TRUEX Processing of Plutonium Analytical Solutions at Argonne National Laboratory

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ABSTRACT

The TRUEX (TRansUranic EXtraction) solvent extraction process was developed at Argonne National Laboratory (ANL) for the Department of Energy. A TRUEX demonstration completed at ANL involved the processing of analytical and experimental waste generated there and at the New Brunswick Laboratory. A 20-stage centrifugal contactor was used to recover plutonium, americium, and uranium from the waste. Approximately 84 g of plutonium, 18 g of uranium, and 0.2 g of americium were recovered from about 118 L of solution during four process runs. Alpha decontamination factors as high as 65,000 were attained, which was especially important because it allowed the disposal of the process raffinate as a low-level waste. The recovered plutonium and uranium were converted to oxide; the recovered americium solution was concentrated by evaporation to approximately 100 mL.

The flowsheet and operational procedures were modified to overcome process difficulties. These difficulties included the presence of complexants in the feed, solvent degradation, plutonium precipitation, and inadequate decontamination factors during startup. This paper will discuss details of the experimental effort.
INTRODUCTION

A three-year program was funded by the Office of Waste Operations and the Office of Technology Development, Environmental Restoration and Environment and Waste Management, to process approximately 118 liters of waste solution generated during the analysis of plutonium samples at the New Brunswick Laboratory (NBL) and Argonne National Laboratory (ANL). These residues, stored in over three hundred sample bottles, contained varying concentrations of nitric, sulfuric, phosphoric, and hydrochloric acids, as well as uranium, plutonium, neptunium, and americium. The TRUEX (TRansUranic EXtraction) process was used to convert the bulk of this waste into a nonTRU low-level waste. The goal was to reduce the TRU elements to a concentration less than 10 nCi/mL so that the waste could be disposed of as non-transuranic waste.*

The objectives of this program were fivefold. First, we wanted to demonstrate the applicability of the TRUEX process to handle a variety of real waste solutions. This program also was designed to give us experience in using the Generic TRUEX Model for designing flowsheets for specific feeds and process goals.

Second, we wanted to treat these waste solutions in order to solve a waste-treatment/storage problem here at ANL. These waste solutions were being stored in small polyethylene bottles (typically 250-mL). These bottles were wrapped in plastic, sealed inside a plastic pouch, and stored inside 5-gallon carbon-steel pails. As these wastes contained both high acid concentrations and high alpha-activity levels, the bottles were beginning to degrade and become brittle. Either recovering the TRU as useful products or converting them to a stable, solid waste form would alleviate ANL's waste storage problem.

Third, we wanted to produce a raffinate that was suitable for conventional low-level waste disposal. The initial goal of this process was to generate a nonTRU raffinate that was less than 10 nCi/mL. During the processing of batch 1, our Environment and Waste Management (EWM) organization required us to lower the TRU limit by a factor of 100, to 0.1 nCi/mL. At this level, the waste could be concentrated in the existing ANL low-level waste evaporators without any other treatment. Equipment and process limitations, however, prevented us from reaching

* The TRU limit for waste is 100 nCi/g; our 10 nCi/mL limit is well below this limit.
this goal. The raffinate generated by our processing ranged from 1 nCi/mL to approximately 10 nCi/mL.

Fourth, we wanted to recover plutonium, uranium, and americium from these waste solutions and return them to the DOE complex. It was initially planned to convert the recovered plutonium to a metal. Shortly after the start of the program, however, the political climate changed, eliminating the demand for plutonium. Therefore, most of the recovered plutonium and uranium was returned to EWM for disposal. The americium recovered was retained for use in on-going experiments at ANL.

Fifth, we wanted to pave the way for others contemplating the installation of a TRU EX facility. This demonstration showed the applicability of using the TRU EX process for treating similar wastes at Rocky Flats, Los Alamos, Hanford, and Idaho.

