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Impact on Plutonium Residue Processing*

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Impact on Plutonium Residue Processing*

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Vitrified Magnesia Dissolution and Its Impact on Plutonium Residue Processing .

by

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Abstract

Aqueous chloride operations at the Los Alamos Plutonium Facility cannot directly dispose of acidic waste solutions because of compatibility problems with existing disposal lines. Consequently, all hydrochloric acid must be neutralized and filtered prior to exiting the facility. From a waste minimization standpoint, the use of spent magnesia pyrochemical crucibles as the acid neutralization agent is attractive since this process would take a stream destined for transuranic waste and use it as a reagent in routine plutonium residue processing.

Since Los Alamos National Laboratory has several years of experience using magnesium hydroxide as a neutralizing agent for waste acid from plutonium processing activities, the use of spent magnesia pyrochemical crucibles appeared to be an attractive extension of this activity. In order to be competitive with magnesium hydroxide, however, size reduction of crucible shards had to be performed effectively within the constraints of glovebox operations, and acid neutralization time using crucible shards had to be comparable to neutralization times observed when using reagent-grade magnesium hydroxide. The study utilized non-plutonium-contaminated crucibles for equipment evaluation and selection and used nonradioactive acid solutions for completing the neutralization experiments. This paper discusses our experience in defining appropriate size reduction equipment and presents our results from using the magnesia crucibles for hydrochloric acid neutralization, a logical precursor to introduction into glovebox enclosures.

Introduction and Background

Los Alamos National Laboratory operates a full suite of aqueous nitrate and aqueous chloride recovery processes for the recovery and purification of plutonium from a variety of different matrices or residues. Spent acid solution from nitrate operations is treated by evaporation to concentrate total dissolved solids and residual actinide values prior to immobilization by cement fixation and final disposition as transuranic waste. Since our processing facility is essentially a stainless steel facility, aqueous chloride operations are not able to share the spent nitric acid evaporator. Consequently, all waste hydrochloric acid is neutralized and filtered prior to disposal as waste caustic solution.

Historically, spent hydrochloric acid was neutralized using potassium hydroxide. However, in the mid-1990's magnesium hydroxide was evaluated and deployed to a limited extent as the neutralizing agent (Palmer and Fife, 1995). Magnesium hydroxide offers several potential advantages: on a molar basis, it contains twice the neutralization capacity of KOH; it is a solid, and therefore no water is added during the neutralization step; it produces a precipitate with generally a larger particle size thereby lowering filtration time; and it exhibits self-buffering capacity at a pH between 9 and 10 leaving many dissolved salts in solution. In contrast, there are also a few disadvantages to using magnesium hydroxide as a neutralizing agent. First, it is a solid, and bulk solid introduction into glovebox enclosures poses a problem. Second, neutralization times may be considered prohibitive when comparing it to KOH. Third, when neutralizing high-acid solutions significant magnesium is introduced into the solution. And finally, the inadvertent mixing of buffered solutions containing dissolved solids with other high-pH solutions can cause postprecipitation of dissolved salts.

These disadvantages with the use of magnesium hydroxide were initially overcome by administrative protocol, and the use of magnesium hydroxide to neutralize spent acid was introduced into the Los Alamos Plutonium Facility. In addition to use at Los Alamos, the Rocky Flats Environmental Technology Site introduced the flowsheet into their site for nitric acid solution stabilization activities (Schreiber et al., 1995, 1996; and Ames et al., January and July 1999).

Generally, the performance of magnesium hydroxide was viewed as a positive improvement over the use of KOH, and it was suggested as part of a waste minimization activity that spent magnesia pyrochemical crucibles be evaluated as a reagent for neutralization instead of disposing of them as a transuranic waste.

Pyrochemistry is a generic term for the molten salt processing and purification of plutonium metal and compounds resulting in pure metal for manufacturing purposes. Because molten plutonium metal is so reactive, finding a container that will remain inert at 800°C in the presence of molten chloride salts and molten plutonium metal is a significant challenge. One of the few materials found to be satisfactory under these extreme processing conditions is vitrified magnesia. These crucibles are prepared from material with a minimum MgO composition of 97% and are fired at ~1600°C to sinter the magnesia. The crucible manufacturer also has the option to add 3% yttria to the greenware to lower the sintering temperature and to inhibit grain growth by pinning the grain boundaries.

