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Argonne National Laboratory**

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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.

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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 TRUEX facility. This demonstration showed the applicability of using the TRUEX 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

TRUEX 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 TRUEX-nDD. A simplified schematic of a TRUEX process is shown in Fig. 1. All of the typical sections of a TRUEX process were required to process these wastes, including extraction, scrub, americium and plutonium strips, and solvent cleanup. Details of the TRUEX process are described elsewhere [11, 12, 13].

The TRUEX process is ideally suited for processing these wastes solutions; nonTRU raffinates were generated, while the americium and plutonium were recovered separately for reuse. The TRUEX 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 fissile 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.

* 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 $\text{Am}(\text{NO}_3)_3$ plus HNO_3 , 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 $\geq 600^\circ\text{C}$ to produce PuO_2 . 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

save room in the glovebox. This arrangement will be shown later in a figure describing the batch 2 flowsheet.

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 nCi/mL to < 0.1 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 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.

Variable Batch Composition

The compositions of the four batches processed are given in Table 1. As described above, the differing batch compositions necessitated adjustments to the TRUDEX flowsheet for each batch. Flowsheet changes were especially significant for this program because the limited number of stages available decreased the flexibility of a particular flowsheet to handle various feeds. For a TRUDEX process installed in a reprocessing plant, these feed variations would be taken into account during flowsheet development, and additional stages would be designed into the system.

Each batch of waste was processed using a slightly different flowsheet. For example, batch 2 contained $1.12\overline{M}$ H_3PO_4 , which had not been present in any of the previous pilot-scale tests. Based upon initial modeling runs using the GTM, we found that the presence of phosphoric acid played a significant role in the extraction section because the phosphate complexes with both plutonium and americium. Therefore, we improved the model for phosphoric acid to better predict process behavior. Based upon results using the improved GTM, we found that aluminum nitrate added to the extraction feed complexed the phosphate and improved the extraction of both plutonium and americium. Another possible alternative, adding more extraction stages, could not be accomplished because of the limited space available. The downside to adding aluminum nitrate was increased waste volume.

Oxalic acid ($0.01\overline{M}$), which was present in most of the feed solutions, was added to the spent carbonate solvent wash solutions before acidification to recycle them to the feed of the next run. This addition was done to attempt to complex the plutonium and prevent polymer formation. The technique appeared to work, though only qualitative information is available.

To counteract the presence of oxalic acid in the feed, a new scrub feed was incorporated into the flowsheet. This feed, $2\overline{M}$ $Al(NO_3)_3$, increased the distribution ratio of plutonium in the extraction section (due to the presence of H_3PO_4 and $H_2C_2O_2$) and stripped oxalic acid from the solvent before it entered the americium strip section. If the oxalic acid were not scrubbed from the solvent, too much plutonium would be stripped from the solvent in the americium strip section. For batch 2, the high oxalic acid concentration in the feed ($0.1\overline{M}$) severely complexed the plutonium, which prevented its extraction. The GTM calculations and the batch extraction tests on the feed verified that adding $Al(NO_3)_3$ increased the plutonium and americium D values by complexing oxalate.

TABLE 1. COMPOSITION OF BATCHED WASTE PROCESSED USING THE TRUOX PROCESS

	Batch				Total
	1	2	3	4	
Volume of original waste, L ^a	1 ^b	34.3	41.8	41.0	118.1
No. bottles of original waste ^c	1	55	135	145	336
Elemental analysis, g					
Total Pu	12	13.28	33.93	28.50	87.71
Pu-239	11.3	11.99	31.13	26.14	80.56
Pu-240	0.7	1.19	2.50	2.28	6.67
Pu-241	0	0.10	0.30	0.07	0.47
Am-241	--d--	--d--	--d--	1.17E-06	
Total U	0	16.27	25.73 ^e	28.79 ^f	70.79
U-233	0	0.00	0.48	0.00	0.48
U-235	0	10.03	0.19	0.80	11.02
U-238	0	6.24	25.06	27.99	59.29
Np-237	0	0	1.57	0	1.57
Acids, M					
HNO ₃	4	2.39	1.69	4.51	--
HCl	4	0.04	0.003	0	--
H ₂ SO ₄	0	0	0.11	0	--
H ₃ PO ₄	0	1.29	1.13	0.61	--

^aThese volumes are of the original waste solutions and do not include recycled solutions such as acidified carbonate or cleaning solutions.

^bThis waste was diluted to 24 L before processing to reduce corrosion rates to acceptable levels.

^cThis row has the number of bottles received that contained waste.

^dNone reported.

^eBased upon ICP analysis of the batched waste, only 7 grams of uranium actually present.

^fBased upon ICP analysis of the batched waste, only 3 grams of uranium actually present.

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 oxalate would not precipitate quickly and that a limited amount of precipitate could be handled by the strip solution.

