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Purification of Plutonium Chloride Solutions via Precipitation and Washing

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Abstract: Pyrochemical operations at Los Alamos Plutonium Facility use high temperature melts of calcium, sodium, and potassium salts in the plutonium metal purification process. Aqueous chloride operations recover the remaining plutonium from the residue salts, generating copious quantities of corrosive aqueous waste while occupying a large area of the facility. To minimize these problems, an alternative flow sheet was tested in which dissolved salts were precipitated and washed to remove interstitial chloride before further processing in aqueous nitrate operations. Results of the tests will be discussed from the perspective of chloride removal, plutonium recovery, filterability, and waste minimization.

Keywords: Plutonium, chloride, aqueous, purification

INTRODUCTION

Pyrochemical operations at Los Alamos Plutonium Facility (TA-55) use high temperature melts of calcium chloride for the reduction of plutonium oxide to plutonium metal (DOR) and the extraction of americium (MSE) and high temperature combined melts of sodium chloride and potassium chloride mixtures for the electrorefining purification (ER) of plutonium metal. Fig. 1 is an illustration of the pyrochemical flow sheet that is currently employed at TA-55 for production of plutonium metal. The remaining plutonium and americium are

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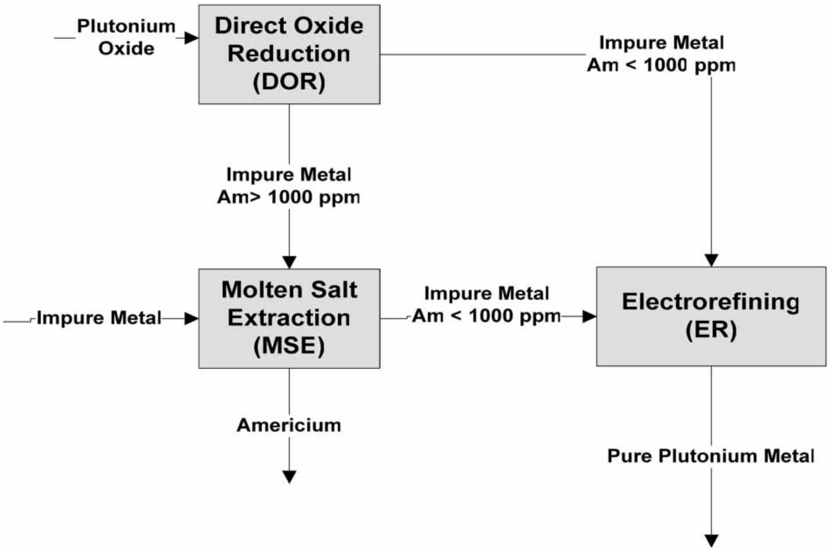

Figure 1. Principle unit operations of the current Los Alamos pyrochemical flow sheet.

recovered from these pyrochemical salt residues by dissolution in hydrochloric acid followed by purification in either solvent extraction or ion exchange. Oxalic acid is added to the purified Pu(III) solution to precipitate Pu(III) oxalate. The oxalate precipitate is calcined to produce plutonium oxide. Fig. 2 illustrates the current aqueous chloride flow sheet used at TA-55. Aqueous operations occupy a large portion of the Los Alamos Plutonium facility. In addition, aqueous chloride operations generate copious quantities of corrosive aqueous wastes. An alternate chloride flow sheet, that would minimize the space needed for aqueous chloride operations, reduce the volume of aqueous chloride waste generated and allow chloride residues to be sent to the mainstream aqueous nitrate operations for processing was tested.

The alternate flow sheet is illustrated in Fig. 3. After dissolution, the plutonium is precipitated[a] and the precipitate is washed to remove accumulated chloride. The washed plutonium precipitate is sent for re-dissolution and purification in the nitric acid flow sheet. Aqueous nitrate operations, which have a flow sheet similar to chloride operations, are generally used to recover plutonium for residues that do not contain chloride. Residues are dissolved in nitric acid, and then the plutonium is purified, precipitated as an oxalate, and calcined. Aqueous nitrate operations are the preferred recovery option compared to chloride because nitric acid is less corrosive

[a] Alternate precipitating agents should be tested to determine the optimal flow sheet. Initial trials used oxalic acid and sodium or potassium hydroxide as the precipitating agents.