The crucibles are a sacrificial component of the pyrochemical process (Figure 1). After a batch processing run either to convert plutonium oxide to metal or to purify plutonium metal, the crucible is broken away from the solidified salt and metal and later leached in hydrochloric acid to remove as much of its residual plutonium as possible, and the crucible shards are discarded as transuranic waste.

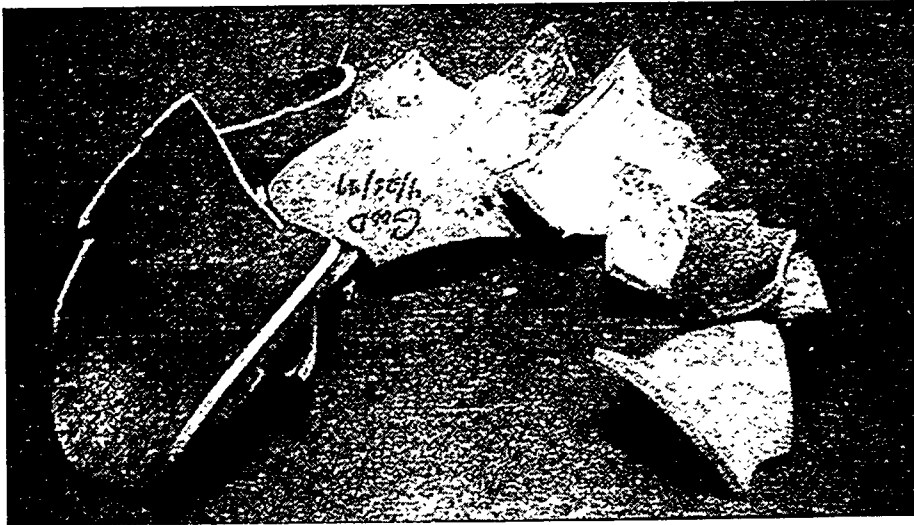


Figure 1. An example of magnesia crucible shards from plutonium pyrochemical operations.

It was recognized that if we could identify appropriate size reduction equipment amenable to glovebox operations that could produce magnesia powder from the crucible shards, we could recycle the spent crucibles and use them as a reagent for spent hydrochloric acid neutralization. Early unpublished work by Palmer (1994) indicated a definite influence of magnesia particle size on the amount of time required to neutralize stoichiometric amounts of 1M HCl (Figure 2). This result is not surprising considering the effect of surface area on the kinetics of heterogeneous chemical reactions.

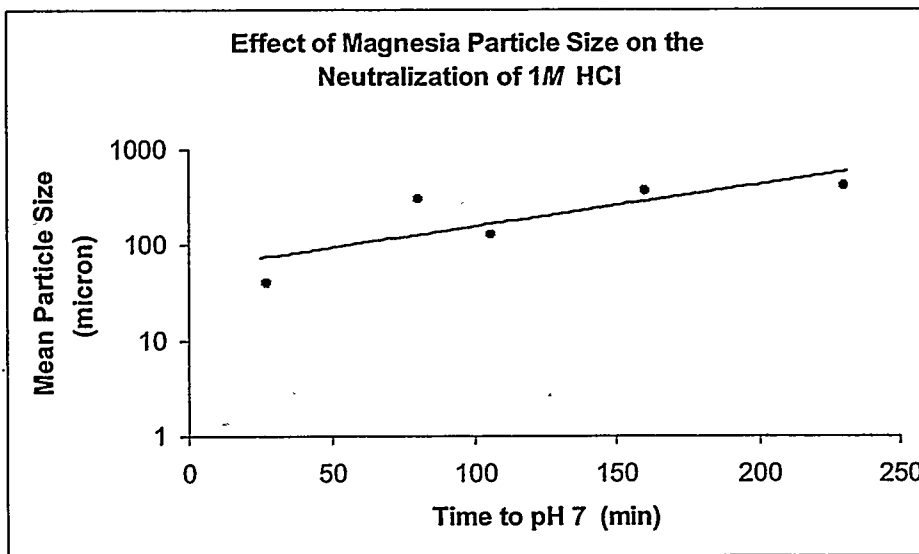


Figure 2. Effect of magnesia particle size on the stoichiometric neutralization of 1M HCl.