In this paper, we will discuss a variety of process- and operational-related challenges that were encountered in this program. These challenges included (1) space limitations, (2) batch operation, (3) variable batch composition, (4) high plutonium concentration, (5) need to limit product volumes, (6) foam generation, (7) solvent cleanup, (8) poor process results during startup, and (9) suspended solids. Methods employed to overcome these challenges are described, as are some of the processing results. For more detailed information on this program, see [1, 2, 3, 4, 5, 6, 7, 8, 9, 10].

**APPROACH**

TRU EX is a solvent-extraction process developed at ANL to remove and recover transuranic material from acid waste solutions. It uses a solution of 1.4M tributyl phosphate (TBP) and 0.2M n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) diluted by n-dodecane (nDD). This solvent is commonly called by the abbreviated name TRU EX-nDD. A simplified schematic of a TRU EX process is shown in Fig. 1. All of the typical sections of a TRU EX process were required to process these wastes, including extraction, scrub, americium and plutonium strips, and solvent cleanup. Details of the TRU EX process are described elsewhere [11, 12, 13].

The TRU EX process is ideally suited for processing these wastes solutions; nonTRU raffinates were generated, while the americium and plutonium were recovered separately for reuse. The TRU EX process was run in a 20-stage 4-cm centrifugal contactor installed in a plutonium glovebox. Because of space limitations in the glovebox and criticality-control requirements, the amount of material that
could be processed at one time was limited to 50 L of solution containing less than 50 grams of fissionable material (Pu plus $^{235}$U). Because the amount of waste to be processed exceeded both these limits, it was split up into six different batches. Wastes were batched together based upon (1) similar characteristics, such as acid and actinide content, (2) presence of complexants, (3) the need to keep batch size as close to 50 L as possible, and (4) the need to limit the HCl concentration so that acceptable corrosion rates in stainless steel equipment were maintained. Of the six batches available, four were processed in this program. The remaining waste will be treated using more traditional means without attempting to recover any of the TRU components [14]. In addition to these four batches, three additional runs were completed to process secondary wastes generated during processing and cleanout of the system.

The process steps required to process these waste solutions are shown in Fig. 2. A brief description of these steps follows. Based upon the waste forms, the waste was segregated into batches; then one batch contained in several 5-gallon storage pails was moved from EWM to our laboratory for transfer into the glovebox. Each 5-gallon pail, containing up to 26 waste bottles, was unpacked by removing each bottle of waste and bagging it into the glovebox. Once inside the glovebox, the waste was transferred into the 50-L feed (batch) tank. The empty bottles were rinsed with nitric acid, then bagged out of the glovebox. After mixing, sampling, and bagout of the sample vial, a sample aliquot was counted using high-resolution gamma spectroscopy to determine the americium content. An aliquot was also counted by liquid scintillation to estimate the plutonium content. Batch extractions were then completed. The Generic TRUEX Model (GTM) [15, 13, 16] was used to design the extraction, scrub, and americium strip sections. The plutonium strip could not be modeled because neither sodium oxalate nor ammonium oxalate were included in the GTM. Once the flowsheet was designed to meet process goals, a sensitivity analysis was completed to determine which variables in the flowsheet were most likely to affect the process.* For the initial waste solutions processed, a series of batch extractions, scrubs, and strips were completed to estimate the expected distribution coefficients (D values) in the various sections of the flowsheet and to verify the GTM predictions.**. Based upon the GTM sensitivity analysis and the batch-extraction data, a flowsheet was developed to satisfy the operational requirements for that particular batch. The equipment in the laboratory was then set up, pumps calibrated, and feed solutions prepared.

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* For more information on how a sensitivity analysis is completed, see [17].
** A distribution coefficient, or D value, is defined as the concentration of an element in the organic phase divided by its concentration in the aqueous phase.
The time needed to actually process the waste depended upon the feed flow rate and the amount of solution requiring processing. Processing 50 L of waste at a flow rate of 100 mL/min took 500 minutes (8.3 hours). Startup, shutdown, and system cleanout at the end of the run often added 3-4 more hours to the test. Thus, each batch was typically processed over the course of 2-3 days.