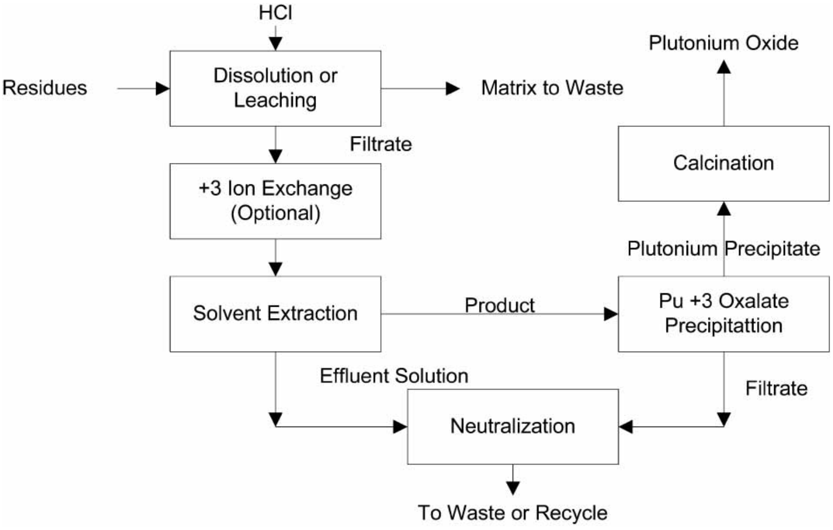

Figure 2. Principle unit operations in the current aqueous chloride flow sheet.

than hydrochloric acid and nitrate operations generate less liquid waste than chloride operations.[b] Demonstration of the alternate flow sheet would also increase the flexibility of aqueous chloride operations. Should the chloride purification unit operations be unavailable, the alternate flow sheet could be implemented to allow aqueous processing to continue. Two disadvantages of implementing the flow sheet are that corrosion problems may result if a significant amount of chloride is inadvertently introduced into nitrate operations and the total number of processing steps increase, probably increasing plutonium losses and worker exposure. To minimize potential corrosion issues, most of the chloride must be removed from the pyrochemical residues before they are sent to nitrate operations.

Two direct oxide reduction (DOR) residues and one electrorefining (ER) residue were processed using the alternate flow sheet. Results are discussed from the perspective of:

- Chloride removal efficiency: Was a sufficient amount of chloride removed from the pyrochemical residues to allow further processing in the aqueous nitrate module with out causing significant corrosion issues? (<3 mg Cl^-/g of Pu)[c]

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[b] The nitrate operations flow sheet includes nitric acid recycle while hydrochloric acid recycle is still in development.

[c] The <3 mg Cl^- per g of Pu is somewhat arbitrary and is based on operator processing experience. Should this flow sheet be pursued, conducting experiments to better quantify acceptable chloride levels in nitrate operations is recommended.

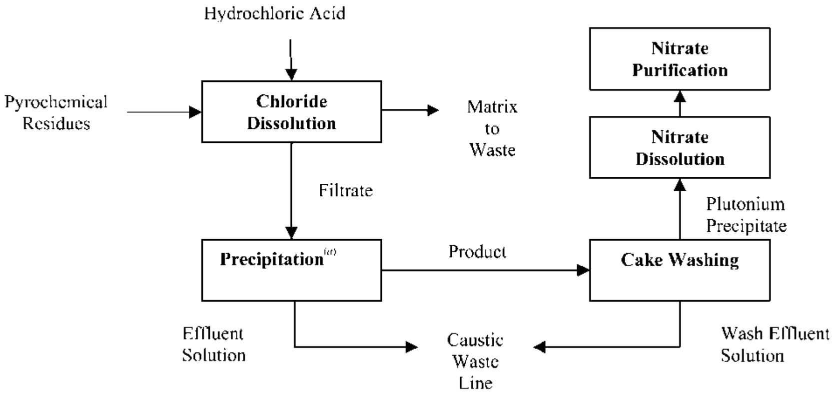

Figure 3. Principle unit operations in the alternate aqueous chloride flow sheet.

- Plutonium recovery: Were plutonium losses kept to a minimum? Was the alpha activity in the process effluents low enough to allow for routine disposal of the aqueous waste? (<4.5 mCi/L alpha activity)
- Filterability: Could the precipitates be filtered rapidly? Potentially, the slowest step in the alternate flow sheet is filtration of the precipitate.
- Waste Minimization: Does the alternate flow sheet result in a significant reduction in the amount of aqueous chloride waste generated?