Therefore, for batch 1, oxalic acid was used as the plutonium precipitation expected. Indicated that the centrifugal contactors should be able to handle the amount of plutonium and a four-stage centrifugal contactor tests using a rare-earth simulant plutonium metal. We were left with oxalate-base stripping agents. Batch tests with stripping agent because we could not complete the fluoride processes need to produce implement with little difficulty and expense. The use of HF was eliminated as a wanted the plutonium strip solution to be compatible with processes that we could limited solubility. Since the initial plan was to recover the plutonium for recycle, we stripping agent for the high plutonium concentrations in these feeds; $Pu(C_2O_4)_2$ has stripping agent for plutonium is oxalic acid. However, oxalic acid was not a suitable concentration created solubility problems in the plutonium strip section. A typical plutonium-recovery process instead of in its usual role as a polishing step. This high typically seen in waste streams. For this program, TRU-EX was used as a front-end The plutonium content in this waste was 10 to 100 times greater than what is

High Plutonium Concentration

concentration was lowered to levels that were seen in the other three batches. diluted to 24 liters. Corrosion was reduced to an acceptable rate, and the Pu concentration was too high to be processed in the stainless steel contactor so it was additional solid waste. The first batch, however, contained 4M HCl in solution. This Removal of the chloride from these solutions would be difficult and would generate higher than usual, we accepted them because of the limited duration of this program. 0.1M HCl - 2M HNO₃ - 0.1M Al(NO₃)₃. Although these corrosion rates were coupon placed in 0.1M HCl - 2M HNO₃ and 1.09% for the coupon in composition. In a 2.7-day corrosion test, coupon weight losses were 0.845% for the for the centrifugal contactor, a corrosion test was performed at a typical HCl dissolution of the plutonium samples at NBL. To see if corrosion rates were too high Hydrochloric acid is also present in these solutions because it is used in the

plutonium in the plutonium strip section. the flowsheet for batch 2 was modified, and the uranium was stripped with the we were no longer required to separate the plutonium from the uranium. Therefore, of waste solution (batch 1). After this flowsheet was developed, our criteria changed-- separated uranium from plutonium. This flowsheet was used to process the first batch batches 2, 3, and 4). Work in FY-90 focused on the development of a flowsheet that Uranium is a major constituent in several of the waste solutions processed

centrifugal contactors, a precipitate did form quickly in batch 1 and affected operation of the system. In this run, about one-third of the plutonium collected inside the plutonium-strip centrifugal contactor stages. Recovery from this precipitate was difficult. It required dismantling the four-stage plutonium strip section contactor and physically scraping the solids from the inside of the rotors. A diagram of the plutonium strip section for batch 1 is given in Fig. 3. Most of the precipitate was located in the first stage of the strip section. Chemical dissolution using 5M nitric acid and 0.28M ammonium oxalate was also used in an attempt to recover the plutonium. Ammonium oxalate was much more effective than nitric acid at recovering the precipitate. In the end, only 8 g of the initial 12 g of plutonium in the feed was recovered.

To eliminate this precipitate, the plutonium strip section was modified in processing later batches. The batch strip tests showed (1) ammonium oxalate is an effective stripping agent, and (2) plutonium oxalate does not precipitate from solution. Plutonium solubility is due to the formation of the soluble anion species $\text{Pu}(\text{C}_2\text{O}_4)_3^-$ and $\text{Pu}(\text{C}_2\text{O}_4)_4^{4-}$. For a single contact of 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ with TRU-EX-NPH, the D value for plutonium was 2E-6. As an added benefit, ammonium oxalate is not extracted by the TRU-EX-NPH solvent,* and by inference, the TRU-EX-NPH solvent, which greatly simplified the design of the strip section. The distribution ratio for 0.1M $\text{H}_2\text{C}_2\text{O}_4$, calculated using the GTM (Version 3.1), was 1.5; the distribution ratio for $(\text{NH}_4)_2\text{C}_2\text{O}_4$ was estimated to be less than 0.038 [6].

In the flowsheet for batch 1, two plutonium strip feeds were incorporated (Fig. 3). A low-flow, high-concentration oxalic acid feed was pumped into the first strip stage because oxalic acid extracts into the organic solvent. If all of the oxalic acid were added in the fourth strip stage, none would be left to strip plutonium in the first stage. Because of the potential precipitate formation, we wanted most of the stripping to occur in this first stage. A second oxalic acid feed was added in the last stage to strip any residual plutonium from the solvent. Nitric acid was added to this solution to maintain a high D value for uranium so that it is not stripped from the organic phase with the plutonium.

The revised plutonium strip section, using ammonium oxalate instead of oxalic acid, is much simpler; only one feed is required, and the solution volume generated is about 1/3 that in the initial flowsheet. The implementation of ammonium oxalate also eliminated the precipitate from the remaining runs. The revised plutonium strip section will be shown later in a figure describing the batch 2 flowsheet.

* TRU-EX-NPH consists of 0.2M CMPO and 1.4M TBP in a normal paraffinic hydrocarbon (NPH) diluent.

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 HNO_3 . Since the TRUEN 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 HNO_3) 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

through the acid and collected on top of the nitric acid. This contact proved to be adequate and eliminated the foam problem for the remainder of the runs.

Solvent Cleanup

Because of the limited volume of solvent available and the length of each run, the solvent had to be recycled during each run. To achieve very low activity levels in the extraction section raffinate, a very good solvent cleanup system was needed. Two independent sodium carbonate wash stages were used to clean the solvent before recycle. To reduce the volume of waste generated, only a small volume of solution was prepared, about 1 L, and the solution was recycled. When the alpha activity in the organic solvent exiting the second carbonate wash stage started increasing, the carbonate solutions were replaced with fresh feed. For runs that lasted more than one day, the carbonate (and acid rinse) solutions were replaced at the beginning of each day. To limit the volume of waste produced, the sodium carbonate being recycled at stage 20 (the second carbonate wash stage) was often reused as the new feed to stage 19 (the first carbonate wash stage).

