

DEVELOPMENT AND DEMONSTRATION OF THE TRU EX SOLVENT EXTRACTION PROCESS*

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ABSTRACT

The Generic TRU EX Model (GTM) was developed for use in designing site- and feed-specific TRU EX flowsheets and in estimating the space and cost requirements for installing a TRU EX process. This paper will discuss data collected in support of the GTM and its use in 1) designing process flowsheets and 2) performing sensitivity analyses. Demonstration of the TRU EX process is underway at Argonne National Laboratory (ANL), where plutonium-containing analytical waste solutions generated at the DOE New Brunswick Laboratory (NBL) are being converted from TRU waste (~1 g Pu/L), with no current means of disposal, to solutions that contain less than 10 nCi of transuranic elements per milliliter of waste solution. Results and implications of this demonstration will be discussed.

INTRODUCTION

The TRU EX process is a solvent extraction procedure capable of separating, with very high efficiency, small quantities of transuranic (TRU) elements (e.g., Np, Am, Pu, Cm) from aqueous nitrate or chloride solutions that are typically generated in reprocessing plant operations or in plutonium production and purification operations. The resulting solutions can be sufficiently separated from TRU elements to warrant disposal as nonTRU wastes. Further, transuranic elements can be recovered and purified by this process. The ability of the TRU EX process to remove, separate, and recover TRU elements from aqueous media with a wide range of compositions gives it the potential for becoming a generic process for treating the entire range of TRU waste streams generated at DOE facilities. The key ingredient in the TRU EX solvent extraction process is octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is generally called simply CMPO. This extractant is combined with tributyl phosphate (TBP) and a diluent to formulate the TRU EX solvent. The diluent is typically a normal paraffinic hydrocarbon (NPH).

The Generic TRU EX Model (GTM) was developed for use in designing site- and feed-specific TRU EX flowsheets and in estimating the space and cost requirements for installing a TRU EX process. The GTM continues to be enhanced through collection of laboratory and pilot-plant data and through improvements in the thermodynamic modeling and computer codes. User friendliness, accuracy of predictions, and compatibility with both Macintosh and IBM PCs are keys to its usefulness. This paper will discuss data collected in support of the GTM and its use in 1) designing process flowsheets and 2) performing sensitivity analyses.

Demonstration of the TRU EX process is underway at Argonne National Laboratory (ANL), where plutonium-containing analytical waste solutions generated at the DOE New Brunswick Laboratory (NBL) are being converted from TRU waste (~1 g Pu/L), with no current means of disposal, to

solutions that contain less than 10 nCi of transuranic elements per milliliter of waste solution. Plutonium and uranium recovered from processing will be used for fuel in the EBR-II reactor, and other actinides will be used in R&D programs at ANL. This demonstration, which is being run in a twenty-stage Argonne design centrifugal contactor, is providing important data and Argonne design building confidence in TRU EX process chemistry and in the use of the centrifugal contactor for future waste processing at Los Alamos National Laboratory, Rocky Flats Plant, Oak Ridge National Laboratory, the Hanford site, and Idaho National Engineering Laboratory. Results and implications of this demonstration will be discussed.

The Generic TRU EX Model

The GTM is composed of four major sections, SASSE, SASPE, SPACE, and INPUT/OUTPUT, which interact together and are executed by Microsoft Excel software. At the center of flowsheet calculations is the SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) section, which calculates multistage, countercurrent flowsheets based on distribution ratios calculated in the SASPE (Spreadsheet Algorithms for Speciation and Partitioning Equilibria) section. The third section of the GTM, the SPACE (Size of Plant And Cost Estimation) section, estimates the space and cost requirements for installing a specific TRU EX process using centrifugal-contactor, mixer-settler, or pulsed-column equipment in a glovebox, shielded-cell, or canyon facility. The interactions of these sections are schematically represented in Fig. 1.

