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Development Program for ^{238}Pu Aqueous Recovery Process

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Abstract. Aqueous processing is necessary for the removal of impurities from ^{238}Pu dioxide ($^{238}\text{PuO}_2$) fuel due to unacceptable levels of ^{234}U and other non-actinide impurities in the scrap fuel. Impurities at levels above General Purpose Heat Source (GPHS) fuel specifications may impair the performance of the heat sources. Efforts at Los Alamos have focused on developing the bench scale methodology for the aqueous process steps which includes comminution, dissolution, ion exchange, precipitation, and calcination. Recently, work has been performed to qualify the bench scale methodology, to show that the developed process produces pure $^{238}\text{PuO}_2$ meeting GPHS fuel specifications. In addition, this work has enabled us to determine how waste volumes may be minimized during full-scale processing. Results of process qualification for the bench scale aqueous recovery operation and waste minimization efforts will be presented.

INTRODUCTION

For the last several years the Power Source Technologies group at Los Alamos has explored aqueous processing methods for purifying ^{238}Pu scrap material during the development of the ^{238}Pu Aqueous Recovery Line. The process methods are specific to the glovebox environment at the Technical Area 55 Plutonium Facility, and have been optimized for high process efficiencies, minimized waste generation rates, and product purity.

The choice of methods for performing these runs was based on many years experience processing material at Los Alamos and elsewhere. Well-understood and previously tested methods were selected as the most appropriate choices for our glovebox environment.

The process methods include milling and dissolving the incoming feed, ion exchange, oxalate precipitation, and calcination to the oxide.

Recently, six process runs were performed to demonstrate that the LANL aqueous process consistently produces flight quality fuel. One hundred grams of impure feed oxide was processed per process run. The material was processed with and without ion exchange to compare purity of product and liquid waste generated by each method. Ion exchange processing produces up to 3 times more liquid waste compared to processing by oxalate precipitation alone.

Compilations of feed and product impurity analyses, process efficiencies, and amounts of generated waste volumes are presented. The relevance of the results to the qualification of the bench-scale aqueous line and application of the methods to the full-scale aqueous line (7 kg $^{238}\text{PuO}_2$ yearly throughput; 500 grams feed per run) are also discussed.

DESCRIPTION OF WORK

Two methods were used to process the feed and they differed on whether or not ion exchange was performed, as shown in Figure 1. After the feed lot was milled, the powdered oxide had a mean particle size less than 5 μm (micron). For each run, approximately 100 grams of the powdered oxide was dissolved in refluxing concentrated nitric acid and ~ 0.10 mole/liter (M) hydrofluoric acid. After the solution was cooled and filtered, 25% of the dissolution filtrate underwent ion exchange processing (Method 1), the remaining 75% was not processed through ion exchange and underwent direct oxalate precipitation (Method 2).

