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Magnesium Hydroxide as the Neutralizing Agent for Radioactive Hydrochloric Acid Solutions

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MAGNESIUM HYDROXIDE AS THE NEUTRALIZING AGENT FOR RADIOACTIVE HYDROCHLORIC ACID SOLUTIONS

BY

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ABSTRACT

The current technology at Los Alamos for removing actinides from acidic chloride waste streams is precipitation with approximately 10 M potassium hydroxide. The hydroxide precipitation filtrate meets the liquid waste stream discharge goal of 5×10^9 counts/min/L total alpha activity and is relatively simple to perform. This alpha activity translates into roughly 31 mg/L Pu^{239} or less than 1 mg/l Am^{241}. Although successful, there are many inherent drawbacks to this precipitation technique which will be detailed in this paper.

Magnesium hydroxide ($K_{sp} = 1.3 \times 10^{-11}$) (Ref. 1) has limited solubility in water and as a result of the common ion effect, cannot generate a filtrate with a pH greater than 9. At a pH of 9, calcium ($K_{sp} = 5.5 \times 10^{-6}$) (Ref. 2) will not coprecipitate as the hydroxide. This is an important factor since many acidic chloride feeds to hydroxide precipitation contain significant amounts of calcium.

In addition, neutralization with $Mg(OH)_2$ produces a more filterable precipitate because neutralization occurs as the $Mg(OH)_2$ is dissolved by the acid rather than as a result of the much faster liquid/liquid reaction of KOH with the waste acid. This slower solid/liquid reaction allows time for crystal growth to occur and produces more easily filterable precipitates. On the other hand, neutralization of spent acid with strong KOH that yields numerous hydroxide ions in solution almost instantaneously forming a much larger volume of small crystallites that result in gelatinous, slow-filtering precipitates.

Magnesium hydroxide also offers a safety advantage. Although mildly irritating, it is a weak base and safe and easy to handle. It can be introduced into the glove box line as a solid that eliminates the pressurized delivery system required to supply potassium hydroxide to the glove box.

From a waste minimization perspective, $Mg(OH)_2$ offers many advantages. First, the magnesium hydroxide is added as a solid. This step eliminates the diluent water used in KOH neutralizations. Secondly, because the particle size of the precipitate is larger, more actinides are caught on the filter paper resulting in a smaller amount of actinide being transferred to the TA-50 Liquid Waste Treatment Facility. Third, the amount of solids that must be reprocessed is significantly smaller resulting in less waste generation from the downstream processes.

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[1] *Handbook of Chemistry and Physics,* 59th Ed. (CRC Press, West Palm Beach, Florida, 1979).
[2] *Lange's Handbook of Chemistry* (McGraw-Hill, New York 1973).

I. BACKGROUND

The preferred method for the recovery of plutonium from pyrochemical residues involves dissolution and processing in hydrochloric acid. Figure 1 is a generic flow sheet for aqueous chloride operations.

Figure 1 illustrates that all liquid chloride waste streams must be neutralized before being transferred to the liquid waste treatment facility. The primary reason for the required neutralization is that current chloride recovery operations do not lower actinide concentrations to a level low enough to permit direct transfer of the waste stream to the facility. The final solution exiting the chloride recovery operations must have a total alpha content less than 5×10^9 counts/min/L. This translates into approximately 31 mg/L of plutonium or 0.7 mg/L of americium. In addition, the transfer lines to the liquid waste treatment facility are fabricated from monel; therefore, the acidic chloride solution must be neutralized to avoid corrosion of the transfer line.

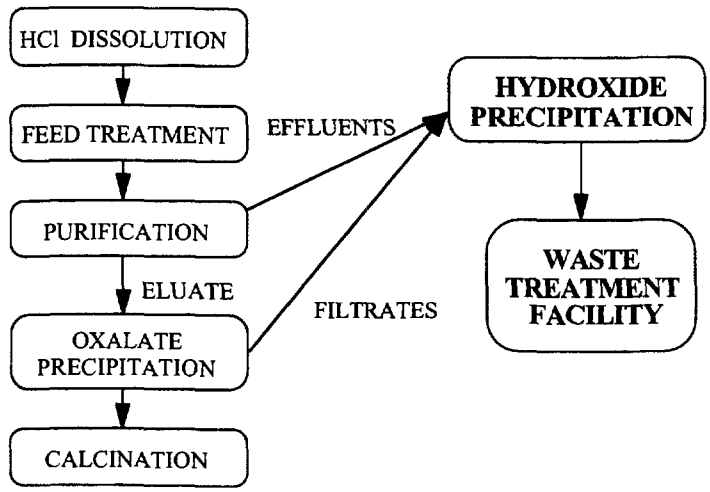

Figure 1: Generic aqueous chloride flow sheet.