EXPERIMENTAL PROCEDURE

Two DOR residues containing primarily magnesium oxide crucible pieces, calcium chloride salts, calcium oxide and plutonium chloride salt (Fig. 4) and one ER residue containing roughly equi-molar quantities of sodium chloride and potassium chloride, as well as plutonium chloride salt, were processed as the feed material. The salts were pulverized, dissolved in 6 M hydrochloric acid, and filtered. Crucibles were separated from the salts, leached in 12 M hydrochloric acid, and the solution was strained and filtered. Leaching and dissolution solutions were combined to form the stock solution for the experimental runs.

A two-liter portion of the stock solution was removed for each experimental run, except for Run 3A which used 400 ml. For runs in which an oxalate precipitation was conducted, the acid molarity was adjusted to between 1–2 M by adding either deionized water, hydrochloric acid, or potassium hydroxide. After hydroxylamine hydrochloride was added to reduce the Pu from the +4 to the +3 oxidation state, oxalic acid was added to form an oxalate precipitate. The solution was filtered using

Figure 4. DOR residue.

20 micron filter paper and filtration time as a function of volume was recorded.[d]

A hydroxide precipitation was then conducted to precipitate most of the plutonium remaining in solution. Potassium hydroxide (~10M) or sodium hydroxide of varying molarities was used as the neutralizer. An approximate pH was determined using bromocresol purple indicator, which turns purple at a pH of about 6.8. In addition, either pH indicator strips or an AST Smartstik hand held pH meter was used to determine solution pH more accurately. The desired pH varied with experimental runs but was a minimum of pH 8. Neutralizer was added until a color change was observed in the bromocresol purple indicator or until the desired pH was measured.[e] All precipitations were conducted at room temperature (approximately 21–24°C) except the 2D hydroxide precipitation, which was conducted at 60°C. For Run 2D, the flask and contents were heated using a heating mantle and J-KEM Scientific Model 210 controller, equipped with a thermocouple. Once at temperature, the neutralizer was added slowly to the oxalate solution until the desired pH was reached. For all runs, the solution

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[d] This is the same procedure used for oxalate precipitation in the baseline aqueous chloride flow sheet.

[e] The pH of the solution would often drop with time. The solution was observed for varying lengths of time to determine if the pH of the solution would drop to neutral or acidic. If the pH dropped below 8 or the solution turned yellow, neutralizer was added to return the solution to the desired basic pH prior to filtration. The pH of the filtrate solution, measured at least 24 hours after filtration, was pH 7 or less for all solutions containing oxalate. This suggests that additional time should have been allowed for the system to equilibrate and additional base should have been added prior to filtration. This would have significantly increased processing time but should have significantly reduced Pu losses in the filtrate. Because of the complexity of the system and the many competing reactions occurring, it is difficult to give a clear explanation for the slow drop in pH. Because the pH drop was most significant in solutions containing oxalate, changes in the speciation of oxalate complexes is probably a significant factor. Hydrolysis may also contribute to the pH drop.

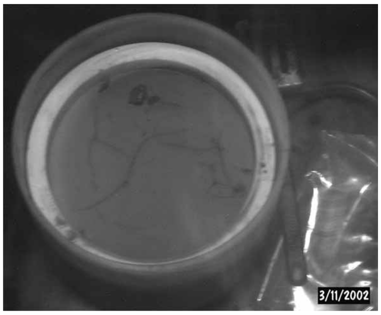

Figure 5. Run 1B oxalate/hydroxide precipitate.

was filtered using 20 micron filter paper and the filtration time as a function of volume was recorded. The hydroxide precipitate was filtered on top of the oxalate precipitate to form one cake. This was done to simplify processing so that only one filtration boat and wash step were necessary (Fig. 5).

The precipitate wash solutions were made from deionized water. The pH of the wash solution was increased by adding potassium hydroxide. The wash solution was poured over the precipitate and the solution was stirred thoroughly to create a slurry before the solution was filtered. The washed precipitate was dried in the oven for approximately four hours at 200°C. The dried precipitate was dissolved in nitric acid.