Five solutions were generated during operation: nonTRU raffinate, americium strip, plutonium strip, carbonate wash, and the acid rinse waste. The nonTRU raffinate was further treated to make it acceptable for handling by EWM. The solution was neutralized with NaOH so that the final pH was between 6 and 9. The americium product stream, which contained Am(NO₃)₃ plus HNO₃, was concentrated by evaporation and stored in a lead-lined safe for future use. The plutonium product stream, which also contained the uranium, was processed by evaporating it to dryness, then calcining the solids in an oven at ≥600°C to produce PuO₂. Most of the oxide was returned to EWM for storage and subsequent disposal; some of the material was stored for ongoing experiments. The sodium carbonate solutions were acidified by adding nitric acid, then recycled to the TRUEX process by mixing them with the feed for the next batch. The acid rinse solution was combined with the acidified carbonate. Recycling these solutions was completed to recover the TRU content of this waste.

A fifth waste solution was generated during the cleanup of the centrifugal contactors after each run. This flush solution was typically acidic (nitric acid), though carbonate solutions were also used. They were added with the acidified carbonate solutions to the next batch.

**PROCESS AND OPERATIONAL CHALLENGES**

**Space Limitations**

Because of limited space in the existing glovebox, we had to limit the number of stages in the flowsheet to 20. Installation of 20 centrifugal contactor stages and a 50-L feed tank left very limited additional room for other equipment and tanks. To collect the extraction section raffinate, a 110-L container was needed. Because a tank this large would not fit into the glovebox, a line was installed connecting the glovebox to an adjacent hood. As the raffinate was generated, it was pumped into 20-L carboys in this hood. This arrangement facilitated sampling of the raffinate, since the need to bag samples out of the glovebox was eliminated. We also placed all of the non-radioactive feed tanks and pumps outside of the glovebox to ease handling and help
Batch Operation

Splitting the waste into batches created a number of unique obstacles and challenges in this program. Batch operation required much more time to complete this program than a continuous process would have. Some of the factors that extended the program included (1) the need to develop and test four different flowsheets, one for each batch of waste, (2) the need to prepare for each run, including equipment setup, calibration, and solution preparation, and (3) the need to clean up after each run and process the resulting wash/product solutions. Blending of all of the waste solutions was considered, but the appropriate facilities to complete this type of operation were not available.

Batch operation also created a larger volume of waste. The centrifugal contactors were started up with a nonradioactive feed solution. Once the operation was stable, the radioactive feed was cut in. In spite of these actions, some of the initial extraction section raffinate had to be recycled. (This is discussed in more detail later.) Shutting down the system also generated waste. Once all of the feed was processed, the system was operated for another 10-20 minutes to help clean it out. After shutdown, the stages were drained; in some instances, decontamination flushes were completed to reduce the activity in the extraction and carbonate wash sections and solvent holding tank. All of these actions create additional waste.

Changing the extraction-section nonTRU raffinate criteria (by EWM) from $< 100 \text{ nCi/mL}$ to $< 0.1 \text{ nCi/mL}$ created a great deal of additional waste. All of the raffinate from batch 1 was reprocessed using a modified TRUEX process. Because of equipment contamination, operational problems, flowsheet limitations, and attempts to limit the volume of waste generated, the lower limit could not be achieved. After several unsuccessful attempts to reach $0.1 \text{ nCi/mL}$, the lower limit was abandoned.

Splitting the waste into batches had some positive consequences. Because we had to develop four different flowsheets, we gained some experience in using the GTM, and we learned which parts of the GTM were more accurate than others. Operating the centrifugal contactors with four different flowsheets enabled us to demonstrate the flexibility of both the equipment and the TRUEX process. Lessons learned from one batch was also used to improve the flowsheet for subsequent batches.
and americium D values by comparing oxalic acid with americium.