Size Reduction Technologies

Size reduction of the crucible shards was the first challenge we had to overcome to be able to realize the use of spent magnesia pyrochemical crucibles as an acid neutralizing agent. In this study, all tests of size reduction equipment and neutralization efficiency used non-plutonium-contaminated magnesia crucible shards. From the preliminary results indicated in Figure 2, we felt that size reduction from shards down to powder with a mean particle size less than 10 microns would be required to complete acid neutralization in an acceptable timeframe. Initially, the Fitzpatrick Company (Chicago, IL), maker of the FitzMill[®], appeared to manufacture equipment amenable to glovebox operations while producing a fine powder. Unfortunately, the FitzMill[®] equipment did not produce a suitable product. Based on laser diffraction particle size analysis (Coulter model LS 230 particle size analyzer from Beckman Coulter, Inc., Chaska, MN), the mean particle size from the FitzMill[®] was 314 μ (90% was less than 592 μ and 10% was less than 69 μ). As a result of the particle size analysis, we decided to use FitzMill[®] product as the feed to two other size reduction systems to evaluate their performance.

Spex CertiPrep, Inc. (Metuchen, NJ) manufactures a *shatterbox* system that uses vibrating concentric discs to accomplish size reduction. Although this is a small-volume batch operation (<100 mL), it successfully size reduced the magnesia shards to produce a powder with a mean particle size less than 10 μ (90% of the powder was less than 20 μ and 10% was less than 2.5 μ). CCE Technologies, Inc. (St. Paul, MN) combines closed circuit *particle-to-particle* impact of opposing gas jets coupled with high efficiency classification to produce a product with narrow size distributions. This technology can produce a powder product at the rate up to 4.5 kg per hour with a mean particle size less than 10 μ (90% of the powder was less than 15 μ while 10% was less than 2 μ).

Results of evaluating these size reduction technologies were very promising. Although testing was not accomplished in glovebox enclosures, we felt that the most challenging aspect of this entire project—magnesia shard size reduction to less than 10 μ —appeared very viable and could be accomplished with equipment that could be successfully installed and operated in glovebox enclosures.

Material Characterization and Acid Neutralization Performance

Prior to conducting acid neutralization experiments, the baseline reagent-grade materials and all samples of ground magnesia crucibles were characterized by particle size analysis using the Coulter model LS 230 particle size analyzer and were photographed by scanning electron microscopy. To compare the performance of the powder product generated from Spex CertiPrep and the CCE Technologies, simple neutralization experiments were performed comparing the performance of reagent-grade materials (Table I) with ground crucible samples (Table II). The data presented are results of neutralizing 50 mL of 0.01 M HCl with magnesia or magnesium hydroxide at concentrations 1.5 times the stoichiometric amount of acid.

As discussed earlier, dissolution data were obtained by acquiring pH versus time data during the neutralization of low-molar HCl as illustrated in Figure 3. Unfortunately, no surface area determinations were performed on any of these samples, which makes it very difficult to assess any effect of surface area on dissolution or neutralization performance. However, scanning electron micrographs were obtained on all samples in an attempt to infer morphology and, therefore, the effect of surface area on neutralization performance. Several typical micrographs are presented in Figures 4–7.

Table I: Performance of Reagent-Grade Materials

Sample	Preparation Method	Size Distribution	Neutralization Time (hr:min:sec)
MgO (light) (Fisher 974923)	Low-temperature dehydration of Mg(OH) ₂ .	8.51μ mean particle size 90%<15.7μ, 10%<2.6μ	pH7 00:00:38 pH9 00:00:40 pH10 00:00:58
MgO (Fisher 975418)	High-temperature calcination of Mg(OH) ₂ .	6.94μ mean particle size 90%<14.2μ, 10%<0.7μ	pH7 00:03:25 pH9 >8 min pH10 N/A
Mg(OH) ₂ (Fisher 951364)	Japanese source, no other Information available.	9.86μ mean particle size 90%<17.2μ, 10%<2.1μ	pH7 00:09:33 pH9 00:10:31 pH10 >15 min
MgO (Fisher 976947)	Hydroxide precipitation from Dead Sea brine followed by dehydration.	5.86μ mean particle size 90%<12.4μ, 10%<1.4μ	pH7 00:00:28 pH9 00:00:35 pH10 00:00:69
MgO (heavy) (Fisher 977820)	Hydroxide precipitation followed by dehydration.	4.30μ mean particle size 90%<7.0μ, 10%<1.9μ	pH7 00:00:30 pH9 00:00:36 pH10 00:00:48