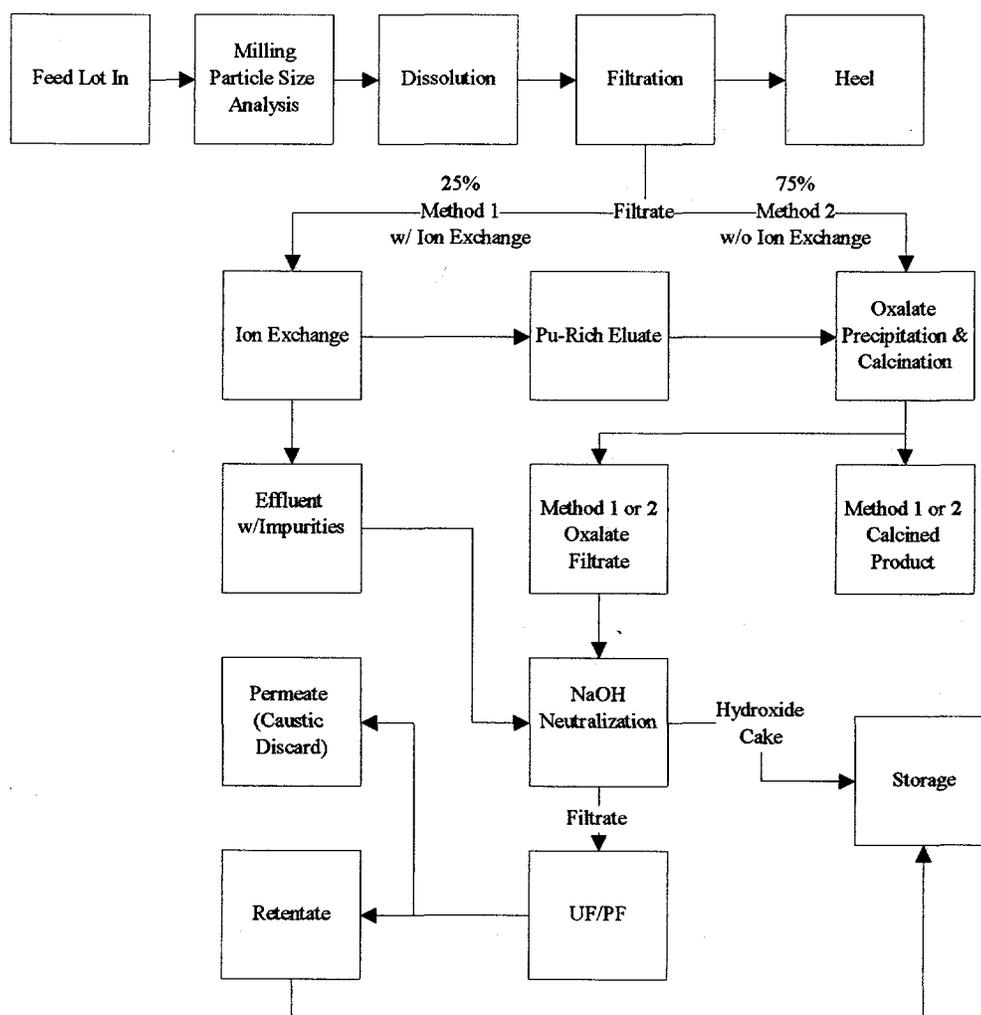


FIGURE 1. Flow diagram for ^{238}Pu Aqueous Scrap Recovery during six demonstration runs.

The purpose of using two methods was to determine if oxalate precipitation alone could produce flight quality fuel because ion exchange processing generates up to three times more liquid waste.

The Method 1 fraction underwent ion exchange as shown in Figure 1. Both the Pu-rich eluate from ion exchange and the Method 2 fraction underwent oxalate precipitation, filtration, and calcination steps, also listed in Figure 1. The ion exchange effluent and oxalate filtrates from both methods were neutralized with sodium hydroxide. The hydroxide filtrates were treated by ultra filtration / polymer filtration (UF/PF). The UF/PF permeate met discharge limits (4.5 mCi/L) and was sent through caustic waste discard to the Radioactive Liquid Waste Treatment Facility at Los Alamos. The Pu-rich retentate was stored, as were the hydroxide cakes, for potential future ²³⁸Pu recovery. Details of the methods shown in Figure 1 have been presented previously (Schulte, 1998 and Pansoy-Hjelvik, 1999).

Sampling points were designated at several steps in order to determine the individual process efficiencies and to ensure that the product lots met GPHS specification.

RESULTS AND DISCUSSION

Figure 2 shows the sum of all non-actinide impurities in the feed and products from both processing methods, as well as the GPHS specification. These results are significant because they show that both methods produce oxide

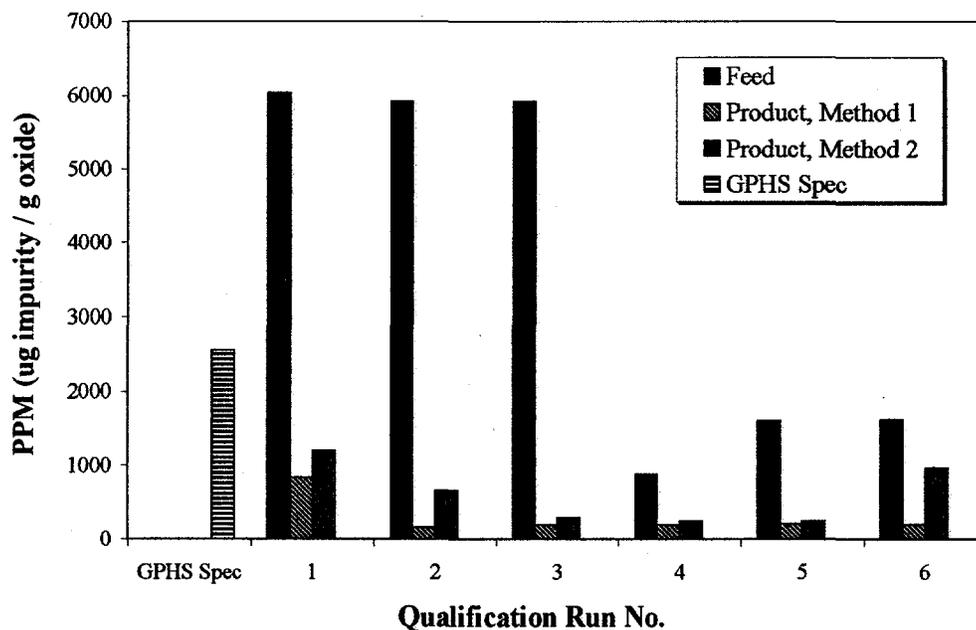


FIGURE 2. Sum of impurity levels in feed and product, in comparison to GPHS specification.

that meet GPHS specifications. Decontamination factors for the sum of all residual impurities differed by about 30% for the two methods. The decontamination factor is the quotient of the total impurity in the feed divided by the total impurity in the product. The sum of the impurities in the product produced through ion exchange are lower, which is expected because of the additional purification provided by ion exchange.