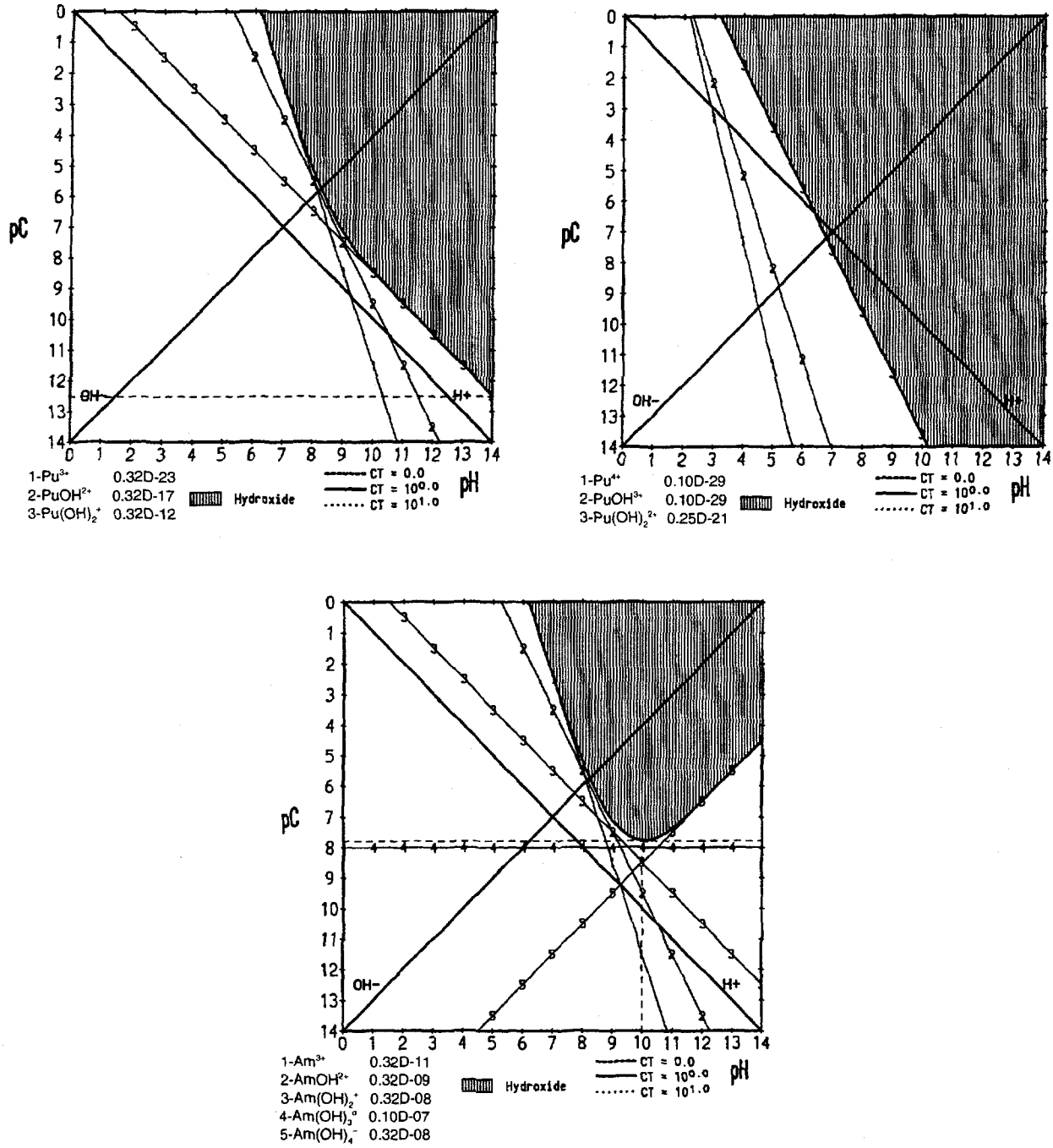

Figure 2 illustrates the solubility diagrams of plutonium and americium hydroxides with respect to pH. The diagrams show that at a pH of 7, the solubilities of these actinide species are below the current discard limits.

The traditional method for achieving these discard limits when treating these acid waste streams is to neutralize the hydrochloric acid with 10 M potassium hydroxide (KOH). When the two major purification methods (ion exchange and solvent extraction) used in chloride solution recovery were in full operation, approximately 20,000 L/year of neutralized filtrate solution was transferred to the liquid waste treatment facility.