During the reprocessing of the batch 1 raffinate, a modified flowsheet was used that eliminated the two strip sections (to reduce waste generation). This flowsheet is shown in Fig. 5. It emphasized the carbonate wash stages because the carbonate wash had to accomplish all of the work that the two strip sections normally accomplish, including the normal cleaning of the organic phase. The Na_2CO_3 normally used was replaced with K_2CO_3 because K_2CO_3 and KHCO_3 have increased solubilities over those of Na_2CO_3 and NaHCO_3 . Because these carbonate wash stages were so important, their composition was modified by adding KOH to react with the nitric acid extracted into the organic in the extraction section that was not removed by the two scrub stages.

Initially, both carbonate wash solutions were the same composition, $0.8\text{M } \text{K}_2\text{CO}_3 - 6\text{M } \text{KOH}$. After foam was generated in the extraction section, the composition of the last wash stage was changed to $0.5\text{M } \text{KOH} - 0.5\text{M } \text{K}_2\text{CO}_3$ to help reduce the amount of KOH dispersed in the organic phase. An acid rinse was also added to the system. We hypothesized that this foam was the KOH reacting with the acidic feed solution.

Following the processing of batch 1 and the batch 1 raffinate and the start of a waste processing run (a period of about 4 months), we found that the solvent had been severely degraded. The viscosity and density of the solvent had changed, and

stripping performance was significantly degraded. This degradation was much higher than expected [18]; additional experiments by Buchholz [9] following this project did not identify any reasons for the amount of degradation seen. To clean the solvent, we investigated alternative wash systems. We wanted a system that could (1) clean up the degraded solvent and (2) be installed in the glovebox for use during the processing runs.

Two papers on the use of solid sorbents were reviewed [20, 21]. In these two studies, a variety of solid sorbents were tested to determine their effectiveness in removing acid degradation products from TRU-EX solvents. Both papers concluded that the use of sodium carbonate as the primary cleanup method is not adequate for returning the solvent to pristine condition; additional solvent cleanup steps are necessary following the sodium carbonate wash. Tse [20] recommended the use of Amberlyst A-26 anion exchange resin or neutral alumina to remove acid degradation products from the solvent. Chiantzia [21] recommended the use of a strong-base anion-exchange resin (like Amberlyst A-26), acid-washed activated charcoal, or acid-washed alumina.

Based upon tests using acid-washed alumina, activated-neutral alumina, and Amberlyst A-26 anion-exchange resin, a column was designed using activated neutral alumina. The system installed in the glovebox for batch 2 is shown in Fig. 6.

Two sodium carbonate wash stages were employed. The solvent exits stage 20 (last carbonate wash) and drops into a small collection container. The solvent is then pumped through a one-micron filter to remove any suspended solids and then passes either through a 1-in.-dia ion-exchange column containing the alumina or directly to the solvent storage vessel. All of the solvent could not be processed through the column because the flow rate was limited to about 15 mL/min; about 35 mL/min on average bypassed the alumina column. For operation, the solvent is directed towards the alumina until the flask located on top of the column is filled. Then the solvent is pumped to the solvent storage tank until the column flask needs to be refilled. During batch 3, the alpha activity in the organic solvent exiting the column averaged 6.4 times lower than the feed to the column; the alpha activity in the cleaned solvent ranged from 0.4 to 2.7 dpm/ μ L, while the feed to the column ranged from 2.3 to 21 dpm/ μ L.

Poor Results During Startup

During the initial startup of the centrifugal contactors for each batch run, we thought that the initial solution exiting the system as the nonTRU raffinate would have the lowest activity of any produced during the test. However, the alpha activity in the raffinate increased rapidly shortly after startup and often peaked at a

concentration that was 20-100 times higher than the steady-state concentration. After peaking, the activity dropped quickly and then tailed exponentially into the "steady-state" value as the run progressed. This spike contaminated the extraction section, collection tank, and transfer tubing, and hindered our ability to generate very low alpha-containing raffinate solutions.

The general procedure used to start up a centrifugal contactor bank is to fill each stage with the heavy phase, aqueous in our case, followed by the addition of the less-dense or organic phase. Usually, each section is filled with the nonradioactive feed solution that will be used in that section during the rest. In some instances, the extraction section is filled with the scrub feed, allowing it to flow from the scrub feed stage down through the extraction section and out the raffinate line. This may have contributed to the activity spike in two different ways. First, the scrub solution flows down from stage 6, the highly contaminated end of the extraction section, to stage 1, the dilute or noncontaminated section. This flow may bring contamination down to the dilute end and cause the spike in activity. Second, D values for TRU components in contact with the scrub solution may be lower than with the waste feed, which may also lead to an initial spike in the activity.

To eliminate this problem, the startup procedure for the extraction section was modified in several ways. First, a nonradioactive feed solution was prepared (typically $2M \overline{HNO}_3$) and fed to the extraction section. This section was also filled backwards, starting from stage one, to help prevent contamination of the initial three stages. Both of these changes helped reduce the spike seen in the initial stages of the run, though the spike was not completely eliminated. Data from batch 3 is shown in Fig. 7. In this figure, the alpha activity in the extraction section raffinate is plotted versus run time. This new procedure was used at system start up, and you can see the initial alpha activity spike in the raffinate. After the failure and replacement of a feed pump 445 minutes into the run, the system was restarted without using a nonradioactive feed; you can see the very large spike in alpha activity that occurred at this time.

Further work is needed to understand the dynamics that occur during startup of centrifugal contactors. During most of the runs, the solution generated during startup was collected and recycled through the extraction section, which increased both the length of each run and the total volume of solution generated.