The oxalic acid was used in the test to verify that the americium (Np) increased the plutonium extraction yield in the test vessel. The CTR calculations and the back path 2, the high oxalic acid concentration in the feed (Np) as well as the americum and the americium strip section. For the back path 2, the high oxalic acid concentration in the feed (Np) and the americium strip section. For the back path 2, the high oxalic acid concentration in the feed (Np) and the americium strip section. For the back path 2, the high oxalic acid concentration in the feed (Np) and the americium strip section. For the back path 2, the high oxalic acid concentration in the feed (Np) and the americium strip section. For the back path 2, the high oxalic acid concentration in the feed (Np) and the americium strip section. For the back path 2, the high oxalic acid concentration in the feed (Np) and the americium strip section.

To consider the presence of oxalic acid in the test, a new sample was taken of the plutonium sample solution before addition to the feed solution. The plutonium and americium solutions were added to the sample canister solution. The plutonium and americium solutions were added to the sample canister solution. The plutonium and americium solutions were added to the sample canister solution. The plutonium and americium solutions were added to the sample canister solution.

Another possible explanation is that the test was successful in producing the plutonium and americium. The test was successful in producing the plutonium and americium. The test was successful in producing the plutonium and americium. The test was successful in producing the plutonium and americium. The test was successful in producing the plutonium and americium.

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Each batch of waste was processed using a slightly different formulation. For example, batch 2 consisted of H2PO4 which had not been present in any of the previous trials.

The compositions of the four batches processed are given in Table 1.
Another challenge in this area was our reliance on waste forms to calculate solution compositions. Because a complete analysis was not completed on each batch (too expensive), we relied on the waste forms to predict what was present in solution. This reliance on waste forms can lead to significant errors and misinterpretation of the data. For example, the uranium concentration actually present in batches 3 and 4 was 27% and 10.4% of the reported amount (Table 1). The presence of unknown species, even at low concentrations, can also significantly affect the operation of the flowsheet. The use of batch extractions on the feed to validate GTM predictions helped to alleviate the potential problem of unexpected feed compositions.
Although laboratory tests indicated that the plutonium oxides would not precipitate quickly and that a limited amount of precipitate could be handled by the treatment process, a significant amount of precipitate was expected. Therefore, it was decided that the centrifugal concentrator should be able to handle the amount of precipitate that was expected. The centrifugal concentrator consists of a rectangular drum and a four-stage centrifugal concentrator that uses the precipitation of the plutonium metal. We were able to achieve these results by using a specific series of steps. Each step involves precipitation of the plutonium and a specific series of centrifugal concentrator operations using a precipitate with a defined chemical composition. The use of IF was determined as a useful technique in this particular application. The precipitate with a defined chemical composition is used as a starting point for the process. Since the initial plan was to recover the plutonium for recycle, we were able to achieve this goal by using a specific series of steps. The precipitate was recovered in the first step, but it was not suitable for the high plutonium concentration in these tests. Therefore, we adjusted the solution used in the second step accordingly. This resulted in a precipitate that was suitable for further processing.

High Plutonium Concentration

Concentration was lowered to levels that were seen in the other test batches. The Plutonium was reduced to 24% of its original concentration. The second test, however, concentrated 24% HCL in solution. The concentration was lowered to levels that were seen in the other test batches. Although these concentrations were lower than usual, we accepted them because of the high plutonium of the high concentration of this procedure. Higher than usual, however, we accepted them because of the high concentration of the high concentration of the high concentration.

Hydrochloric acid is also present in these solutions because it is used in the plutonium in the plutonium strip section to remove the plutonium from the plutonium. The solution is then removed from the plutonium. Therefore, we were no longer required to separate the plutonium from the solution.
The revised plutonium strip section using ammonium oxalate instead of oxalate
organic phase with the plutonium.

The distribution ratio for N(NH4)2CO24 was estimated to be less than 0.038 [6].

Leak was recovered.