Chloride concentrations of the dissolution, filtrate, and wash solutions were measured using a Cole-Parmer combination chloride selective electrode with an Orion Model EA 940 expandable ion analyzer. The Orion ion analyzer was also used for pH determinations. The instrument was calibrated using 3 or 4 chloride standards prepared by diluting a 1000 ppm chloride standard with ultra pure water. Due to the high chloride concentration in most samples, sample dilution with deionized water was often necessary to bring the chloride concentration into a measurable range. To control ionic strength, 1 ml of an ionic strength adjuster (ISA) per 50 ml of solution was added to all standards and samples prior to analysis. The pH of all solutions was adjusted to a 3–6 pH range to minimize variations in chloride concentration reading due to varying pH and to ensure the pH of the solutions were within the operating range of the chloride electrode (2–12 pH units)[f] The Direct Calibration Measurement technique was used so that chloride concentrations could be read directly on the ion analyzer.

Plutonium concentrations for solutions containing between 1 and 200 grams of plutonium were measured with a solution assay instrument (SAI). The SAI is a gamma ray based instrument. Radiochemistry was used to determine plutonium concentrations for solutions with lower plutonium content.

[f] Experiments using the Orion ion analyzer showed that the variation of chloride concentration readings to changes in pH was less than 5% over the pH range from 3–6.

RESULTS AND DISCUSSION

For Run 1 a three-year-old DOR residue containing approximately 1300 g of crucibles and 5000 g of salt was dissolved. The resulting 17.9 liters of 1.2 M acid solution contained 180 g/L chloride and 32.4 g/L plutonium. For Run 2, a two-year-old DOR residue containing 2470 g of crucibles, 4680 g of salt, and 2640 g of MgO was dissolved. The 18.2 liters of 0.3 M acid solution contained 240 g/L chloride and 5.0 g/L plutonium. For Run 3 an electrorefining (ER) residue containing 1000 g of salt was dissolved yielding 6.0 liters of 4.3 M acid solution with 190 g/L chloride and 30.5 g/L of plutonium.

Experimental parameters and precipitate descriptions are summarized in Table 1. Typically, the amount of oxalic acid added for an oxalate precipitate is based on the assumption that all the plutonium and only the plutonium reacts to form $Pu_2(C_2O_4)_3$. In standard runs, a 10% to 15% excess is added.

Table 1. Experimental parameters and precipitate description

Run	Initial g of Pu	% Excess oxalic acid	pH of hydroxide precipitation	Number, volume and pH of washes	Description of precipitate OX-oxalate OH-hydroxide
1A	63	15%	8.3	5 washes 400 ml pH8.6, 6.5	Combined-green, grey paste
1B	63	250%	10.1	10 washes 500 ml 8.2–9 pH	OX-grey, dark green OH-thin green/grey
1C	63	125%	>11	4 washes 500 ml 10.5 pH	Combined-Large grey, $Ca(OH)_2$ co-precipitated
2A	11	28%	8.6	4 washes 500 ml 11.6 pH	OX-very thin brownish green OH-1/4 "brown
2B	11	275%	8.6	4 washes 500 ml 11.6 pH	OX-thin tan OH-1/4 "brown
2C	11	No oxalate added	9.0	4 washes 500 ml 11.0 pH	OH-thin tan, grey
2D	11	No oxalate added	9.0	4 washes 500 ml ~11.0 pH	OH-tan, white hunks
3A	12.2	13%	11.4	4 washes 500 ml 11.5 pH	OX-dark brown OH-avocado green

A considerably smaller amount of plutonium (15%–70%) precipitated as plutonium oxalate in the alternate flow sheet, where a large amount of impurities were present in the solution, compared to the standard flow sheet where >99% of the plutonium precipitates as an oxalate. The amount of oxalic acid added was increased in an attempt to increase the amount of plutonium precipitating as an oxalate. This resulted in increased plutonium losses in the effluent. The amount of oxalic acid was varied in an attempt to balance these competing effects. The pH of the washes was varied to determine the effect of pH on the alpha activity (plutonium losses) in the final wash solutions.

An oxalate precipitation was conducted initially because the oxalate precipitate yields a concentrated plutonium product with reasonably good purification and rapid filtration rates. The additional hydroxide precipitation was necessary in order to recover more of the plutonium, though it yielded a cake that was difficult to filter and wash. The hydroxide cake was filtered on top of the oxalate cake to minimize washing steps. For full scale processing, handling the cakes separately may have a better approach since the oxalate cake should need considerably less washing.

Results of plutonium recovery and chloride washing efficiency are summarized in Table 2.