The SASSE section has been developed to allow the design and detailed evaluation of proposed flowsheets in conjunction with distribution ratios generated in SASPE. In addition to 1) establishing that each feed component will be able to reach its design composition in the extraction raffinate and product streams and 2) providing the compositions of the organic and aqueous solutions in each stage of the flowsheet

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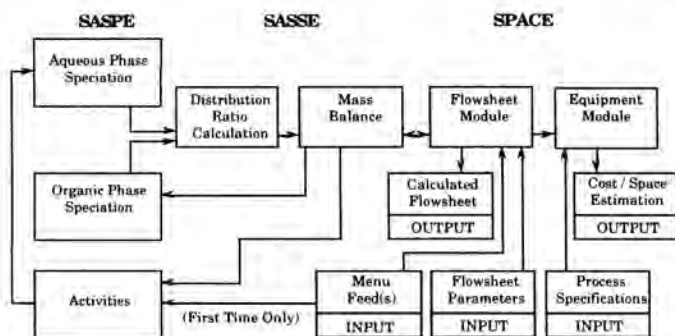


Fig. 1. Interactions among computer program modules of generic TRU EX Model for flowsheet calculations.

at steady state, SASSE can be used to identify key points for process monitoring and control. An early version of SASSE was used to assist Westinghouse Hanford in countercurrent testing of the TRU EX flowsheet (1-4) using actual waste from its Plutonium Finishing Plant. This early work was expanded upon in a recent report that shows the usefulness of the GTM for designing flowsheets and performing sensitivity analyses (5).

The fourth section of the model, INPUT/OUTPUT, is a menu-driven interface that allows the user to choose which option to run, prompts the user for all the information needed by the GTM before calculations have begun, and generates reports (tabular and graphical) of results. In options that use SASSE, an Excel macro will produce an appropriate SASSE spreadsheet for a TRU EX process with an extraction section, up to three scrub sections, up to four strip sections, a sodium-carbonate-wash section, an aqueous-complexant-wash section, and/or an acid rinse, depending on the user's specifications. Any number of stages can be specified in each flowsheet section. (In other options, modules of SASPE will be opened and closed as necessary to make calculations and to generate reports.) The experienced user can perform flowsheet calculations without using the INPUT/OUTPUT interface.

When the GTM is used to calculate flowsheets, the SASPE section of the model will calculate distribution ratio (D) values for each aqueous-phase composition from user-specified feeds (feed menu) and from stage compositions generated in SASSE during SASPE/SASSE iterations. The exceptional accuracy of the SASPE D-value calculations over a wide range of aqueous-phase compositions is due to the use of mechanistically correct models that use thermodynamic activities of major aqueous-phase species (H^+ , NO_3^- , and H_2O). These activities are calculated in SASPE from aqueous-phase compositions using the approach of Bromley (6). Solvent loading is also treated in the GTM. The GTM loading module uses the distribution ratios calculated in SASPE and the aqueous and organic compositions calculated in SASSE to calculate the concentration of CMPO that is available for extracting species into the TRU EX solvent. Distribution ratios calculated in SASPE are then diminished by the ratio $(CMPO_{available}/CMPO_{total})^n$, where n (the number of moles of CMPO per mole of metal salt species extracted) is specified for each extractable species.

The main objective of the GTM is to calculate a TRU EX solvent extraction flowsheet based on input of a specific feed and a specific set of process goals and constraints. The output of this model will be 1) the compositions of all effluent streams, 2) the compositions of both phases (organic and aqueous) in each process stage at steady state, and 3) estimates of the space and cost requirements for installing the flowsheet in a plant situation. Other options are available to calculate aqueous-phase speciation and thermodynamic activities, distribution ratios of extractable species, and solvent radiolytic and hydrolytic degradation. Calculation of these options is based on initial aqueous- and organic-phase compositions and other important variables supplied by the user.

User Options (choose option from menu bar)	
1	calculate complete Generic TRU EX Model for a specific feed solution
2	calculate the following: <ul style="list-style-type: none"> - charge balance check of complex aqueous solution - density of complex aqueous solution - ionic strength of complex aqueous solution - activities of H^+, NO_3^-, and water
3	calculate oxalic acid additions to fission-product-containing waste
4	calculate D values for user-specified aqueous phase (org. phase assumed equilibrated)
5	calculate D values for equilibration of user-specified aqueous and organic phases
6	flowsheet analysis with user-specified distribution ratios
7	generate a TRU EX flowsheet for a user-specified feed
8	estimate space and costs for user-specified flowsheet
9	estimate solvent degradation for specific TRU EX process
10	generate reports from existing TRU EX flowsheets or space and cost calculations

Fig. 2. User options card for generic TRU EX model.