Suspended Solids

In another attempt to lower the alpha activity of the extraction-section raffinate, one-micron filters were installed on a number of process streams. These filters would remove suspended solids from solutions that may contain TRU elements. Whamman Polycap HD filters (Fisher Scientific, 1600 W. Glenlake Ave, Itasca, IL 60143) were

installed on the following lines: the TRU waste feed, the extraction section raffinate, the recycled aqueous phase in the second carbonate wash, the organic phase collected following the second carbonate wash, and the solvent feed to the extraction section. A second, five-micron filter was installed on the TRU waste feed line before the one-micron filter to help prevent the smaller filter from plugging. In spite of this second filter, some plugging of both the five- and one-micron filters was observed during the tests. This was noted by measuring a decrease in the raffinate flow rate exiting the extraction section. To increase the flow rate, the pump settings were increased. All of the filters were installed on the suction side of the pumps. In this manner, the connections to the filter housing are typically under a slight vacuum. When the filters were installed on the pump discharge, the filter housings were under pressure, the connections tended to come apart, and the liquid being pumped would spray into the glovebox.

RESULTS

In this program, about 118 L of waste in 336 bottles was delivered and processed in four batches. Three additional runs were made to process the waste that was generated. The bottles and associated plastic wrappings were returned to EWM as nonTRU waste.

The TRUEX flowsheet for batch 2 is shown in Fig. 8. This flowsheet shows the 20-stage centrifugal contactor in the middle of the figure, with each section broken out into a series of stages. Equipment that was located outside of the glovebox is shown outside of the glovebox boundary. The improved process operations described in this report, such as the americium strip and solvent wash sections, are also shown. The americium and plutonium recovery percentages shown in the product boxes relate to the split between these two sections and not to the amount recovered from the feed solution. Although the equipment setup is fairly typical of the last three batch flowsheets, process concentrations and flow rates varied from batch to batch.

Approximately 360 L of waste was actually processed in seven runs. The original waste comprised about 33% of the total volume processed. The remaining waste consisted of bottle rinses, feed dilution, analytical samples, acidified carbonate raffinate, acid-wash solutions, equipment-decontamination solutions, and recycled

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 84g 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.

* 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

Batch Number	Feed		Alpha Activity (nCi/mL) ^b	Pu Product		Aqueous Raffinate	
	Pu (g) ^a	U (g) ^a		Pu (g) ^a	U (g) ^a	Alpha Activity (nCi/mL) ^b	Alpha Decontamination Factor ^b
1	12	0	40,000	8	0	1.8	22,400
2	13 ^c	16	21,400	13	10 ^d	4.4	4,900
3	28 ^c	7	88,000	30	5	1.3	65,500
4	34 ^c	3	40,000	33	3	10	4,000
Totals	87	26		84	18		

^aBased on ICP analysis unless otherwise noted.

^bBased on scintillation counting results.

^cBased on waste requisition form.

^dBased 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-strip 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

complexes that formed in our feed solution. (3) An on-line alumina column was instrumental in achieving good solvent quality during each process run. (4) Improved startup procedures were established to prevent the generation of out-of-specification material.

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

1. M. J. Steindler, *Chemical Technology Division 1990 Annual Report*, Argonne National Laboratory Report ANL-91/18 (May 1991).
2. M. J. Steindler, *Chemical Technology Division 1991 Annual Report*, Argonne National Laboratory Report ANL-92/15 (March 1992).
3. M. J. Steindler, *Nuclear Technology Programs Semiannual Progress Report April-September 1990*, Argonne National Laboratory Report ANL-92/25 (June 1992).
4. J. E. Battles, *Nuclear Technology Programs Semiannual Progress Report October 1990-March 1991*, Argonne National Laboratory Report ANL-92/44 (December 1992).
5. J. E. Battles, *Chemical Technology Division 1992 Annual Report*, Argonne National Laboratory Report ANL-93/17 (June 1993).
6. J. E. Battles, *Nuclear Technology Programs Semiannual Progress Report April-September 1991*, Argonne National Laboratory Report ANL-93/21 (July 1993).
7. J. E. Battles, *Chemical Technology Division 1993 Annual Report*, Argonne National Laboratory Report ANL-94/15 (April 1994).
8. G. F. Vandegrift, et. al., *Separation Science and Technology Semiannual Progress Report October 1991-March 1992*, Argonne National Laboratory Report ANL-93/38 (January 1994).
9. G. F. Vandegrift, et. al., *Separation Science and Technology Semiannual Progress Report April-September 1992*, Argonne National Laboratory, ANL-94/29 Report (September 1994).
10. G. F. Vandegrift, et. al., *Separation Science and Technology Semiannual Progress Report October 1992 - March 1993*, Argonne National Laboratory Report ANL-95/4 (January 1995).
11. E. P. Horwitz and W. W. Schulz, "The TRUEX Process: A Vital Tool for Disposal of U.S. Defense Nuclear Waste." *New Separation Chemistry*

Techniques for Radioactive Waste and other Specific Applications, Eds L. Cecille, M. Casarri, and L. Pietrelli, Elsevier Applied Science, London, pp. 21-29 (1991).