To eliminate this precipitation, the plutonium strip section was modified in

TRU-EX-NpH consists of 0.2M CMPo and 1.4M TBP in a normal paraffinic

Section will be shown later in a figure describing the batch 2 howse.

eliminated the precipitation from the remaining runs. The revised plutonium

solution 1/3 that in the initial howse. The implication of ammonium oxalate also

and is much smaller only one leaf is reacted, and the solution volume generated is

The revised plutonium strip section using ammonium oxalate instead of oxalate

solution is maintained a high D value for uranium so that it is not stripped from the

since to strip any residual plutonium from the reactor, when added to this

is the first stage. A second oxalic acid leaf was added in the next

stripping to occur in this first stage. A second oxalic acid leaf was added in the next

striping because of the potential precipitation formation, we react most of the

first stage. A low-fourth-concentration oxalate acid leaf was pumped into the first

striping because oxalic acid extracts into the organic solvent. If all of the oxalic

striping is done at this concentration, the problem is solved. (1) Ammonium oxalate is an

processes. Later experiments, the batch strip losses showed (1) Ammonium oxalate is an

n-2 stage of plutonium, the TRU-EX-NpH leachate did not precipitate from

TRU-EX-NpH. The D value for plutonium was 2.0. As an added feature, ammonium

and plutonium. The new TRU-EX-NpH system is to be combined with the solution

ammonium oxalate does not precipitate from

(e.g. 3). A low-five-concentration oxalate acid leaf was incorporated into the

ammonium oxalate was also used in an attempt to recover the

bulk of plutonium in the

ammonium oxalate was much more stable than acrylic acid at

ammonium oxalate was also used in an attempt to recover the

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Combined Scrub/Americium-Strip Section

Nitric acid concentrations in the feed for all four batches were quite high, ranging from 1.7 to 4.5M HNO₃. Since the TRUEX solvent also extracts nitric acid, a robust scrub section was needed to reduce the acid content in the organic so that acceptable americium strip operation was achieved. However, space limitations in the glovebox limited the number of stages that could be allocated to scrubbing.

We developed an innovative scrub/americium-strip section that reduced the number of stages required and significantly reduced the volume of americium product solution generated. The americium strip section was designed to concentrate americium by a factor of ~17. A schematic of the americium strip section for batch 2 is shown in Fig. 4. This section consisted of seven stages, with the americium removed at stage 11. Only a small fraction of the aqueous flow (but most of the americium) is removed from this stage; most of the flow passed on through stages 8-10 and into the scrub and extraction sections. Stages 8-10 act both as a strip section for nitric acid and aluminum and as a scrub section for americium, as it is being concentrated by the pinching action of the extraction section and the americium strip section.

Foam Generation

In the initial tests, foam was observed in both the aqueous and organic interstage lines, with the foaming most prevalent in the extraction section. This foam seemed to start in stage 1 and move slowly up through the system. In some cases, only minor foaming was observed; however, this foam leads to increased other-phase carryover and poor processing results. In an extreme case, the foam caused a contactor stage in the extraction section to overflow. To solve this problem, an acid rinse was added to the flowsheet to acidify the solvent before it was introduced into the extraction section. This stage had been eliminated from the initial test setup because we needed as many stages as possible for the flowsheet, and we thought that the acid concentration in the feed (2-5M HNO₃) would be high enough to adequately acidify the solvent. This assumption proved incorrect, however. To implement an acid wash and not take a valuable stage from the process, nitric acid was added to the bottom of the solvent storage tank. The organic solvent returning from the last carbonate wash stage was pumped to the bottom of the tank; being the less dense phase, it bubbled up
been severely degraded. The viscosity and density of the solution had changed, and
waste processing ran (a period of about 4 months), we found that the solution had
following the processing of batch 1 and batch 1 remained, and the start of a
solution.