By direct addition of KOH to the waste acid, this neutralization technique immediately provides a high concentration of hydroxyl ions in solution. As the acid is neutralized and the metal ions are precipitated, large volumes of very small-particle-size precipitates are formed that are gelatinous. This physical property gives a precipitate that has long settling times, and is slow to filter. Another problem associated with using KOH as the neutralizing agent is that the pH of the solution is very difficult to control in the region of the equivalence point (pH = 7).

Figure 3 is an idealized neutralization curve for 5 liters of 5 M HCl that is neutralized with 10 M KOH. As the plot illustrates, the volume of KOH required to raise the pH from 2 to 12 is small, and controlling reagent addition to reach the equivalence point is not practical in actual glove box operations. Associated with this problem is the fact that any magnesium or calcium present in the feed solution will coprecipitate with the actinides starting at a pH ~10. The formation of these unwanted precipitates will increase the time needed for filtration as well as increasing the amount of precipitate that must be reprocessed or stored.

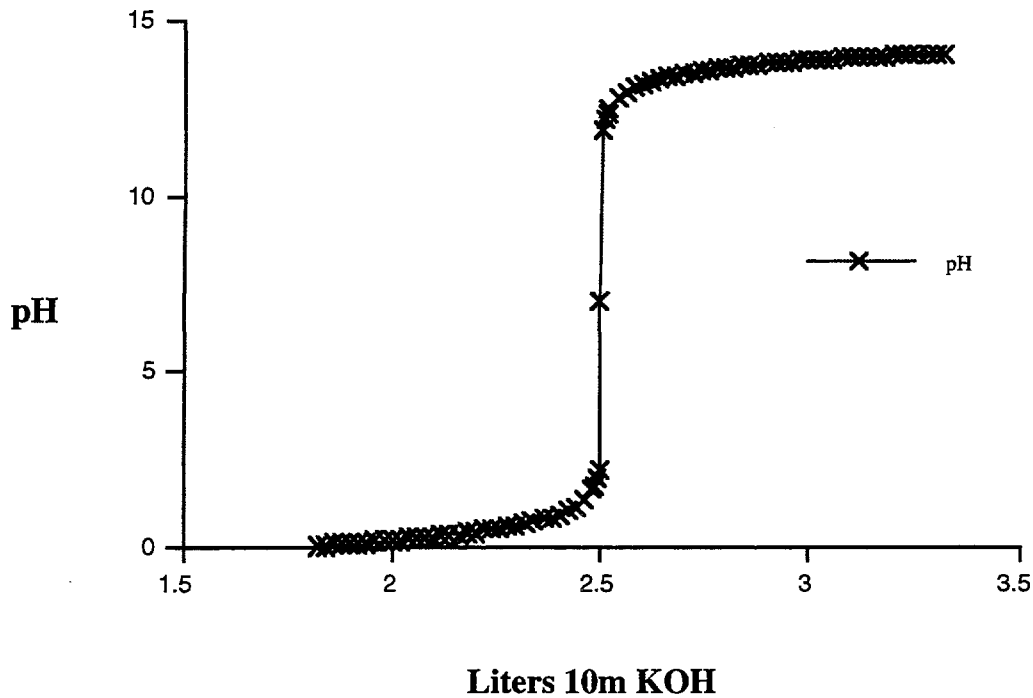

Figure 3: Idealized neutralization of 5 L of 5 M HCl with 10 M KOH

The neutralization step in chloride processing is traditionally a high-radiation-exposure operation for technicians. The process requires almost constant operator attention during neutralization and filtering and, in many cases, the feed contains relatively high concentration of americium; therefore, operator exposure is increased accordingly.

If magnesium hydroxide is used as the neutralizing agent, the reaction proceeds along a significantly different route. Since $Mg(OH)_2$ is slightly soluble in water, the acid first reacts with the $Mg(OH)_2$ reducing the acidity of the solution. As the solution is neutralized, the metal ions then react with the small amount of hydroxyl ions in the solution and are precipitated. This reaction mechanism produces a much larger particle size and traps a minimal amount of water during metal hydroxide precipitation. The resulting settling and filtering times are decreased significantly.