12. G. F. Vandegrift, R. A. Leonard, M. J. Steindler, E. P. Horwitz, L. J. Basile, H. Diamond, D. G. Kalina, and L. Kaplan, *Transuranic Decontamination of Nitric Acid Solutions by the TRUEX Solvent Extraction Process--Preliminary Development Studies*, Argonne National Laboratory Report ANL-84-45 (July 1984).
13. G. F. Vandegrift, D. B. Chamberlain, R. A. Leonard, J. C. Hutter, D. G. Wygmans, C. J. Conner, J. Sedlet, L. Nuñez, J. M. Copple, J. A. Dow, B. Srinivasan, M. C. Regalbuto, S. Weber, and L. Everson, "Development and Demonstration of the TRUEX Solvent Extraction Process", Proc. of the Waste Management '93 Conf. 19th Annual Nuclear Waste Symp., Tucson, AZ, Vol. 2 pp. 1045-1050, February 28-March 4, 1993.
14. S. A. Slater, D. B. Chamberlain, C. Conner, J. Sedlet, B. Srinivasan, and G. F. Vandegrift, *Methods for Removing Transuranic Elements from Waste Solutions*, Argonne National Laboratory Report ANL-94/43 (Nov. 1994).
15. M. C. Regalbuto, S. Aase, and G. F. Vandegrift, *Validation of the Generic TRUEX Model Using Data from TRUEX Demonstrations with Actual High-Level Waste*, Argonne National Laboratory Report ANL-95/21 (August 1995).
16. G. F. Vandegrift and M. C. Regalbuto, "Validation of the Generic TRUEX Model Using Data from TRUEX Demonstrations with Actual High-Level Waste," Proc. of the Fifth International Conference on Radioactive Waste Management and Environmental Remediation, Berlin, Germany, Vol. 1 pp. 457-462, September 3-7, 1995.
17. M. C. Regalbuto, B. Misra, D. B. Chamberlain, R. A. Leonard, and G. F. Vandegrift, *The Monitoring and Control of TRUEX Processes. Volume One-The Use of Sensitivity Analysis to Determine Key Process Variables and Their Control Bounds*, Argonne National Laboratory Report ANL-92/7 (April 1992).
18. N. Simonzadeh, A. M. Crabtree, L. E. Trevorrow, G. F. Vandegrift, *Radiolysis and Hydrolysis of TRUEX NPH Solvent*, Argonne National Laboratory Report ANL-90/14 (July 1992).
19. B. A. Buchholz, L. Nuñez, G. F. Vandegrift, "Effect of Alpha-Radiolysis on TRUEX-NPH Solvent," *Separation Science and Technology* 31 (in press).
20. P.-K. Tse, L. Reichley-Yinger, and G. F. Vandegrift, "TRUEX Process Solvent Cleanup with Solid Sorbents", *Separation Science and Technology* 25 (13-15), 1763-1775 (1990).
21. R. Chiarizia and E. P. Horwitz, "Secondary Cleanup of TRUEX Process Solvent," *Solvent Extraction and Ion Exchange* 8 (6), 907-941 (1990).

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.

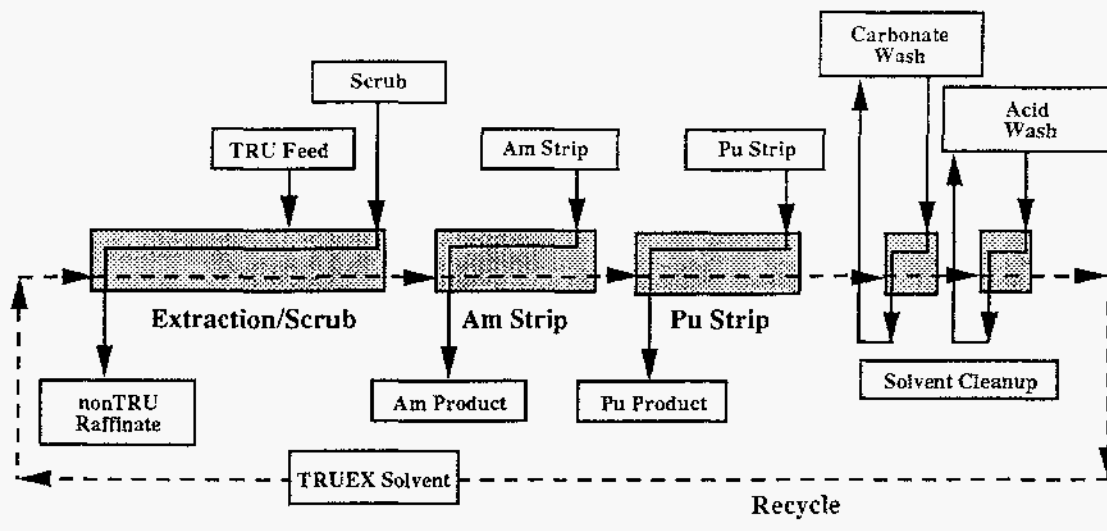
FIGURE 4. Schematic of the americium strip section, batch 2.