We hypothesized that this form was the KOH reaction with the acidic feed
system. It was observed that the KOH was added to the organic phase. In this way, the KOH was added to the
the first wash stage which was changed to 0.5M KOH + 0.5M K2CO3 to help reduce the
after form was generated in the extraction section. The composition of
- 6M KOH. After form was generated in the extraction section, the composition of
initially, both carbonate wash solutions were the same composition, 0.8M K2CO3.

Initially, both carbonate wash solutions were the same composition.

Two wash stages.

After form was generated in the extraction section and was not removed by the
acid extractant into the organic, the extractant in the extraction section which was not removed by the
important, their composition was modified by adding KOH to react with the minor
those carbonate wash stages were used to replace K2CO3 and Na2CO3 because those carbonate wash stages were so
replaced with K2CO3 because K2CO3 and Na2CO3 have increased solubility over
including the normal cleaning of the organic phase. The Na2CO3 normally used was
this was shown in Fig. 5. It emphasizes the carbonate wash stages because the carbonate wash
During the reprocessing of the batch 1 remaining, a modified flowchart was used
19 (the first carbonate wash stage).

19 (the second carbonate wash stage) was then replaced with the new feed to stage
where 20 (the second carbonate wash stage) was then replaced with the new feed to stage
day. To limit the volume of waste produced, the sodium carbonate being recycled at
day, the carbonate (and acid) waste was recycled at the beginning of each
leaving carbonate solutions were replaced with fresh feed. For runs that lasted more than one
organic solution extract into the second carbonate wash stage. Increasing the
was prepared, about 1.5, and the solution was recycled. When the alpha activity in the
because of the limited volume of solution available and the length of each run.

Solvency Cleanup

Incorporation and stabilization of foam problems for the remainder of the runs.
In the following increased rapidly shortly after starting and often peaked at a
high in the latter phase. However, the alpha activity above the lower activity of any produced during the test. However, the alpha activity
throughout the initial solution exchange the system as the neutral final stage would
During the initial stage of the continuous exchange for each batch run we

**Poor Results During Startup**

21 days/ft².

This column ranged from 0.4 to 0.7 days/ft², while the feed to the column ranged from 2.3 to
6.4 times lower than the feed to the column. The alpha activity in the cleaned solution
During 3, the alpha activity in the original solution at the column after the column
pumped to the solution storage tank until the column has been filled. Then the solution is
purified by passing the solution column. For operation, the column is directed toward
washed alumina. The system is installed in the delayed feedbox for each batch is shown in Fig. 6.

Amberlite A-26 anion-exchange resin, a column was designed with activated neutral
ambersite A-26 anion-exchange resin (i.e. Amberlite A-26), acid-washed activated charcoal, or acid-

Washed alumina

\[ \text{Amberlite A-26 anion-exchange resin (i.e. Amberlite A-26}, \text{ acid-washed activated charcoal, or acid-} \]

\[ \text{Amberlite A-26 anion-exchange resin or neutral alumina as activated neutral.} \]

\[ \text{Amberlite A-26 anion-exchange resin or neutral alumina as activated neutral.} \]

\[ \text{Amberlite A-26 anion-exchange resin or neutral alumina as activated neutral.} \]

\[ \text{Amberlite A-26 anion-exchange resin or neutral alumina as activated neutral.} \]

\[ \text{Amberlite A-26 anion-exchange resin or neutral alumina as activated neutral.} \]

Two papers on the use of solid sorbents were reviewed (20, 21). In these two

During the processing runs:

1) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

2) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

3) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

4) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

5) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

6) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

7) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

8) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

9) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

10) clean up the degraded solution and (2) be instilled in the delayed feedbox for use

Supplementary performance was substantially degraded. This degradation was much higher
ured to avoid getting a number of process steps. These filters would
one microfilter were inserted on a number of process steps. These filters would
In another attempt to lower the alpha activity of the extraction section runtime,

Suspended solids

length of each run and the total volume of solution generated.

