on Neutralization Rate for 0.209 M Ce/1 M HNO_3

reasonably may be attributed to poorer mixing during the transition from yellow to tan. A similar decrease in neutralization rate seemed to be occurring in the 50 mL/min flow rate test shown for 0.052 M Ce/0.1 M KNO_3/3 M HNO_3 in Figure G.2.

Filtration Rate

In the baseline tests (Appendix E), it was observed that as the pH 2-4 time interval decreased below about 2 minutes, the filtration time increased. Filtration times also were found to increase for pH 2-4 intervals less than 1 minute in the prototype tests (Figure G.4). The data, however, are sparse and scattered.

Vessel Plugging

As described under Air Flow Control, the precipitation vessel plugged during neutralization of the 0.209 M Ce/1 M HNO_3 solution at a 120-mL/min air sparge flow rate. The plugging occurred in the pH regime (~pH 4-5) in which gel forms. The slurry from the same test also plugged after the slurry was allowed to settle for several minutes at the conclusion of the test and prior to draining the precipitation vessel. The slurry did not flow when the drain was opened. Reestablishing airflow up through the bottom of the reactor cleared the line and allowed draining from the reactor. Plugging did not occur in other tests of the same solution, but the other tests were not allowed to settle. Plugging also did not occur with any of the solutions containing 0.052 M Ce in 1 M HNO_3, with or without potassium, and with or without flocculating agent.

Calcined Filtercake Properties

Wet filtercakes from several of the prototype tests were dried and calcined to further investigate the effects of neutralization rate on the calcined filtercake properties. The properties of interest were tapped density and volume, and weight gain of calcined material upon exposure to ambient air.

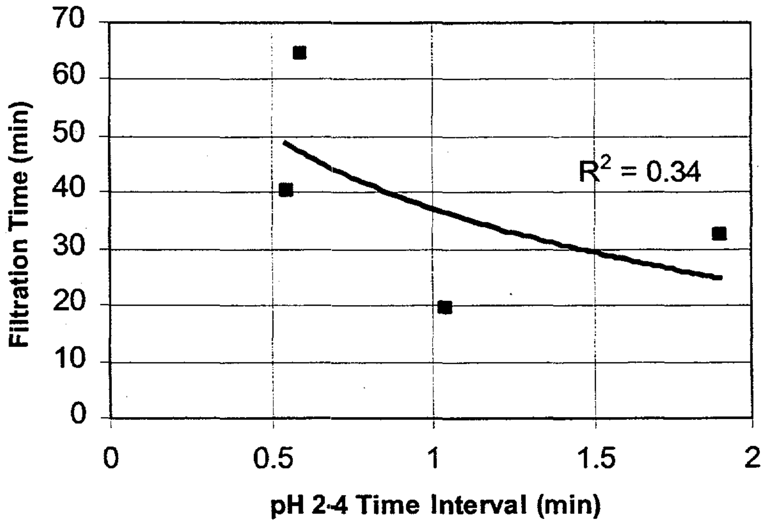


Figure G.4. Filtration Time as a Function of pH 2-4 Neutralization Time

Tapped Density and Volume

The pH 2-4 neutralization times for the filtercakes prepared from 0.052 M Ce in 3 M HNO_3 in the prototype reactor were very short (less than 2 minutes). It was of interest to compare the tapped densities and volumes of the calcined filtercakes to those obtained from filtercakes prepared in the beaker tests. Because the results are based on single tests conducted at different air sparge flow rates to control the neutralization rate, more data are needed to confirm the observed trends. Therefore, the following conclusions must be considered provisional.

As the pH 2-4 neutralization time increases, the tapped density decreases and the volume of the calcined filtercake increases (Figure G.5). These trends are consistent with those observed in the baseline and neutralization test series. The data for the tests with solutions not containing potassium generally fit within the data for the solutions containing potassium. However, the data are scattered too much over a narrow time interval to draw final conclusions.

Flocculent addition and drying method also were briefly examined for their effects on the calcined filtercake volume. The graph of the calcined filtercake volume vs. the pH 2-4 interval in Figure G.5 shows no break in the trend for the single test conducted with flocculating agent, even though the wet filtercake weight with flocculent was about 50% greater for this particular test. The flocculent concentration was about 100 times greater than is typically added to a precipitating system; lower concentrations would likely minimize any effect.