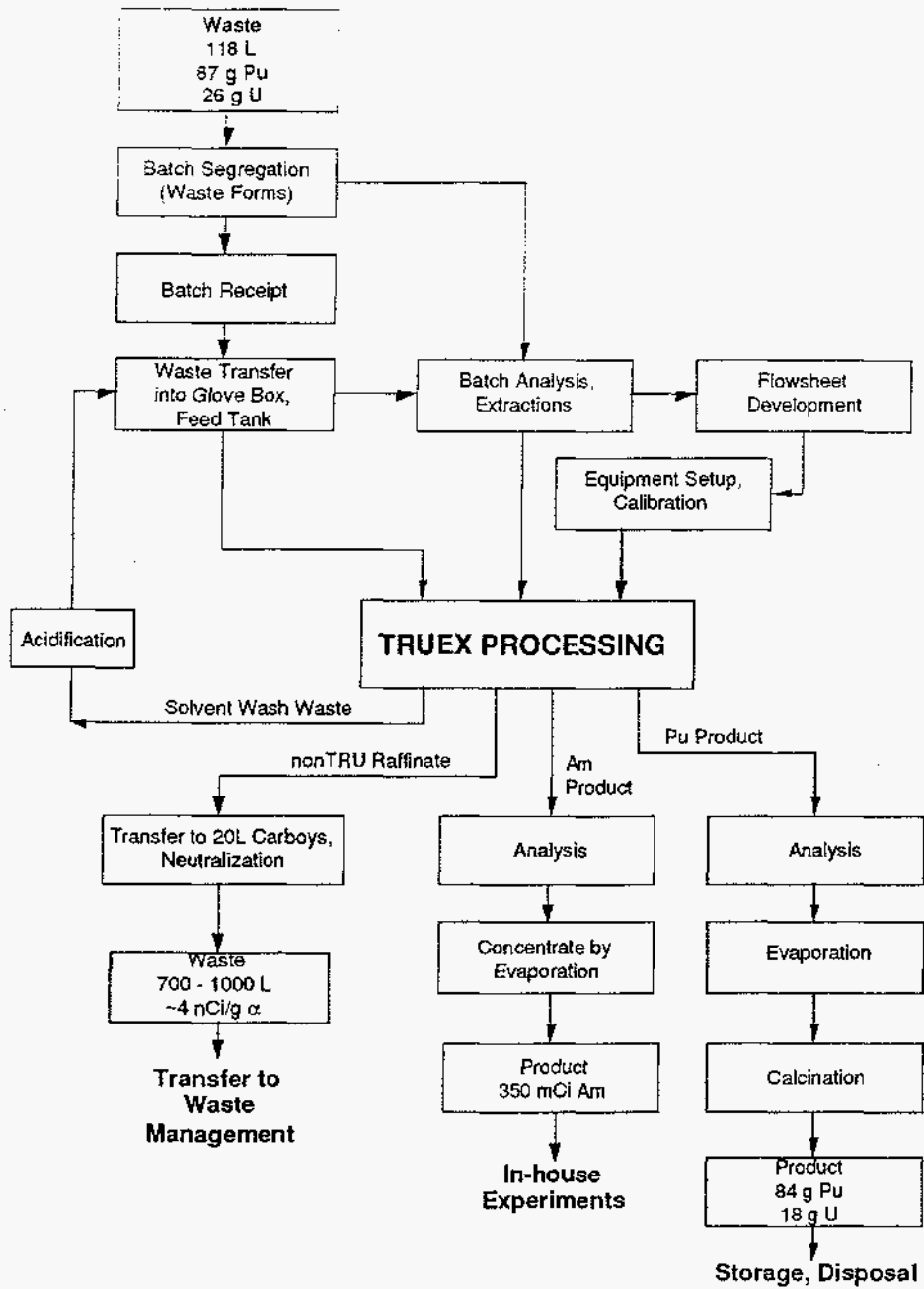
FIGURE 5. Flowsheet for processing the raffinate solution from batch 1.

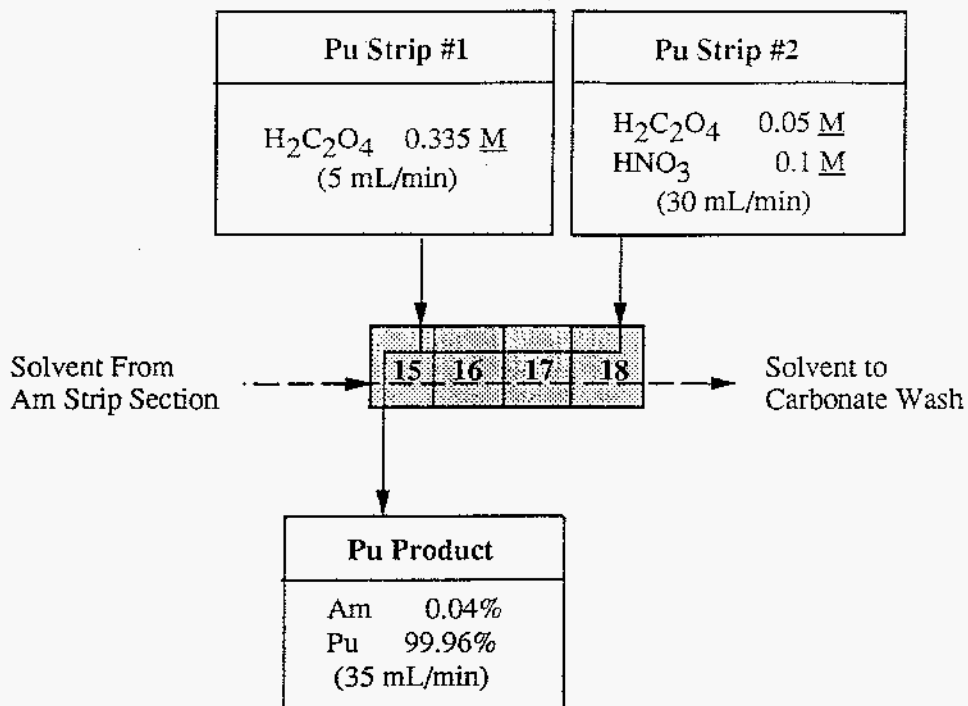
FIGURE 6. Solvent purification system installed for batch 2.