Another benefit of using $Mg(OH)_2$ is a result of the common ion effect. The theoretical solubility of $Mg(OH)_2$ would give a solution pH of 10.5. However, as a result of the common ion effect of the hydroxyl ion, the pH of the solution will not be greater than nine. At this pH all of the dissolved calcium and magnesium remains in solution. This ultimately reduces the amount of solids precipitated, which will decrease the filtering and subsequent handling time required for these solids. As a result of decreasing the settling and filtering times for the hydroxide precipitates, technician exposures will decrease accordingly. Other problems associated with chloride salt formation traditionally seen when using the KOH precipitation technique are nonexistent when using $Mg(OH)_2$. This is a result of the higher solubility of $MgCl_2$ as opposed to KCl (about 50% more).

II. EXPERIMENTAL

A. Nonradioactive Cold Studies

These cold studies were designed to test the applicability of $Mg(OH)_2$ as an effective neutralizing agent for acidic chloride waste streams and to determine if the neutralized filtrate would meet the Resource Conservation and Recovery Act (RCRA) discard limits for designated metal impurities.

PROCEDURE

Part 1: Proof of principle

Two feed streams were prepared for the comparison studies consisting of 6 M HCl with 0.35 M Fe and a second stream consisting of 6 M HCl, 0.35M Fe, and 2 M Ca. For these initial experiments, two 100 ml aliquots of each solution were neutralized. The first sample was neutralized with 10 M KOH, and the second was neutralized with $Mg(OH)_2$. After mixing, the neutralized solutions were transferred to separate 100-ml graduated cylinders, where the solids were allowed to settle, and the settling times, solid volumes, and total volumes were recorded. The solutions were then re-slurried and filtered. The times required for free liquid removal were measured, and samples of the filtrates were collected for analysis. Additionally, the precipitates from neutralizing the calcium feed stream were washed with water, and the wash was sampled for analysis.

To study the effects of excess base addition, separate 100-ml samples of the calcium feed stream were neutralized excess of $Mg(OH)_2$ and with excess KOH to a pH of 10. Appropriate analyses were performed on all the liquid and solid samples, and the results are detailed in Tables I through IV.

Part 2: Precipitation of RCRA metals.

These experiments were performed to determine if RCRA elements present in chloride feed for hydroxide precipitation would be removed using $Mg(OH)_2$. For these experiments, chloride salts of RCRA elements were dissolved, and the solution was made approximately 2 M HCl before neutralization with $Mg(OH)_2$. The initial feed solutions and final filtrate solutions were analyzed for the element of interest.

B. Experiments with Radioactive Solutions

The hot experiments were set up to determine if indeed $Mg(OH)_2$ would generate a filtrate that meets the discard requirement for the liquid waste treatment facility. The first comparison was performed on a chloride waste stream. After the acidity of the solution was determined, two 100-ml batches were neutralized, the first with KOH and the second with $Mg(OH)_2$. As in the cold experiments the settling times, solid volumes, total volumes and filtering times were recorded. The feed stream and both filtrates were analyzed for Pu, Am, and other elements of interest.

A second set of neutralizations was performed to determine the relative difference between the particle-size distributions of precipitates formed by the two neutralizing agents. Two neutralizations were carried out comparing KOH and $Mg(OH)_2$. The particle-size distributions of the respective precipitates were determined.

III. RESULTS AND DISCUSSION

A. Proof-of-Principle Cold Studies

Table I describes the settling times, solid volume, and the filtration times of the different systems studied.

Table I: Settling and Filtration Times of Various Precipitates

Feed precip. agent	Fe/HCl KOH	Fe/HCl $Mg(OH)_2$	Fe/Ca/HCl KOH	Fe/Ca/HCl $Mg(OH)_2$
settling time	overnight	2 hrs	overnight	2 hrs
solid level	114 ml	28 ml	130 ml	32 ml
filtering time	105 min	30 min	150 min	30 min

Table I compares some precipitate characteristics between KOH precipitation and $Mg(OH)_2$ precipitation of feed with and without calcium. Not only are the settling times significantly less, but the volume and the filtration times of the precipitate are each approximately 75% less when using $Mg(OH)_2$ than the precipitate from KOH precipitation. The KOH precipitate was left standing overnight while the $Mg(OH)_2$ precipitate reached an equilibrium level in approximately two hours. This large decrease in settling and filtration times should greatly improve the efficiency of hydroxide precipitations of glove box solutions and help to eliminate this process bottleneck in chloride operations.

Table II presents the weight of the precipitates as well as their chloride and calcium concentrations. As the data show the precipitate from $Mg(OH)_2$ weighs 10% less than the precipitate from the KOH experiment. Also, the oxide from the $Mg(OH)_2$ contains significantly less calcium and chloride than the KOH precipitate.