Impurity results for the actinides showed that feed oxide with thorium and americium above GPHS specification requires ion exchange purification. These results are discussed elsewhere in these proceedings (Pansoy-Hjelvik, 2001).

Process Step Efficiencies

Process step efficiencies are a measure of how well the process methodology has been designed, so that the maximum amount (preferably $\gg 90\%$) of ^{238}Pu coming into a results in the desired intermediate or final product form. For example, the ion exchange process efficiency is the fraction of ^{238}Pu recovered by the ion exchange method divided by the amount of plutonium sent to the ion exchange column.

The process efficiencies for dissolution of the feed oxide during the six runs is shown in Figure 3. These results show that the process efficiencies averaged 96.1%. The efficiencies were based on the amount of ^{238}Pu in the feed minus the amount in the heel, divided by ^{238}Pu in the feed. Part of the development work was determining the milling process and the optimal amount of hydrofluoric acid to use during the dissolution process to achieve high dissolution efficiencies (greater than 90%). Figure 3 shows that our process meets this goal.

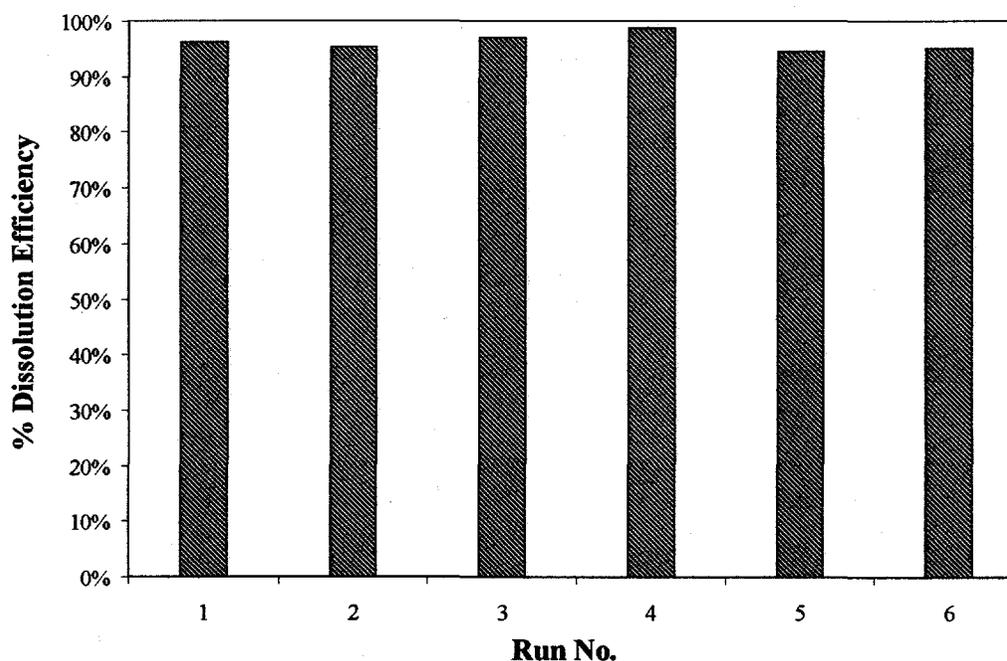


FIGURE 3. Dissolution process efficiencies per demonstration run.

The process efficiencies for the amounts of ^{238}Pu material processed through both methods is shown in Figure 4. These results show that the developed methods are satisfactorily efficient. The process efficiencies were based on the measured amount of ^{238}Pu processed by each method divided by the amount of ^{238}Pu in the product. Process efficiencies for Method 1 (with ion exchange) averaged 86.4%; for Method 2 (without ion exchange), the average was 96.1%.

Generated Waste Volumes

Another goal of the six demonstration runs was to determine the optimal route for aqueous purification that would result in minimal generated waste solution volumes, as well as producing pure product oxide. The impurity results

showed that flight quality oxide meeting GPHS specifications is indeed produced by processing with or without ion exchange. The significance of these results is mainly the determination that ion exchange is only necessary when processing feed oxide with thorium and americium impurity levels above GPHS specifications.