Chloride Removal

For each run, the chloride concentrations in all solutions were measured to determine the efficiency of the chloride removal.[g, h] The target maximum level of chloride in the washed precipitate was 3 mg Cl^- per gram of plutonium.[i] Chloride concentrations in the DOR oxalate/hydroxide precipitates were reduced to desired levels by washing with caustic water of varying pH, except for Run 1C when a large amount of calcium hydroxide was co-precipitated. More Cl^- was trapped in the precipitate when a significant amount of calcium hydroxide was present, making it harder to remove the chloride. Calcium hydroxide precipitate formation can be minimized during the hydroxide precipitation by maintaining the pH of the solution to less than

[g] For routine implementation of the alternate chloride flow sheet, only the chloride concentration in the nitric acid dissolution solution of the washed cakes must be checked to ensure that solutions exceeding the acceptable limits are not sent for processing in the nitric acid line without further dilution.

[h] Obtaining reliable readings with the chloride electrode was difficult with increasing age of the electrode. In particular, the time needed to reach stable readings increased significantly. A chloride mass balance was conducted for each the first 5 runs. Losses of 1%, 1% and 8.5% were observed for Run 1A, 1B and 1C respectively and gains of 12% and 28% were observed for Runs 2A and 2B.

[i] The <3 mg Cl^- per g of Pu is somewhat arbitrary and is based on operator processing experience. Should this flow sheet be pursued, conducting experiments to better quantify acceptable chloride levels in nitrate operations is recommended.

Table 2. Plutonium recovery and chloride washing efficiency results

Sample ID	Total g of precipitate	g of Pu in washed precipitate	g of Pu in filtrate and wash solutions	Alpha Activity of combined solutions (mCi/L)	mg of Cl^- in washed precipitate	mg Cl^- per grams of Pu in washed precipitate
Target				<4.5		<3.0
Run 1A	72	41	0.42	4.6	39	0.95[a]
Run 1B	148	53	2.3	14	13.8[b]	0.27[b]
Run 1C	200	44	1.2	12	500	11
Run 2A	30	11	1.3	15	6.3	0.50
Run 2B	46	11	1.7	20	8.1	0.73
Run 2C	23	13	.057	1.8	84	7.6
Run 2D	40	13	.049	0.88	340	31
Run 3A	27.9	12	.047[d]	2.0	23	2.7

[a] Values in Bold were below the target levels and met acceptance criteria.

[b] Run 1 was washed with 5.1 liters instead of 2 liters.

[c] Run 1B data is corrected back to the chloride levels after 2 liters of washing for better comparison with other run.

[d] Washes only-no value for filtrate available.

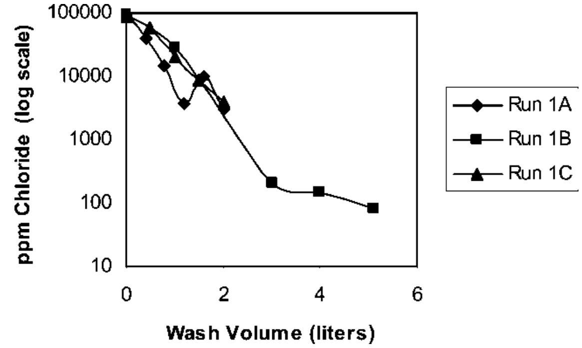

Figure 6. Run 1 chloride wash concentration.

11. Run 2 illustrates that chloride concentrations in precipitates containing both oxalate and hydroxide were reduced by at least an order of magnitude more than precipitates containing hydroxide only, when washed with identical amounts of solution. For Run 3 (the ER oxalate/hydroxide run), the chloride concentration in the washed cake was barely below the target level, suggesting that chloride removal from ER residues may be more difficult. Figures 6, 7 and 8 illustrate the log of chloride concentration in the wash solution per volume of wash.

Plutonium Recovery

The alpha activity in the combined filtrate and wash solutions was measured to determine plutonium concentration. Alpha activity of the solutions must be

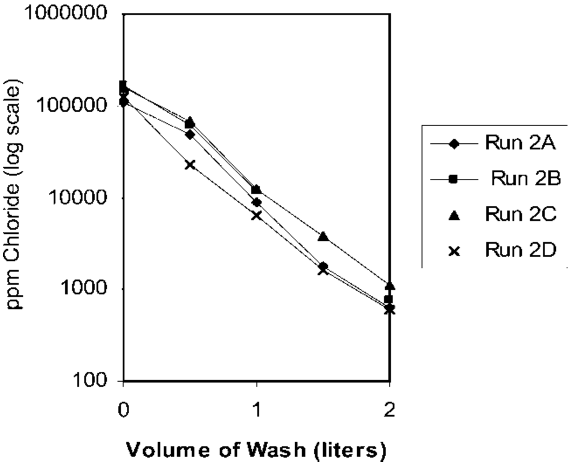

Figure 7. Run 2 chloride wash concentration.