Table II: Calcium and Residual Chloride Content of the Hydroxide Precipitates

	KOH precipitate	KOH precipitate	$Mg(OH)_2$ precipitate
pH of filtrate	7	10	7
wt (g)	6.1	9.3	5.4
Ca (wt %)	2.3		0.7
Cl (wt %)	3.98		1.85

This weight difference is probably a result of water retention as well as coprecipitated calcium and residual chloride contaminating the precipitate. Not surprisingly, the weight of the precipitate also increased when the pH was raised to 10. The increase is a result of the coprecipitation of calcium. These data are presented in Table III.

Table III: Analysis of Filtrates from 10 ml HCl Feed Containing 1.86 g/l Iron and a Mixture of 1.60 g/l Iron and 4.5 g/l Calcium

	HCl with Iron		HCl with Iron and Calcium			
	KOH	$Mg(OH)_2$	KOH	$Mg(OH)_2$	Excess KOH	Excess $Mg(OH)_2$
Final pH	7.9	7.7	7.0	7.4	10.5	8.4
Final Volume (ml)	133	110	135	110	160	110
Iron (g)	BDL	BDL	BDL	BDL	BDL	NA
Magnesium (g)	NA	5.6	NA	5.6	NA	5.6
Calcium (g)	NA	NA	3.57	4.10	0.98	4.05

BDL is *below detection limits*
NA is *not analyzed*

Table III describes the results of experiments in which 100 ml of feed solution (HCl with iron and separately, HCl with iron and calcium) are neutralized with KOH and $Mg(OH)_2$. The table presents final pH values, final slurry volumes, and filtrate analyses for the species of interest. The iron, calcium and magnesium values were calculated by determining the concentrations of the respective elements by ICP (inductively coupled plasma) and then calculating gram amounts in the feed. These data show the increased slurry volume resulting from KOH precipitation (as much as 30% more filtrate) and that calcium is effectively removed from solution if the final pH reaches values around 10. The self-buffering resulting from common-ion effect of the $Mg(OH)_2$ slurry has two immediate benefits: dissolved calcium or magnesium will not coprecipitate, and since the pH of the filtrate does not exceed 9, the solution cannot be classified as hazardous based on RCRA guidelines (pH > 12 is hazardous). Neither of these advantages is currently achieved consistently when using KOH as the neutralizing agent.

Table IV presents data taken from analyzing the water from washing the hydroxide precipitates and refiltering. The table illustrates the tendency of KOH precipitates to entrain both chloride and calcium in the solid. The trait, while also present with $Mg(OH)_2$ precipitation, occurs to a much lesser extent.

Table IV: Analysis of Precipitate Wash Filtrate

	KOH Precipitate		$Mg(OH)_2$ Precipitate	
	Wash 1	**Wash 2**	**Wash 1**	**Wash 2**
Chloride (M)	0.8	0.22	0.35	0.06
Calcium (g)	0.55	0.15	0.32	0.04
Magnesium (g)	NA	NA	0.05	0.45

NA is *not analyzed*

The initial concentration of calcium in the KOH precipitate was 2.3% by weight, while the $Mg(OH)_2$ precipitate the calcium concentration was 0.7% by weight. Several observations can be made from observing the behavior of the $Mg(OH)_2$ precipitate during washing. Residual chloride can be effectively removed using much less wash than from KOH precipitates. Not only is this an advantage from a waste minimization standpoint, but this is an advantage if the precipitates are scheduled for recycling into nitrate operations, where residual chloride can be a corrosion concern. With additional washing, it also appears that the magnesium can be made soluble again and effectively removed to lower the final precipitate mass for storage or reprocessing.

Physically the dried $Mg(OH)_2$ precipitate tends to be a free-flowing powder after drying while the KOH precipitate tends to dry in chunks. This may indicate that the magnesium hydroxide precipitate can be dried at lower temperatures. If further development proves this to be true, plutonium-bearing hydroxide can be dried at a temperature that is low enough to prevent the conversion from hydroxide to oxide, which may permit redissolution of the precipitate in warm nitric acid (maybe low-molar nitric acid and maybe without the need for fluoride addition) and not leave residues requiring additional processing. Currently, these KOH precipitates are

dissolved in boiling nitric acid, and efficient dissolution is sometimes difficult. If the $Mg(OH)_2$ precipitation scheme is successful, another option is to dissolve the hydroxide precipitate in HCl and run the resulting solution through the chloride recovery sequence. This would have the advantage of providing a closed-loop cycle for the recovery of a chloride waste.