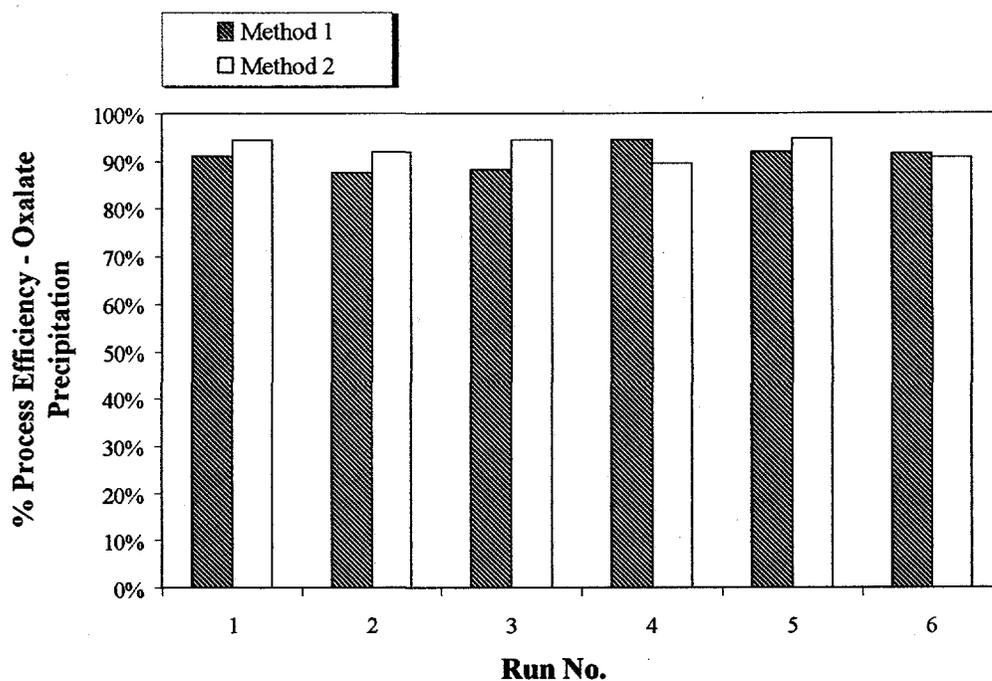


FIGURE 4. Overall Process Efficiencies During Six Demonstrations Runs.

TABLE 1. Actual and Calculated Volumes of Hydroxide Filtrates (Liquid Waste) Generated.

Averaged Total Volumes (L) Hydroxide Filtrate Generated						
100 g oxide feed (per 6 runs)				7 kg oxide feed (yearly throughput)		
Run No.s	Method 1 (Actual for 25% fraction)	Method 2 (Actual for 75% fraction)	Method 1 (Calculated presuming 100%)	100% Processed Through Ion Exchange (Calculated)	100% Processed Without Ion Exchange (Calculated)	Volume Difference Between Two Methods
1-3	5.8	5.4	23.0	1611.5	507.9	1103.6
4-6	8.7	5.0	34.5	2432.7	467.0	1965.8

The feed oxide that is expected to be processed during initial full-scale production efforts do not have high thorium and americium impurity levels. Thus, ion exchange processing is not expected to be used during the start-up of the full-scale production aqueous line.

Table 1 shows the average volume of waste solution (hydroxide filtrates) generated for the six runs, and the calculated volumes scaled to the amounts generated during full-scale processing of 7 kg feed oxide per year. The feed material in runs 1-3 was different from than feed in runs 4-6, and the volumes generated during these runs are averaged, as shown in Table 1. The calculated volumes of hydroxide filtrate generated during full-scale operations are based on the measured volumes during the demonstration runs.

The data show that during full-scale operations, processing through oxalate precipitation alone generates up to 500 L of waste volumes, in comparison to 2400 L generated through ion exchange plus oxalate precipitation processing, depending upon the feed type and for the same amount of material. These results indicate that the generation of up to 2000 L of waste solutions per year can be avoided by processing the feed types tested without ion exchange.

SUMMARY

Demonstration tests illustrate the feasibility of purifying ^{238}Pu oxide scrap. In 6 demonstration runs, feed material (scrap oxide) was processed by two methods which differed on whether or not ion exchange was used. The results showed that both methods produce flight quality oxide meeting GPHS specification. Milling, dissolution, and oxalate precipitation are essential steps, but ion exchange purification is optional and is to be used for feed containing americium or thorium above GPHS specification. Omission of ion exchange greatly reduces the amount of liquid waste that must be treated and disposed. The work demonstrates that the majority of feed material can be purified sufficiently to meet the GPHS specification without ion exchange.

ACKNOWLEDGMENTS

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