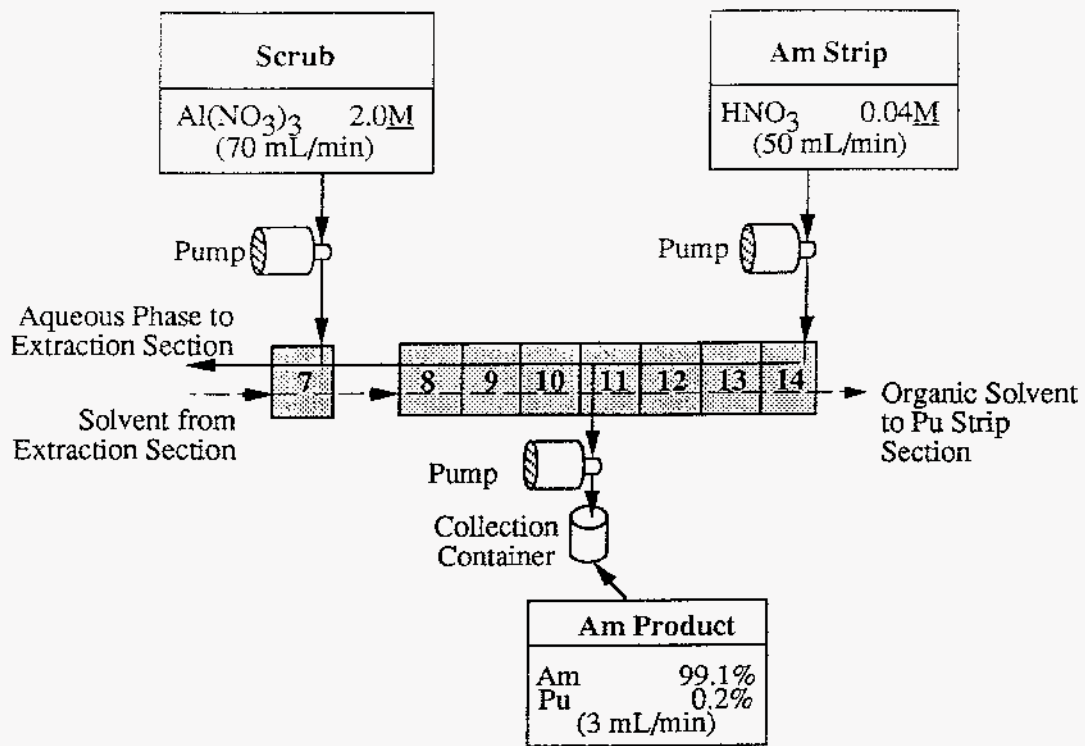
FIGURE 7. Alpha activity in the extraction section raffinate during processing of batch 3.

FIGURE 8. TRUEX flowsheet for processing batch 2 waste.

