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Purification of Aqueous Plutonium Chloride Solutions Via Precipitation and Washing

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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 and high temperature combined melts of sodium chloride and potassium chloride mixtures for the electrorefining purification of plutonium metal. The remaining plutonium and americium are recovered from these salts by dissolution in concentrated hydrochloric acid followed by either solvent extraction or ion exchange for isolation and ultimately converted to oxide after precipitation with oxalic acid. Figure 1 illustrates the current aqueous chloride flow sheet used for plutonium processing at TA-55.

Figure 1. Principle unit operations in the current aqueous chloride flow sheet.

Aqueous chloride operations generate copious quantities of secondary wastes and are difficult to manage from a materials corrosion perspective. Two goals of this research are to minimize the waste generated and the glovebox space needed to process chloride residues. These goals may be achieved by modifying the existing flow sheet so that residues can be sent to the mainstream nitrate operations for processing. Before the residues can be sent to nitrate operations, most of the chloride must be

removed. The proposed modification to the existing flow sheet, illustrated in Figure 2, would eliminate the chloride anion exchange and solvent extraction steps. After dissolution, plutonium precipitation is conducted, followed by a series of precipitate washings to remove accumulated chloride. The washed plutonium precipitate would be sent for re-dissolution and purification in the nitric acid flow sheet.

Figure 2. Illustration of the proposed modifications to the aqueous chloride flow sheet.

This paper discusses results obtained by processing two direct oxide reduction (DOR) residues, containing plutonium, calcium chloride and calcium oxide, using the flow sheet illustrated in Figure 2. Results are discussed from the perspective of chloride removal efficiency, filterability, and plutonium recovery.

Experimental Procedure

Two DOR salt residues were pulverized, dissolved in 6M HCl and filtered to form stock solutions for precipitation experiments. Hydroxylamine hydrochloride was added to a stock solution to reduce the plutonium to the +3 oxidation state. Varying amounts of oxalic acid were added to form a plutonium oxalate precipitate. Potassium hydroxide or sodium hydroxide was added to precipitate any remaining plutonium as a hydroxide. The precipitate was washed with deionized

water of varying pHs to remove interstitial chloride. The precipitate was dried, dissolved in nitric acid and chloride concentrations of the resulting solutions were measured. Two liters of stock solution containing 63 g of Pu and 480 g of chloride were used for each experiment in Run 1. Two liters of stock solution containing 11 g of Pu and 370 g of chloride were used for Run 2 experiments. Seven experiments with the following varying experimental parameters were conducted.

For Run 1A a 15% molar excess of oxalic acid was added and the hydroxide precipitation pH was 8.3.

For Run 1B a 250% molar excess of oxalic acid was added and the hydroxide precipitation pH was 10.1.

For Run 1C a 125% molar excess of oxalic acid was added and the hydroxide precipitation pH was greater than 11. A considerable amount of calcium hydroxide co-precipitated with the plutonium hydroxide.

Run 2A a 28% molar excess of oxalic acid was added and the hydroxide precipitation pH was 10.

Run 2B a 275% molar excess of oxalic acid were added and the hydroxide precipitation pH was 8.6.

Run 2C no oxalate precipitation was conducted. The hydroxide precipitation pH was 9.0.

Run 2D no oxalate precipitation was conducted. The hydroxide precipitation was conducted at 60 C and pH 9.0.

Results and Discussion

Results of plutonium recovery and chloride washing efficiency are summarized in Table 1.

Sample ID	Total grams of precipitate	Initial grams of Pu	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	72.4	63	41	.42	4.6	39 (4, 65)	.95*
Run 1B	148	63	53	2.31	14.2	13.4	.26
Run 1C	200	63	44	1.25	11.6	500	11
Run 2A	30	11	11	1.34	14.8	6	.5
Run 2B	46	11	11	1.72	19.6	8	.73
Run 2C	23.3	11	13	.057	1.83	84	7.6
Run 2D	39.8	11	13	.049	.877	340	31

Table 1. Plutonium recovery and chloride washing efficiency results *Values in red were below the target levels and met acceptance criteria

For each run, the chloride concentrations in all solutions were measured to determine the efficiency of the chloride removal. The target maximum level of chloride in the washed precipitate was 3 mg Cl⁻ per gram of plutonium. Chloride concentrations in plutonium oxalate/hydroxide precipitates were reduced to desired levels by washing with water. When washed with identical amounts of water, chloride concentrations were reduced by at least an order of magnitude more in precipitates containing both oxalate and hydroxide versus hydroxide precipitates only. During the hydroxide precipitation, it was possible to minimize calcium hydroxide precipitate formation by keeping the pH of the solution less than 10. When a significant amount of calcium hydroxide was precipitated with the plutonium hydroxide, chloride concentrations in the washed precipitate were over an order of magnitude greater.

Minimizing plutonium losses in processing and, in particular, minimizing the alpha activity of the filtrate and wash solutions to less than 4.5 mCi/L to meet waste line discard limits, was an important experimental goal. Table 1 summarizes the plutonium recovery and activity of the combined filtrate and washes solutions for all runs. Results indicate that increased plutonium oxalate precipitate formation resulted in increased plutonium losses in the filtrate and washes. This may be due to the small particle size of the oxalate precipitate passing through the 20 micron filter. For oxalate/hydroxide precipitations, all combined solution activities exceeded the desired level. For hydroxide only precipitations, filtrate/wash solution activities were below desired levels. For Run 1, a large amount of plutonium was not recovered in the solutions or the precipitate. The plutonium may have been lost in the filter paper, filter boat, spillage, etc.

Filtration rates were maximized when the amount of calcium precipitated as a hydroxide was minimized and when the amount of plutonium precipitated as an oxalate rather than a hydroxide was maximized.

The chloride washing flow sheet resulted in approximately a 50% reduction in aqueous waste generation as compared with processing by the standard flow sheet.

These studies support the feasibility of using the chloride washing processing flow sheet, Figure 2, as an alternative to the existing flow sheet to process chloride residues resulting from plutonium metal production operations.