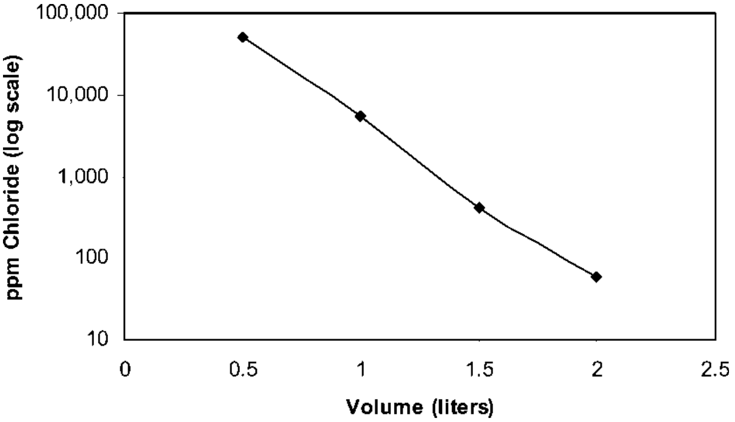

Figure 8. Run 3 chloride wash concentration.

below 4.5 mCi/L to allow for easy disposal of the waste to the Los Alamos Radioactive Liquid Waste Treatment Facility. The low activity level also ensures minimal loss of plutonium in the waste solutions. Table 1 summarizes the plutonium recovery and alpha activity of the combined filtrate and wash solutions for all runs. Figures 9 and 10 illustrate the activity of the filtrate and wash solutions for the DOR runs. For the DOR runs, the alpha activity (plutonium concentration) in the combined solutions for the oxalate/hydroxide solutions was consistently higher than the target level, however Run 1A was close. Excess oxalate ion causing high plutonium losses to the filtrate has been observed previously (1). The excess oxalate competes with the hydroxide for binding the plutonium that is in solution. Keeping the

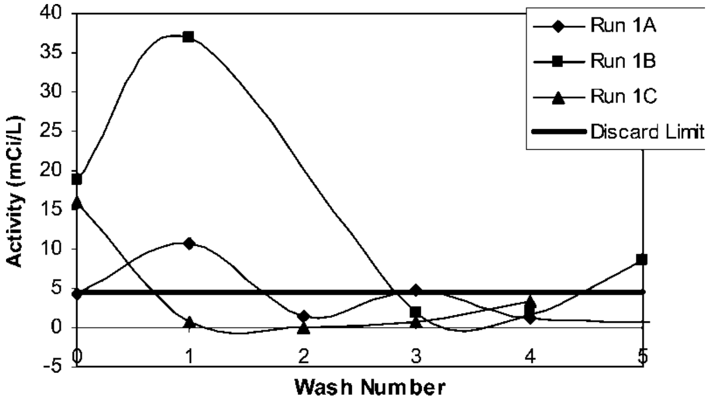

Figure 9. Run 1 wash activity.

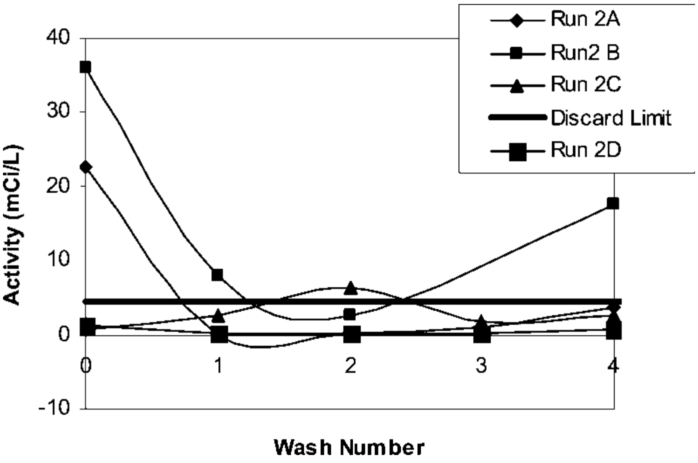

Figure 10. Run 2 wash activity.

amount of excess oxalate to a minimum should reduce this problem. The combined filtrate and wash solution for the ER oxalate/hydroxide run was below the target activity level. (Fig. 11) Since sodium and potassium do not precipitate as a hydroxide at pH less than 14, the ER hydroxide precipitation could be conducted at a higher pH than the DOR runs. The higher hydroxide concentration in solution along with the low oxalate concentration probably allowed for more favorable competition with the oxalate for the binding of the plutonium.