Table II: Performance of Ground Crucible Samples

Sample	Preparation Method	Size Distribution	Neutralization Time (hr:min:sec)
MgO Crucible	Spex product, 100g FitzMill® charge, 5 min grind time, no grinding aid.	9.80μ mean particle size 90%<18.9μ, 10%<2.4μ	pH7 ~00:26:00 pH9 ~00:40:00 pH10 N/A
MgO Crucible	Spex product, 2 each 50g FitzMill® charges, each 5 min grind time, no grinding aid.	5.23μ mean particle size 90%<12.5μ, 10%<0.5μ	pH7 00:07:08 pH9 00:09:58 pH10 00:16:50
MgO Crucible	Spex product, 2 each 50g FitzMill® charges, each 5 min grind time, ethylene glycol as a grinding aid.	7.88μ mean particle size 90%<18.6μ, 10%<1.1μ	pH7 00:17:59 pH9 00:30:39 pH10 >60 min
MgO Crucible	CCE product.	6.89μ mean particle size 90%<12.3μ, 10%<1.5μ	pH7 00:03:32 pH9 00:04:57 pH10 >11 min
MgO Crucible	FitzMill® product.	314μ mean particle size 90%<592μ, 10%<69μ	pH7 >100 min pH9 N/A pH10 N/A

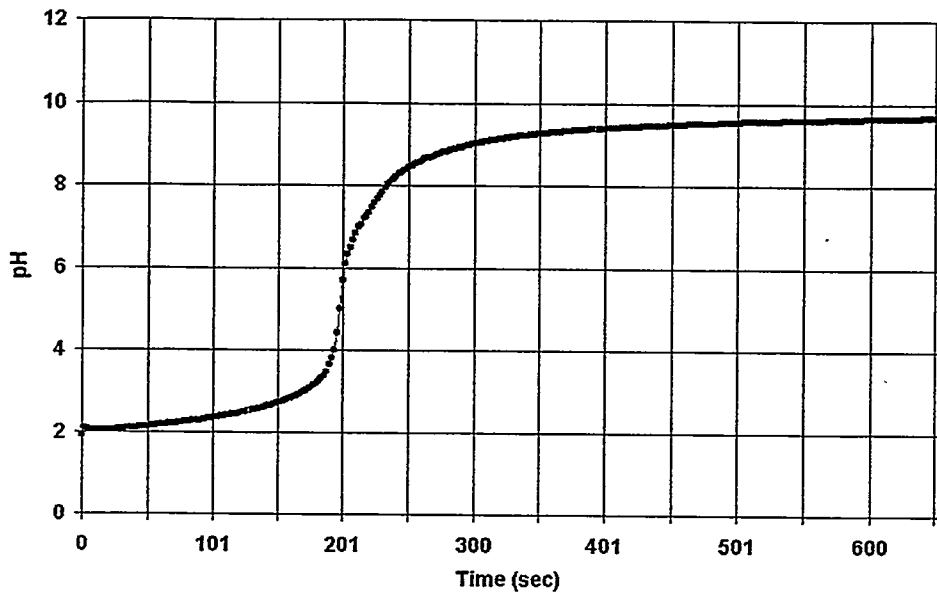


Figure 3. The pH versus time data from the neutralization of HCl with 1.5 × stoichiometric addition of ground magnesia produced from CCE particle impact technology.