B. Cold Studies using RCRA Constituents

Table V details the results of trial neutralizations of 2 M HCl containing certain RCRA elements (Ni is not, at this time, a RCRA metal, but there are indications that it may be added to the RCRA list in he future). As these filtrate analyses indicate, the concentration of RCRA elements in the neutralized waste stream are below 5 ppm. Therefore, caustic precipitation (either with KOH or with $Mg(OH)_2$) should provide an acceptable technique for processing feeds that produce a filtrate that can be directly transferred to TA-50.

Table V: RCRA Metal Behavior in $Mg(OH)_2$ Precipitation

Element	Feed Composition (g/l)	Filtrate Composition (mg/l)
Chromium	4.9	<1
Lead	8.8	<1
Cadmium	8.0	<0.2
Nickel	7.7	<1

C. Experiments with Radioactive Solutions

Table VI details the settling characteristics of the $Mg(OH)_2$ and KOH precipitates. The acid concentration of the waste stream was determined to be 6.7 M by titration with standard NaOH.

Table VI: Settling Data for Neutralized Solutions

	Reagent	
	$Mg(OH)_2$	KOH (~10 M)
Amount of reagent added (g)	20	83
Settling time (min)	30	240
Total Volume (ml)	102	178
Solid Volume (ml)	<10	33

These results are similar to the previous experiments with nonradioactive solutions (Table I), and indicate the relative differences between the two precipitation techniques. The $Mg(OH)_2$ precipitates settle faster and produce less solid and liquid volume.

Table VII shows the analysis of the feed solution as well as both the KOH and $Mg(OH)_2$ filtrates.

Table VII: Analyses of Acidic Feed and the Neutralized Filtrates

Element	Feed (ppm)	$Mg(OH)_2$ Filtrate (ppm)	KOH Filtrate (ppm)
Plutonium	64	0.04	0.36
Americium	28	0.15	0.76
Silver	2.2	<1	<1
Calcium	2800	2900	530
Chromium	22	<1	<1
Iron	3.0	<1	<1
Potassium	9400	8500	140000
Magnesium	1700	81000	15
Sodium	5000	5000	3100
Nickel	180	<5	<5

As the results shown in Table VII indicate, filtrates from both precipitation techniques will meet the current discard limits for caustic waste solutions. However, filtrates from $Mg(OH)_2$ precipitation are an order of magnitude lower in plutonium and a factor of five lower in americium. This decrease in the plutonium and americium concentrations will result in lower alpha activities for solutions sent to the waste treatment facility. Also, calcium and magnesium levels in the KOH filtrate are significantly lower than the $Mg(OH)_2$. This is as result of coprecipitation of these species with KOH through improper pH control as discussed earlier.

As previously discussed, the neutralization reaction with $Mg(OH)_2$ appears to generate a precipitate with a larger particle size as evidenced by faster settling rates, smaller total-solids volume, and faster filtration rates. Figure 4 shows the comparison of the particle-size distributions resulting from precipitations by both KOH and $Mg(OH)_2$. The mean particle size was 25.8 microns for the $Mg(OH)_2$ precipitate while potassium hydroxide yielded a precipitate that had a mean particle size of 6 microns.

From these distribution data, 66% of the hydroxide precipitate from KOH is <5 micron material while only 17% of the $Mg(OH)_2$ precipitate has a particle size of <5 micron. Because of this high fraction of small precipitate and our inability to effectively remove this fraction from solution during our solid-liquid separation step, this may account for the higher activity level in the KOH filtrate and for the differences in plutonium and americium concentrations seen in Table VII.