Further work is needed to understand the dynamics that occur during sampling of

45 minutes into the run, the system was restored without using a nonradioactive
alpha activity spike in the effluent. After the delivery and reposition of a feed amp
alpha activity spike in the effluent. After the delivery and reposition of a feed amp


To eliminate this problem, the sampling procedure for the extraction section was
also read in an initial spike in the activity.

in concert with the expected solution may be lower than the weak feed, which may
the dilution and cause the spike in activity. Second, D values for TET components
the dilution or nonradioactive section. This flow may bring contamination down to
the dilution or nonradioactive section. This flow may bring contamination down to


The general procedure used to start up centrifugal contactors is to fill each

collection tank and transfer balance and hydrated orange compound to nonradioactive
section while the tank is pressurized by a pump and a number of process steps. These filters would
was consisted of brine, naph, and the organic phase collected.

The aqueous phase in the second extraction section was processed in a similar fashion. The aqueous phase collected in the second extraction section was processed in a similar fashion.
Approximately 700-1000 L of liquid low-level waste was generated. If this TRUEx flowsheet were implemented on a larger scale, the final volume of liquid low-level waste would be three times that of the feed solution volume. For example, using the 118 L of waste delivered, plus the 23 L of nitric acid used to dilute batch 1, a volume increase to 426 L would have been expected. This assumes that all of the feed solutions were batched together and processed in one run. The larger waste volume generated can be explained by (1) seven runs were completed instead of one, (2) equipment decontaminations were completed between runs, and (3) no aqueous TRU wastes were produced in this program. A precipitation process like that discussed by Slater [14] would increase the volume of waste generated by a factor of two times the initial feed volume; however, even though the final waste volume would be less, none of the actinides would have been recovered from this process. Recovery of Pu, U and Am was one of the original goals of the project.

In addition to the low-level waste generated, approximately 84 g of plutonium was recovered as plutonium oxide along with 18 grams of uranium. About 350 mCi of $^{241}$Am was recovered in the americium strip solution.

Results from the four batch processing runs are listed in Table 2. The alpha activity in the raffinate solutions ranged from 1.3 nCi/mL in batch 3 to 10 nCi/mL in batch 4. Decontamination factors for alpha ranged from 4,000 in batch 4 to 65,500 in batch 3. Decontamination factors relate somewhat to the initial activity in the feed solution feed solutions; the higher the initial activity, the higher the decontamination factor that was achieved.

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*This volume includes the sodium hydroxide that was added to the raffinate after TRUEx processing to adjust the pH to 6-9.*
Table 2: Data from TRUEX Processing of NBL Waste Solutions

<table>
<thead>
<tr>
<th>Batch Number</th>
<th>Feed Pu (g)</th>
<th>Feed U (g)</th>
<th>Alpha Activity (nCi/mL)</th>
<th>Pu Product Pu (g)</th>
<th>Pu Product U (g)</th>
<th>Alpha Activity (nCi/mL)</th>
<th>Aqueous Raffinate</th>
<th>Alpha Decontamination Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>0</td>
<td>40,000</td>
<td>8</td>
<td>0</td>
<td>1.8</td>
<td>22,400</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>13&lt;sup&gt;c&lt;/sup&gt;</td>
<td>16</td>
<td>21,400</td>
<td>13</td>
<td>10&lt;sup&gt;d&lt;/sup&gt;</td>
<td>4.4</td>
<td>4,900</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>28&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7</td>
<td>88,000</td>
<td>30</td>
<td>5</td>
<td>1.3</td>
<td>65,500</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>34&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3</td>
<td>40,000</td>
<td>33</td>
<td>3</td>
<td>10</td>
<td>4,000</td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td>87</td>
<td>26</td>
<td>84</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Based on ICP analysis unless otherwise noted.
<sup>b</sup>Based on scintillation counting results.
<sup>c</sup>Based on waste requisition form.
<sup>d</sup>Based on mass spectroscopy analysis.