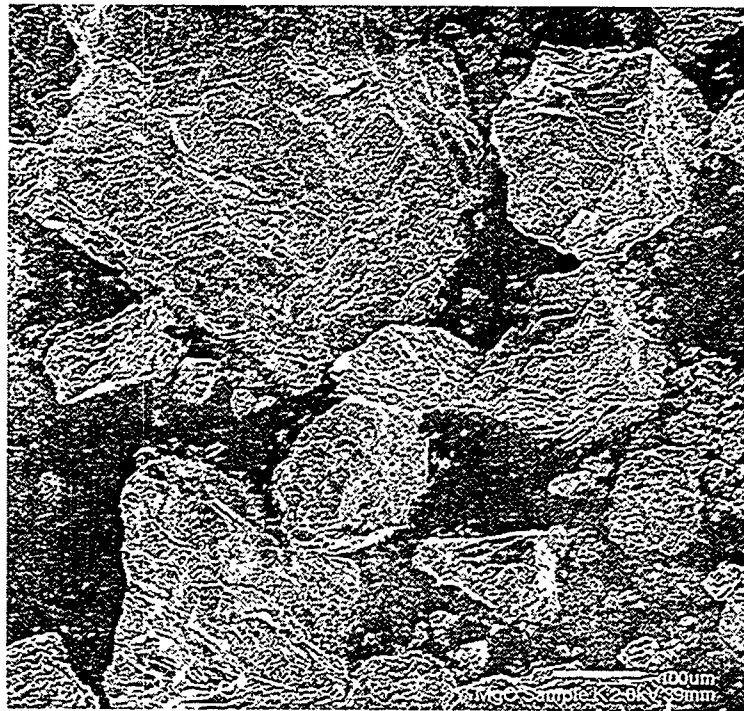


Figure 4. MgO crucible size reduced using FitzMill® technology (100× magnification).

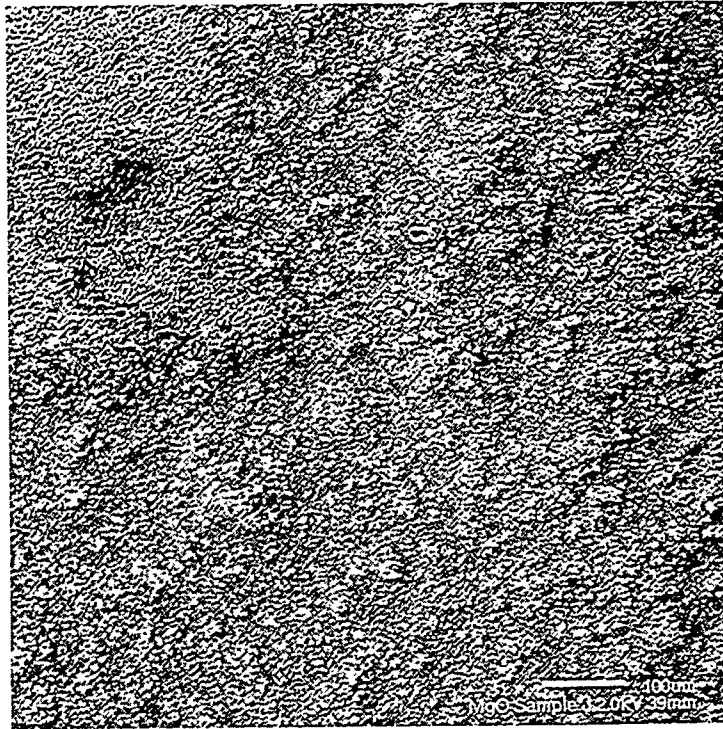


Figure 5. Reagent-grade MgO (heavy), Fisher 977820 (100× magnification).

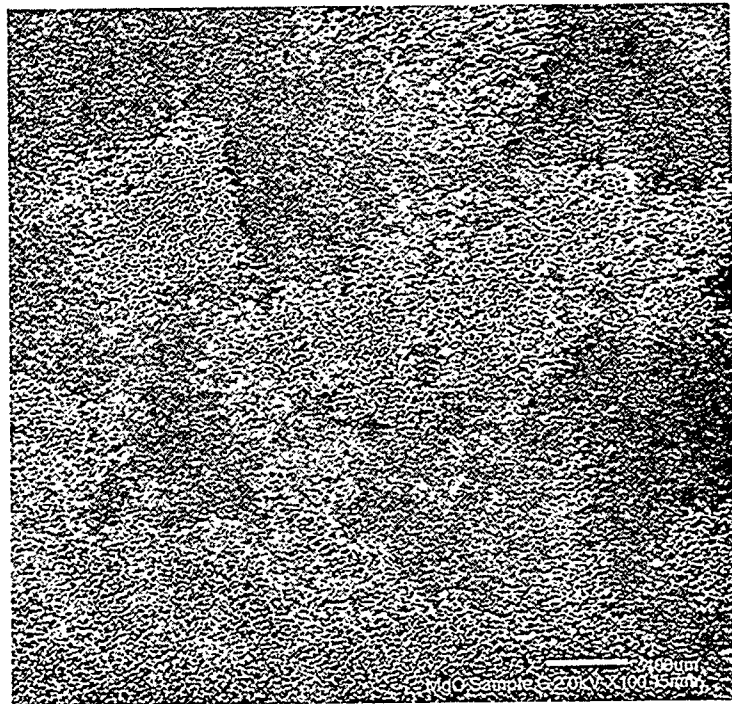


Figure 6. MgO crucible material size reduced using CCE particle impact technology (100× magnification).