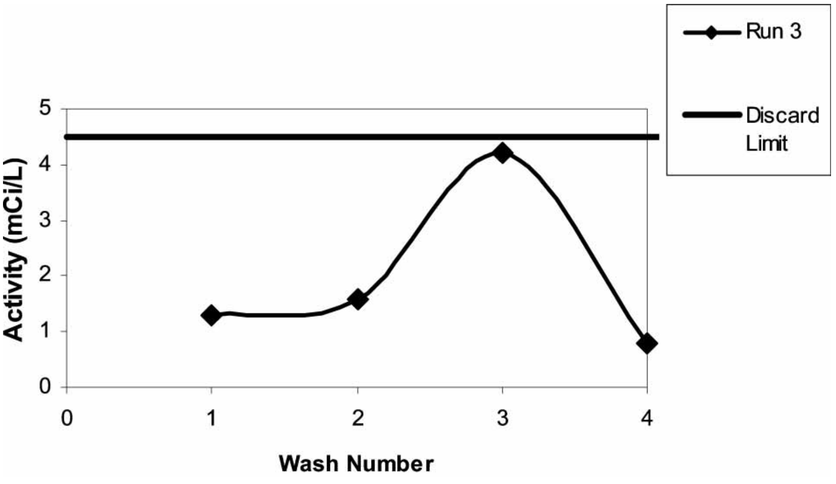

Figure 11. Run 3 wash activity.

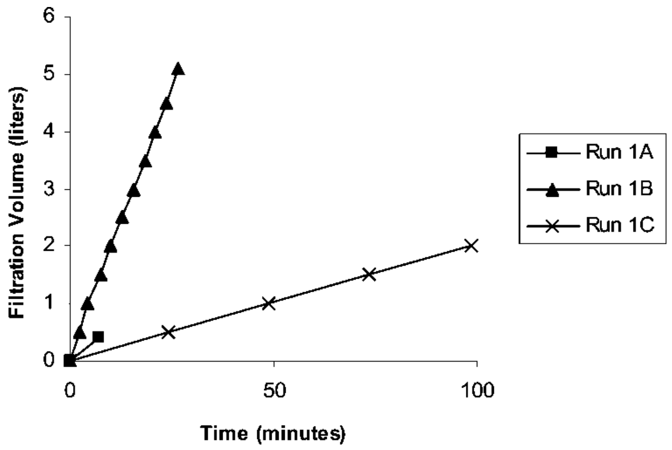

Figure 12. Run 1 filtration rates.

If a small particle size of the oxalate precipitate was a contributing factor to the higher alpha activity in the solutions, a finer filter paper could trap more of the precipitate, however, this would result in considerably slower filtration rates.

The pH of the filtered sample often lowered significantly between the time of the hydroxide precipitation and the time the radiochemistry analysis was completed. This generally resulted in higher alpha activity. This effect was also observed by Alwin et. al. in hydroxide precipitation reactions only (2). Allowing a longer time for the solution to equilibrate prior to terminating the hydroxide precipitation should minimize this problem. Increasing the pH of the washes also tended to reduce the activity of the washes. For hydroxide only precipitations, filtrate/wash solution activities were below discard activity level.

For Run 1, a large amount of plutonium was not recovered in the solutions or the precipitate. The filter paper contained 15 g of recoverable Pu. Additional plutonium may have been lost due to spillage or hold up in the equipment. Careful handling the subsequent runs, significantly reduced these losses.

Filtration Rates

Figures 12 and 13 illustrate the variation in filtration rates within a run. (The hydroxide filtration rates are for filtration through the combined oxalate/hydroxide cake.) Table 3 summarizes the mass of the precipitate and the filtration rates.[j]

[j] No correlation was observed between plutonium losses and filtration rates.