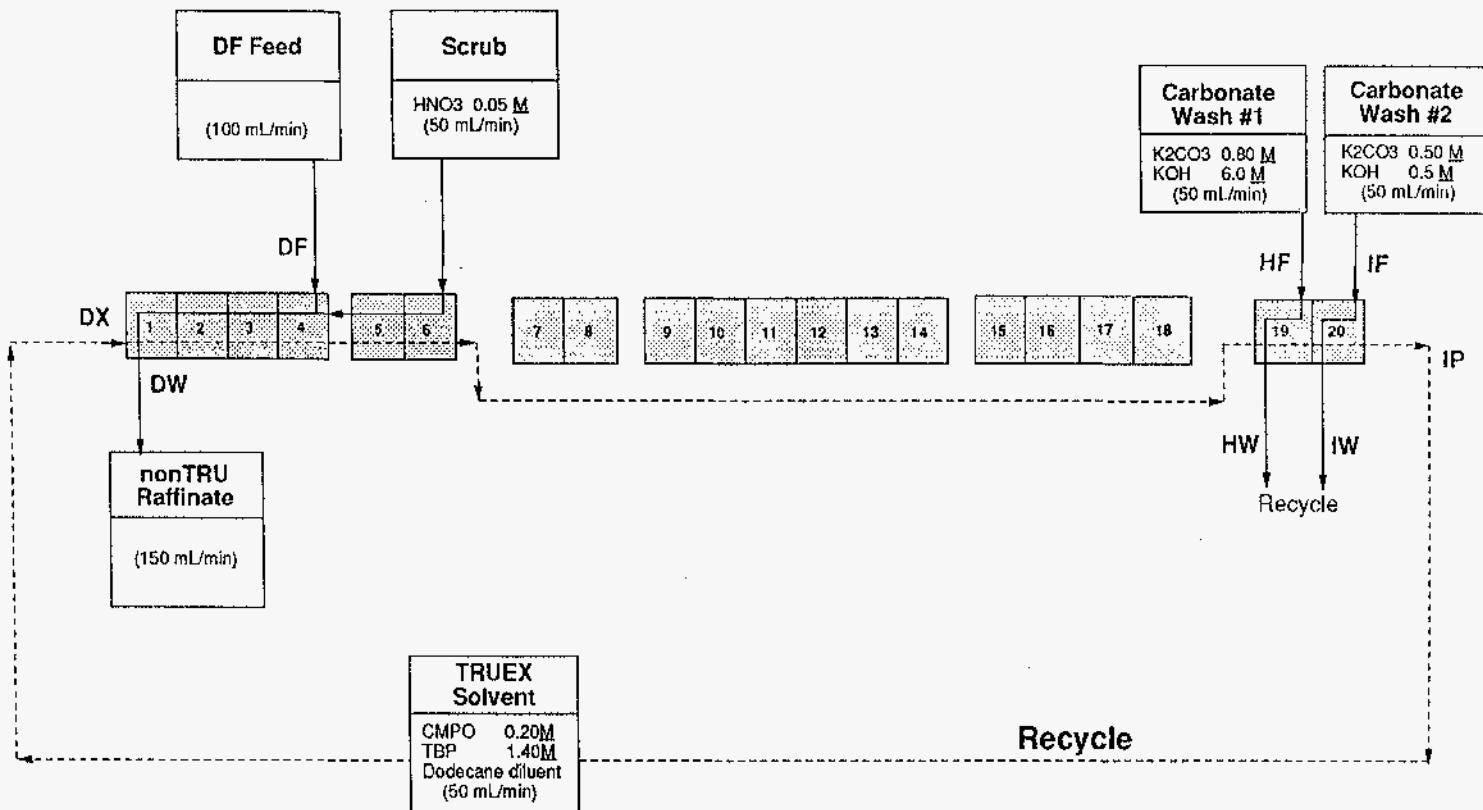


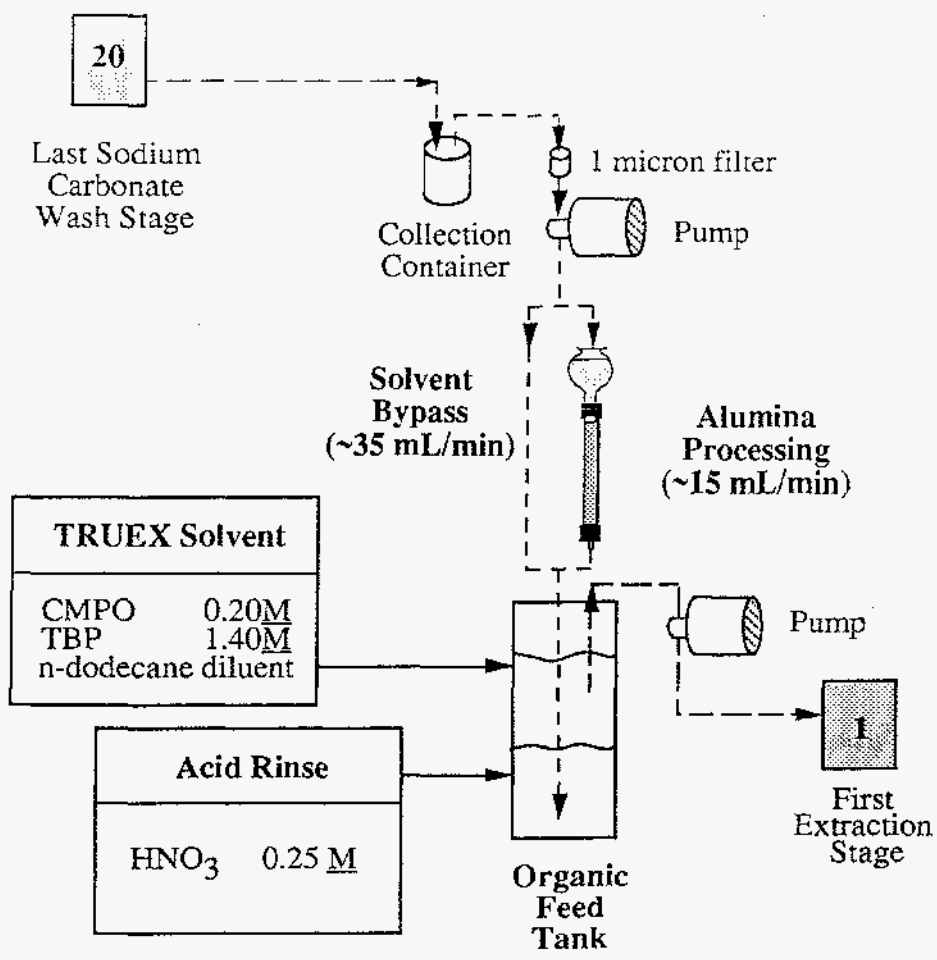


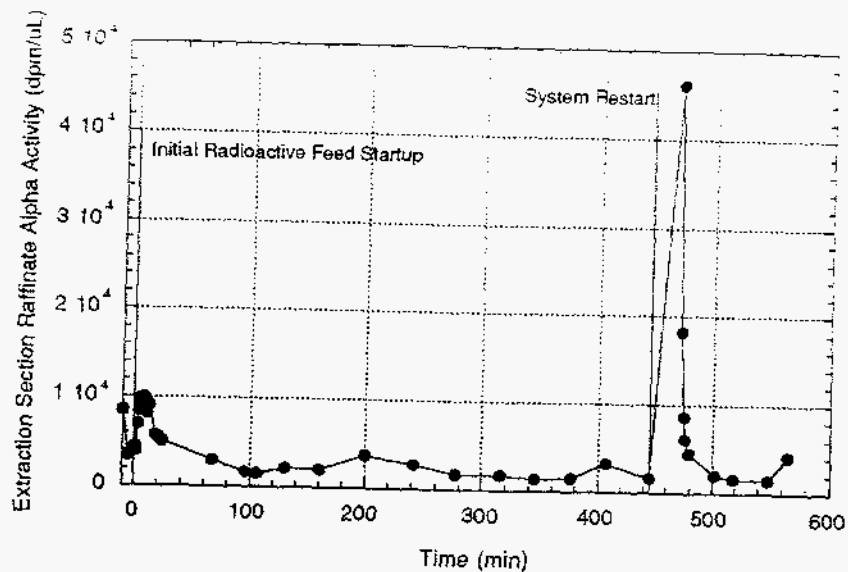




Process for the Treatment of Batch #1 Extraction Raffinate Waste







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