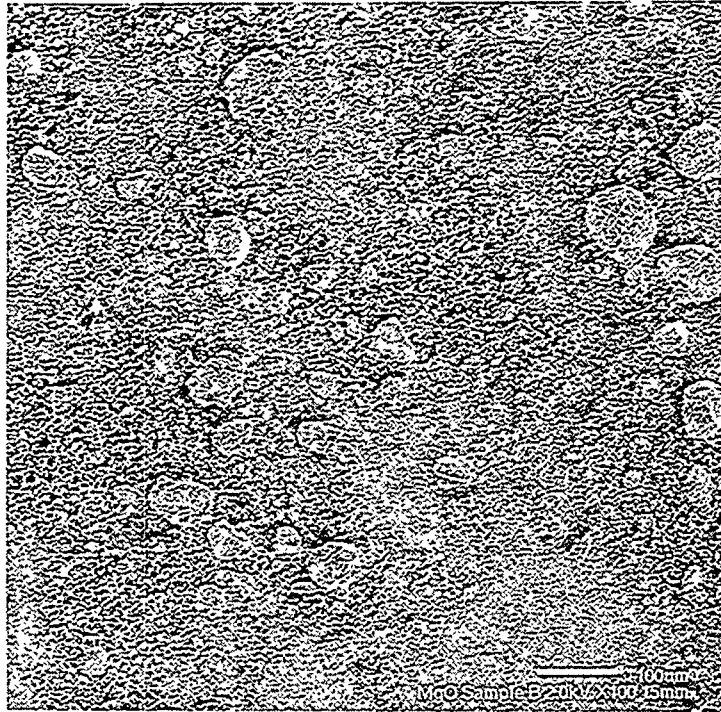


Figure 7. MgO crucible material size reduced using Spex CertiPrep technology; two each 50g batches, no grinding aid (100× magnification, showing evidence of agglomeration).

Dissolution Theory and Discussion

In 1969, Vermilyea conducted research on the dissolution of magnesia and magnesium hydroxide in aqueous solutions. He not only concluded that the hydrolysis of the magnesia is fast and that the dissolution of the resulting magnesium hydroxide is the rate-limiting step, but he also suggested that the resulting magnesium hydroxide dissolution is controlled by surface reaction at $\text{pH} < \sim 5$ and by proton diffusion control for $\text{pH} > \sim 5$. From Terry (1983), the extent of diffusion resistances responsible for measured dissolution rates is available providing that numerical values of the diffusion coefficient are known. In the absence of mass transfer correlations, the Nernst equation can provide a crude estimate of proton diffusion and hence the dissolution rate controlled by diffusion.

$$R_D = AD\Delta C / \delta \quad , \quad (1)$$

where R_D = rate of diffusion, mol/sec,
 A = surface area, cm^2 ,
 D = diffusion coefficient, cm^2/sec ,
 ΔC = change in concentration, mol/cm^3 , and
 δ = boundary layer film thickness, cm.

Using typical values for proton diffusion ($6 \times 10^{-5} \text{ cm}^2/\text{sec}$) boundary layer thickness (0.001 cm) and calculating particle surface area based on particle size analysis (assuming spherical particles), the slope of the resulting graph plotting the logarithm of the rate as a function of pH illustrates proton diffusion control in the pH region $> \sim 5$ (Figure 8).