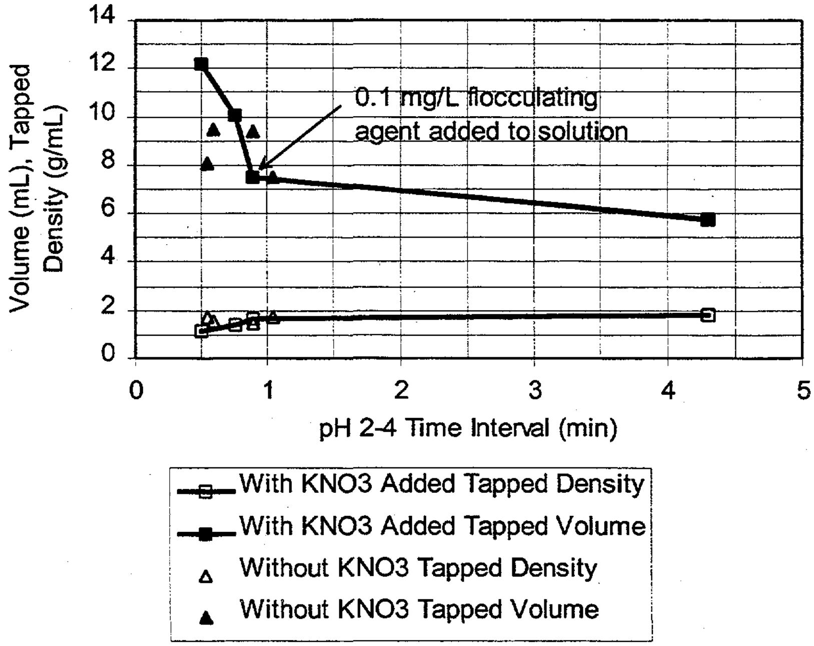


Figure G.5. Effect of pH 2-4 Neutralization Time on Density and Volume of Calcined Filtercake Prepared from 0.052 M Ce/3 M HNO_3

Weight Gain of Calcined Filtercake

The neutralization rate may also have a significant effect on the hygroscopicity of the calcined filtercake. Results of tests on the effects of the pH 2-4 neutralization time on calcined filtercake weight gain upon exposure to air are shown in Figure G.6. The weight gain is greatest at a pH 2-4 interval of about 1 minute for solutions containing potassium. The results for solutions without potassium are too scattered over a short time interval to derive clear conclusions.

However, the presence of a relatively small quantity of KNO_3 decreases the weight gain. The average weight gain values for the two data points in both sets of data at pH 2-4 intervals close to 1 minute show that potassium decreases the 1-hour weight gain by about 30% (relative to the solutions without potassium). Further tests are required to confirm this behavior, to determine the minimum amount of alkali required for this effect, and to identify the effect of rinsing.

The effect of calcination temperature was also examined. Filtercakes for the prototype and beaker tests using 0.052 M Ce/3 M HNO_3 were split with each half placed in a separate crucible. One set of crucibles was calcined at 950°C for 2 hours, and the other set was calcined at 1000°C for 2 hours. The results (Table G.1) indicate that calcining at 1000°C instead of 950°C decreases the 1-hour weight gain by about 19% and the 24-hour weight gain by about 40%.

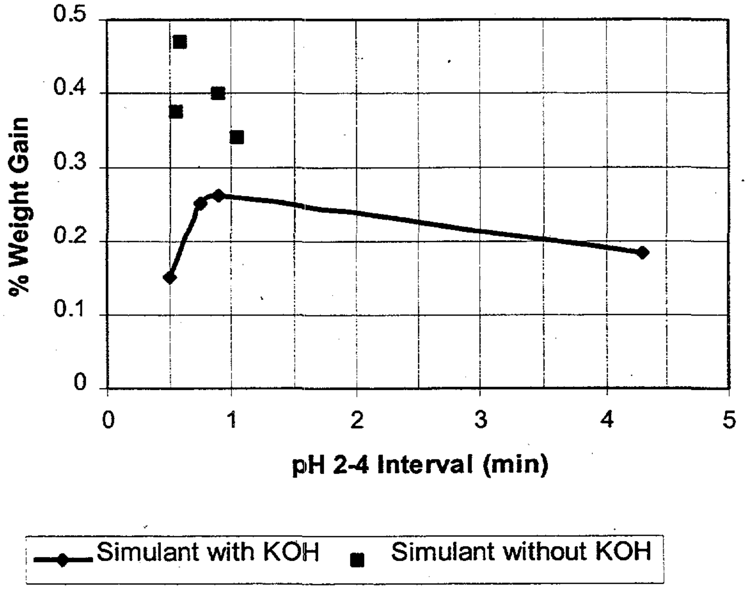


Figure G.6. Effect of pH 2-3 Neutralization Time on Weight Gain on Exposure to Air of Calcined Filtercake Prepared from 0.052 M Ce/3 M HNO_3

Table G.1. Effect of Calcination Temperature on Weight Gain Upon Exposure to Air

Test Conditions 0.052 M Ce/3 M HNO_3	Drying Conditions	Calcining Conditions	Weight Gain, %		Calcined Tapped Density, g/L
			1 hr	24 hr	
Beaker	500°C/2 hr	950°C/2 hr	0.40	NA	NA
		1000°C/2 hr	0.32	0.78	1.49
Prototype, average of 3 tests	500°C/2 hr	950°C/2 hr	0.40	0.77	1.67
		1000°C/2 hr	0.31	0.46	1.69