Conclusions

The major goals of this program were accomplished. The TRU waste was converted to low-level waste and returned to EWM for subsequent disposal. Both plutonium and americium were recovered in separate streams and subsequently processed to make them more amenable for storage. We demonstrated the strength of the TRUEX process by processing actual waste solutions that contained 100-1000 times more plutonium than originally expected of it. We also demonstrated the usefulness of the Generic TRUEX Model in developing flowsheets and in completing a sensitivity analysis on these flowsheet. This analysis helped indicate the flowsheet variables that were most important to achieving our objectives. Lastly, we showed that the GTM predictions for americium were relatively good, especially in the scrub/americium-stripping section. Modeling of the various actinides in the extraction-section raffinate were not as effective; we never could achieve the low levels that were predicted by the model, probably because of (1) contamination of equipment in the glovebox and (2) colloidal plutonium present in the feeds.

During this program, we made several important additions to TRUEX processing experience. (1) Ammonium oxalate was incorporated into the flowsheet as a very good plutonium-stripping agent. (2) Aluminum nitrate was added to the scrub feed to strip oxalic acid from the solvent, reducing the effect of the phosphate-plutonium
Several needs were identified in this program. Solvent degradation due to alpha activity needs to be further evaluated. More accurate complexation constants for typical complexants are needed, and the \((\text{NH}_4)_2\text{C}_2\text{O}_4\) stripping data should be incorporated into the GTM.

REFERENCES


FIGURE 1. A simplified schematic of a TRUEX solvent-extraction flowsheet.

FIGURE 2. General waste treatment flowsheet.

FIGURE 3. Schematic of the plutonium strip section, batch 1. Plutonium recovery values are based upon calculated predictions.

FIGURE 4. Schematic of the americium strip section, batch 2.

FIGURE 5. Flowsheet for processing the raffinate solution from batch 1.

FIGURE 6. Solvent purification system installed for batch 2.

FIGURE 7. Alpha activity in the extraction section raffinate during processing of batch 3.

FIGURE 8. TRUEX flowsheet for processing batch 2 waste.
Waste
118 L
87 g Pu
26 g U

Batch Segregation
(Waste Forms)

Batch Receipt

Waste Transfer into Glove Box, Feed Tank

Batch Analysis, Extractions

Flowsheet Development

Equipment Setup, Calibration

Acidification

Solvent Wash Waste

nonTRU Raffinate

Pu Product

Analysis

Concentrate by Evaporation

Evaporation

Calcination

Product
84 g Pu
384 g U

Am Product

Analysis

In-house Experiments

Transfer to Waste Management

Transfer to 20L Carboys, Neutralization

Waste
700 - 1000 L
~4 nCi/g α

In-house Experiments

Storage, Disposal

Transfer to Waste Management
Pu Strip #1

\[ \text{H}_2\text{C}_2\text{O}_4 \ 0.335 \text{ M} \]

(5 mL/min)

Pu Strip #2

\[ \text{H}_2\text{C}_2\text{O}_4 \ 0.05 \text{ M} \]

\[ \text{HNO}_3 \ 0.1 \text{ M} \]

(30 mL/min)

Solvent From Am Strip Section

Pu Product

- Am 0.04%
- Pu 99.96%

(35 mL/min)

Solvent to Carbonate Wash

15 16 17 18
Process for the Treatment of Batch #1
Extraction Raffinate Waste

- **DF Feed** (100 mL/min)
- **Scrub**
  - HNO₃ 0.05 M (50 mL/min)
- **Carbonate Carbonate**
  - K₂CO₃ 0.80 M
  - KOH 6.0 M (50 mL/min)
- **K₂CO₃ 0.80 M**
- **KOH 6.0 M**
- **KOH 0.5 M** (50 mL/min)
- **Recycle**

**Flow Chart**

- DF Feed
- Scrub
- Carbonate Carbonate
- HF
- IF
- HW
- IW
- Recycle

**Solvent**
- CMPO 0.20 M
- TBP 1.40 M
- Dodecane diluent (50 mL/min)
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