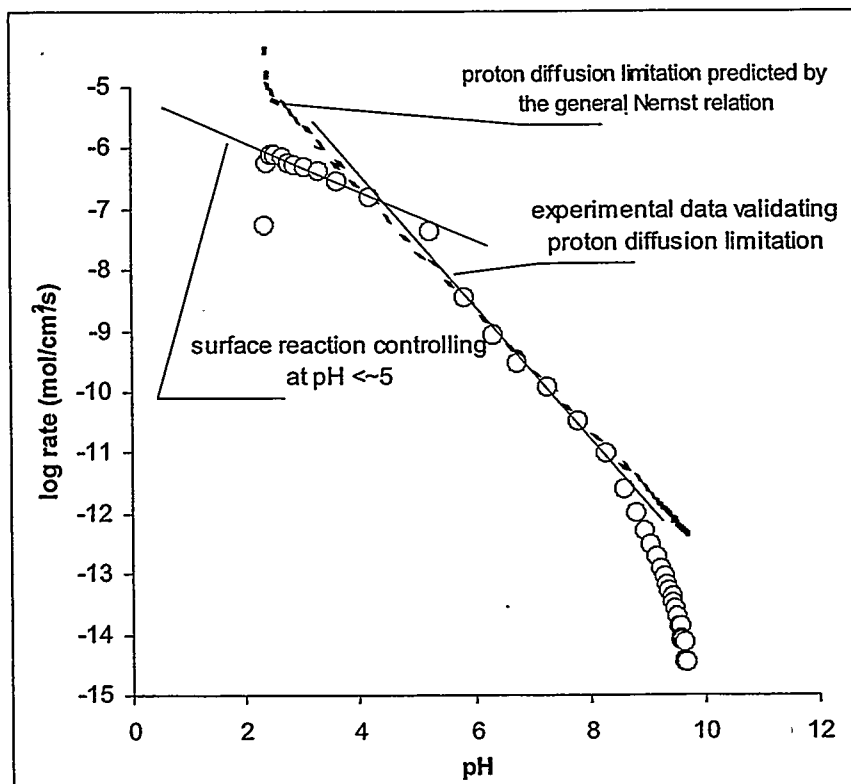
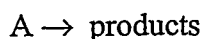


Figure 8. Typical kinetic analysis from neutralization of hydrochloric acid with pulverized magnesia illustrating similarity with Vermilyea (1969).

For constant-volume batch reactors conducting decomposition reactions, as in the dissolution of magnesia or magnesium hydroxide,



$$-r_A = kC_A^\alpha \quad (2)$$

where $-r_A$ = the rate of reaction, mol/cm³/s,
 k = the specific rate constant, (cm³/mol) ^{α -1}/s,
 C_A = concentration of species A in solution, mol, and
 α = the reaction order.

To examine the irreversible dissolution reaction chosen for this study, the differential method of analysis (Figure 9) was used to determine the specific rate constant and the reaction order α by numerically differentiating concentration versus time data (Fogler, 1992). These data were compared

with Terry (1983) who reports that the chemical reaction in the acid dissolution of magnesia is proportional to the proton concentration to the power of 0.47–0.49. Vermilyea (1969) states that there is a definite shift in reaction mechanism at pH ~5 (Figure 9), and the dependence on proton concentration is to the 0.47 power at pH < 5 and directly proportional to the proton concentration at pH > 5 (diffusion control).

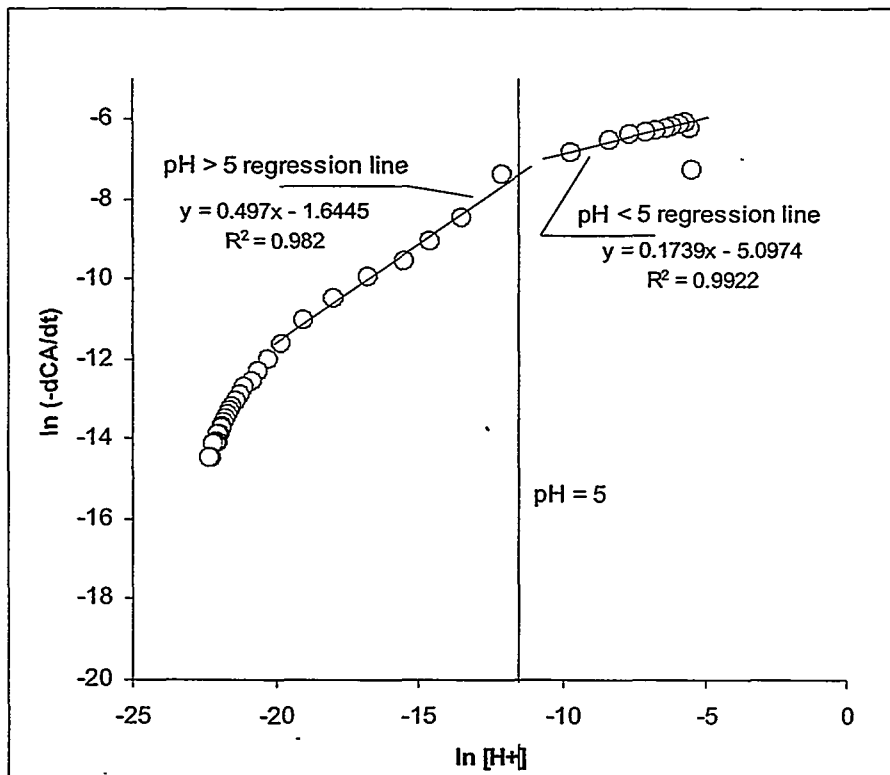


Figure 9. Example of differential rate analysis of the pH versus time data for neutralizing HCl with magnesia and magnesium hydroxide (changes in particle surface area have been included).