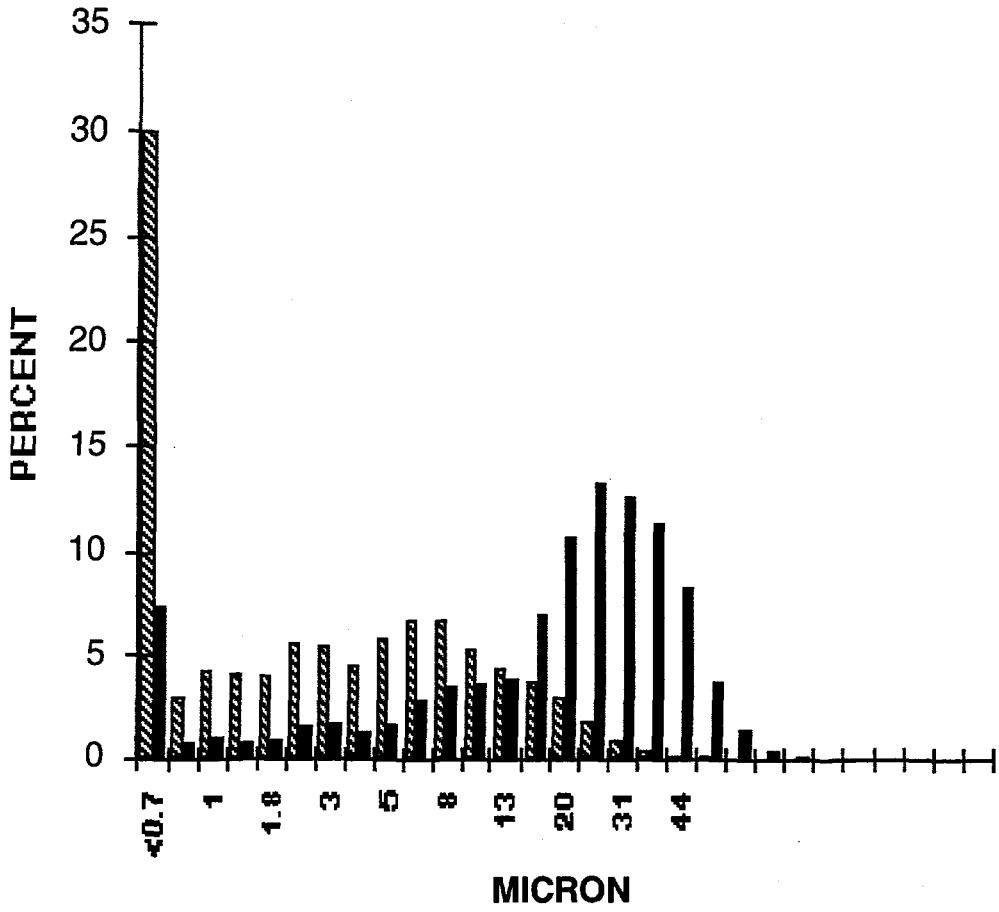

Figure 4. Plot of Particle Size Distributions for $Mg(OH)_2$ and KOH Precipitates (hatched distribution is KOH, solid distribution is $Mg(OH)_2$)

D. Plant Operations

1. Waste Stream Treatment. The following procedure is currently in place for chloride acid waste treatment in Building PF-4.

1. Titrate the waste stream for hydrogen ion concentration with standard KOH.
2. Calculate the amount of magnesium hydroxide needed to neutralize the acid.
3. Add the magnesium hydroxide to the solution and allow to mix thoroughly.
4. Check the pH of the solution. If the pH is below 7, a small amount of magnesium hydroxide should be added to the solution in 10-gram increments.
5. Allow the precipitate to settle.
6. Filter the solution and collect the filtrate.
7. Sample the filtrate and have assayed for total alpha.

Approximately 50 batches at 10 liters per batch have been processes through this method. The batches average approximately 6 M hydrogen ion concentration. All 50 batches have produced a "cold" filtrate when filtered through a 25-micron filter cloth. These filtrates have typically averaged 2×10^8 counts/minute/liter which is an order of magnitude below the discard

limit. When potassium hydroxide is used as the neutralizing agent, the filter cake must be allowed to build up, and the solution must be passed through a 5-micron pall filter. Even then approximately 10% of the solutions must be reprocessed to meet the discard limit for total alpha. Also, the cake buildup results in an even further slowing down of the filtration process.

The other significant factor is that if KOH were used to neutralize the solution, approximately 800 liters of neutralized filtrate would have been transferred to TA-50 instead of the 500 liters that was sent from these solutions. The estimated cost for processing liquid at TA-50 is $50 per liter.[3] This has resulted in a cost savings of approximately $15,000 for these 500 liters.

If magnesium hydroxide had been in place during top production years when 20,000 liters of solution were transferred to TA-50, a conservative estimate of 25% reduction in volume would have been achieved by replacing KOH with $Mg(OH)_2$. Some 5,000 fewer liters would have been transferred to TA-50 and resulted in a savings of $250,000.

2. Residue Stabilization. Magnesium hydroxide also offers the possibility of converting the plutonium into a form suitable for long-term storage. Figure 5 shows a flow sheet for the stabilization of plutonium compounds.