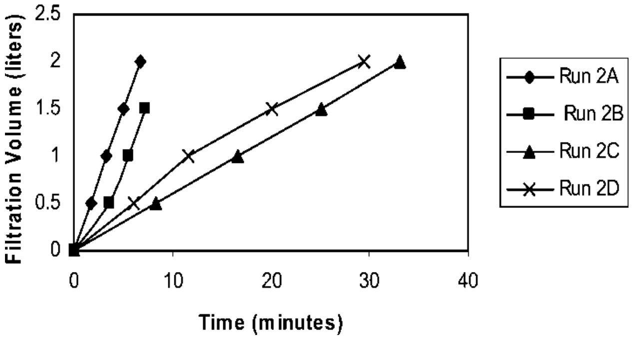

Figure 13. Run 2 filtration rates.

The total mass as well as the nature of the precipitate contributed to the filtration rates. Results from different runs were not compared directly since smaller cakes and less plutonium were present in Runs 2 and 3.

The fastest filtration rates for Run 1 were observed in Run 1B, where more of the Pu was precipitated as an oxalate. The reverse of this effect was observed in Run 2, although the precipitate was very thin in 2A so slowing effects from the precipitate may not have been apparent. Run 1C, where a significant amount of calcium hydroxide co-precipitated, resulted in the slowest filtration rate.

Table 3. Filtration rate comparisons

Sample identification	Total g of precipitate	Oxalate filtrate filtration rate	Hydroxide filtrate filtration rate	Wash filtration rate
Run 1A	72.4		160 ml/min	60 ml/min
Run 1B	148	2000 ml/min	2000 ml/min	190 ml/min
Run 1C	200	2000 ml/min	40 ml/min	20 ml/min
Run 2A	30	Very quick (As rapidly as solution added)	160 ml/min	300 ml/min
Run 2B	46	Very quick (As rapidly as solution added)	130 ml/min	210 ml/min
Run 2C	28.1	NA	18 ml/min	60 ml/min
Run 2D	41.2	NA	140 ml/min	70 ml/min
Run 3A	27.9		240 ml/min	250 ml/min

Runs 2C and 2D compare the effects of conducting the hydroxide precipitation at elevated temperatures on the filtration rates. Room temperature hydroxide precipitation (Run 2C) resulted in the slowest filtration rates. Studies by Alwin et. al. found that filtration rates for plutonium hydroxide precipitates could be increased by approximately a factor of 6 when the precipitation was conducted at 70°C (2). Faster filtration rates were observed when the precipitation was conducted at elevated temperature though the improvement was not as significant as previous observations.

Waste Minimization

Processing 1 kg of plutonium through the standard aqueous chloride flow sheet results in the generation of approximately 120 liters of high activity liquid chloride waste. Based on results from Run 1, the alternate flow sheet would result in approximately 85 liters of high activity waste per kg of plutonium processed, which represents a 30% reduction. Additional liquid effluents would be generated during processing aqueous nitrate operations but nitrate operations include unit operations which recycle nitrate effluents.

CONCLUSIONS

Proof of principle of the proposed alternate aqueous chloride flow sheet, which significantly reduces the number of high-maintenance chloride glove boxes needed for aqueous chloride operations, increases the flexibility of aqueous operations and is anticipated to reduce the amount of chloride liquid waste generated by about 30%, was demonstrated. Results yielded specific information for optimizing process parameters.

To minimize the amount of chloride in the washed precipitate, conduct a combined oxalate/hydroxide precipitation rather than a hydroxide precipitation only. In solutions containing a significant amount of calcium, keep the pH of the hydroxide precipitation less than 11 to minimize precipitation of calcium hydroxide.

To maximize filtration rate of the chloride washing, if calcium is present in significant amounts, keep the pH less than 11 and conduct the hydroxide precipitation at elevated temperatures. (The additional gain in filtration speed gained by precipitating at elevated temperatures must be weighed against the added experimental complexities.)

To minimize the loss of plutonium in the filtrate and wash solutions, conduct the hydroxide precipitation at pH 11 or higher and ensure sufficient time is given for the pH of the system to stabilize prior to filtration, keep the amount of excess oxalate to a minimum, and raise the pH of the washes to at least 12. (While conducting the hydroxide precipitation at a pH greater than 11 does reduce Pu losses it is not recommended for systems containing significant amount of calcium. (DOR and MSE salts) due to the increased difficulty in removing the chloride from the larger cake as well as the reduction in the filtration rate.)

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