Our work did not compare with these previous researchers as illustrated in Table III. We certainly see the diffusion limitation dominate the dissolution reaction at pH >~5, but the reaction order for each pH range did not compare with their work. Instead of values of the reaction order of 0.5 for pH < 5 and 1.0 for pH > 5, our results were between 0.03 to 0.18 for pH < 5 and between 0.47 to 0.57 for pH > 5.

Reasons for this difference may center on the low acid concentration used (nominally pH 2 solution) and the composition and treatment of the magnesia. The presence of 3% yttria may have influenced the dissolution rate as well as the high vitrification temperature (1600°C) used in preparing the crucibles. Certainly the high vitrification temperature experienced by the magnesia will reduce porosity and ultimate surface area, but since we did not gather surface area data for the pulverized shards, we cannot determine if this is sufficient reason for the lower values of reaction order compared with the literature.

Conclusions

We have determined that the technology exists to effectively pulverize magnesia shards to powder nominally less than 10µ in size and that this material can be used to neutralize spent HCl produced in

aqueous plutonium recovery operations. One difficulty, however, is that the neutralization time required for this step is nominally a factor of 10–20 longer than for reagent-grade materials, something that right now is prohibitive for routine processing operations.

Table III. Results of Kinetic Evaluations from Neutralizing HCl with Magnesia and Magnesium Hydroxide.

Sample	Size Distribution	Kinetic Parameters for pH < 5	Kinetic Parameters for pH > 5
Mg(OH) ₂ Reagent (Fisher 951364)	9.86μ mean particle size 90%<15.7μ, 10%<2.6μ	k = 0.0061 α = 0.1739	k = 0.1931 α = 0.4970
MgO Crucible (Spex product)	5.23μ mean particle size 90%<12.5μ, 10%<0.5μ	k = 0.0010 α = 0.1003	k = 0.1753 α = 0.5693
MgO Reagent (Fisher 975418)	6.94μ mean particle size 90%<14.2μ, 10%<0.7μ	k = 0.0012 α = 0.0318	k = 0.2266 α = 0.5389
MgO Crucible (CCE product)	6.89μ mean particle size 90%<12.3μ, 10%<1.5μ	k = 0.0026 α = 0.0332	k = 0.3779 α = 0.5507
MgO Reagent (heavy) (Fisher 977820)	4.30μ mean particle size 90%<7.0μ, 10%<1.9μ	Not enough data— diffusion control appeared to begin ~pH 4.5	k = 0.1889 α = 0.4830
MgO Reagent (Fisher 976947)	5.86μ mean particle size 90%<12.4μ, 10%<1.4μ	Not enough data— diffusion control appeared to begin ~pH 4.0	k = 0.1124 α = 0.4665
MgO Crucible (FitzMill® product)	314μ mean particle size 90%<592μ, 10%<69μ	k = 0.0036 α = 0.1302	k = 0.1731 α = 0.4787

Two complementary mechanisms may account for the difference in overall dissolution performance which entail the use of 3% yttria in the greenware formulation and the high vitrification temperatures used to initially fabricate the crucibles. It is possible that one or both of these steps cause an increase

in density, which ultimately minimizes the surface area of powder produced during any size reduction operation.

Although using spent pyrochemical crucibles as a neutralizing reagent is a very intriguing concept, actual operating experience using magnesium hydroxide at Los Alamos has caused several problems:

- slow neutralization times compared with liquid potassium hydroxide are difficult to overcome in actual process operations;
- neutralization of high-acid solutions adds considerable magnesium to the solution, making the resulting liquid difficult to filter;
- overall, filtration times between KOH neutralized solutions and those neutralized with $Mg(OH)_2$ turn out *not* to be significantly different when we consider the variety of solutions generated during plutonium processing; and
- the inadvertent mixing of magnesium hydroxide filtrates (buffered and containing high dissolved solids) with potassium hydroxide filtrates ($pH \gg 14$) causes postprecipitation and plugging of disposal lines.

As a result of these problems, the concept of recycling spent crucibles as a neutralizing agent has been shelved by the Laboratory, and no additional work is anticipated.

Acknowledgements

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