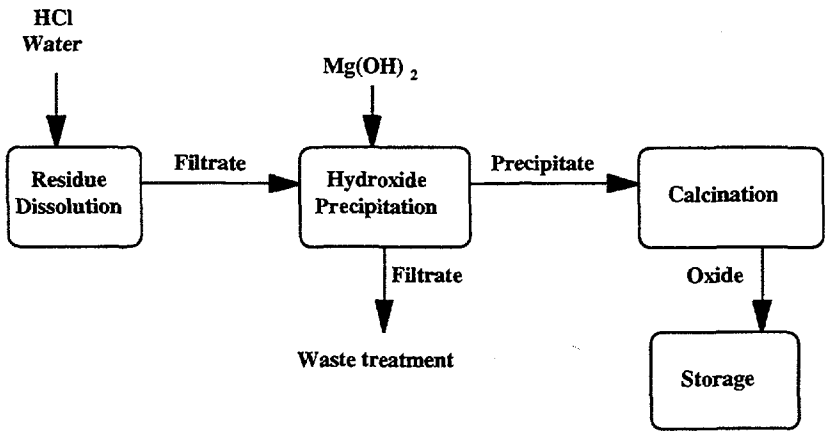

Figure 5. Proposed flow sheet for residue stabilization

As the flow sheet depicts, the residues will be dissolved in hydrochloric acid. The filtered solution is then titrated using a pH electrode to a pH of 7. The calculated amount of magnesium hydroxide is added to the feed stream to precipitate the actinides. The precipitate is filtered and washed. The filtrate is sampled, and, if it meets discard limits, it can be transferred to liquid waste treatment. The plutonium hydroxide can be calcined to the oxide. The hydroxide will convert to oxide when heated to temperatures above 100°C.[4]

To test this flow sheet, a sodium/potassium-based salt was dissolved in dilute HCl. The salt had a bulk weight of 2.3 Kg and contained 210g of Pu. After the salt was dissolved in 15 liters of solution, the calculated amount of $Mg(OH)_2$ was added. The precipitate was allowed to settle, and a solid volume of 1 liter was achieved after settling. The solution filtered quickly and the

[3]W. Schuler, "Waste Disposal Cost, " LANL Memorandum NMT-2-NITR-94-090 to B. J. McKerley (April 1, 1994).
[4]J.M. Cleveland, *The Chemistry of Plutonium,* (American Nuclear Society, LaGrange Park, Il., 1979) p. 311.

precipitate was washed. The filtrate was sampled, and a total alpha measurement was performed. The filtrate had an activity of 2.7×10^7 counts/minute/liter. This activity level is two orders of magnitude below the level needed to discard the solution; therefore, the filtrate was transferred to TA-50. The filtrate was calcined. The oxide was weighed and a sample removed for chemical analysis. The weight of the precipitate was 329.3 g and was approximately 65% plutonium by weight. At this plutonium concentration the oxide meets the criteria for long-term storage

As a proof of principle this batch operation has shown that there is promise for the use of magnesium hydroxide in residue stabilization, and future work is planned in this area.

IV. FUTURE WORK

As just mentioned, one of the areas of future experimentation is to prove using magnesium hydroxide in residue stabilization on a pilot-scale operation. This will involve setting up a daily plant operation for residue recovery.

Also of interest with magnesium hydroxide is to determine if added filtration steps through smaller micron filters will reduce the activity of the solution. The particle-size determinations lead us to believe that if the solution is filtered through a finer frit, the activity of the solution will decrease. This will help NMT Division help reach its stated goal of zero discharge.

One last area of experimentation is to determine if magnesium oxide can be used to neutralize the acid waste stream. Magnesium hydroxide is prepared by hydrating magnesium hydroxide[5] and therefore MgO should neutralize acid solutions. This is of interest because one of the major solid waste streams generated by pyrochemical operations is MgO crucible pieces. If MgO will neutralize the chloride waste streams, then, instead of discarding the crucible as a solid waste, it can be used as a reagent in chloride recovery operations.

V. CONCLUSIONS

This study has shown magnesium hydroxide to be superior to potassium hydroxide as a neutralizing agent for acid chloride waste streams. The reasons are listed below:

1. Less liquid waste that must be sent to liquid waste treatment,
2. Faster-settling precipitates,
3. Faster-filtering precipitates,
4. No unwanted coprecipitation of calcium and/or magnesium,
5. Lower activity levels of the filtrates,
6. Weight of precipitate reduced,
7. $Mg(OH)_2$ is safer to use than KOH, and
8. $Mg(OH)_2$ is less expensive.

ACKNOWLEDGMENTS

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[5]Gmelin, *Handbook of Inorganic Chemistry, Mg.*, (Weinheim/Bergstrasse, Berlin, Germany 1937).