The GTM User Option Card displayed in Fig. 2 shows the calculated options that are available to the user.

Data Collection

Following are three examples of the data collected for use in developing distribution ratio models to be used in SASPE. The data presented for bismuth, H_3PO_4 , and HBF_4 are only part of the data set collected.

The extraction behavior of bismuth in the TRU EX process is important for treating the early Hanford wastes (now in the single shell tanks) because of the great amounts of bismuth in these tanks. The initial method for separating plutonium from neutron-irradiated uranium used bismuth phosphate to coprecipitate Pu(IV) and sodium bismuthate to oxidize Pu(IV) to Pu(VI). Thus, many Hanford waste tanks contain large amounts (on the order of grams per liter) of bismuth (7). Using ^{210}Bi radiotracer, distribution ratios of bismuth (D_{Bi}) were measured as a function of nitric acid concentration for aqueous solutions containing only nitric acid and for solutions containing 1M $NaNO_3$ as well (Fig. 3). With nitric acid alone, D_{Bi} increases sharply with increasing acid concentration until a maximum is reached at about 1M HNO_3 . At higher concentrations of HNO_3 , D_{Bi} decreases rapidly, presumably because much of the CMPO is taken up by its extraction and complexation of nitric acid and is no longer available to complex the bismuth nitrate. The differences between the forward and reverse extractions at low nitric acid concentrations are typical for Bi^{3+} ion and are attributed to its tendency to hydrolyze under such conditions. With 1M $NaNO_3$ present, the distribution ratios are considerably higher than with nitric acid alone because the high nitrate ion activities enhance the extraction of the neutral

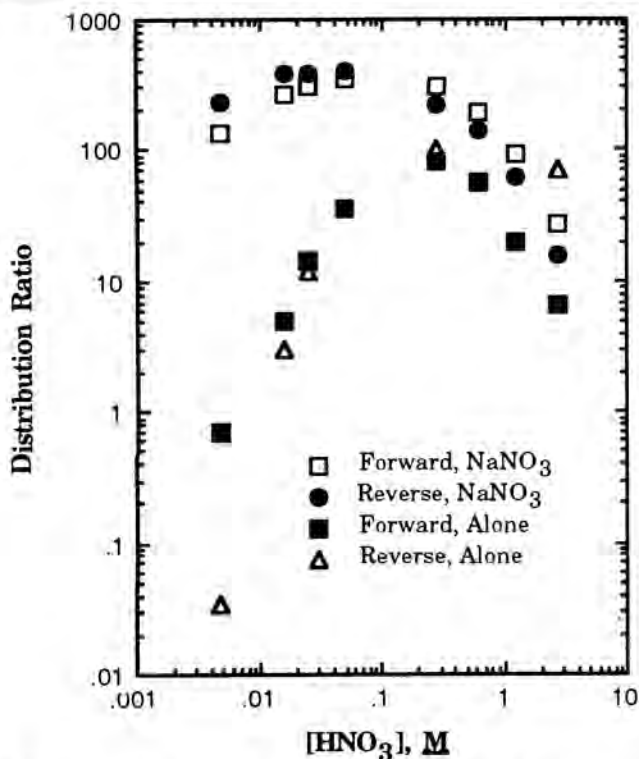


Fig. 3. Distribution ratios for ^{210}Bi as function of aqueous-phase nitric acid concentration before equilibration in TRUEX solvent extraction process. Data marked NaNO_3 are for nitric acid solution containing 1M NaNO_3 ; data marked "alone" are for nitric acid only.

species $\text{Bi}(\text{NO}_3)_3$. A maximum is reached here also, but at 0.1M HNO_3 . Distribution ratio measurements using potentiometric titrations of phosphoric acid in the aqueous and organic phases are presented in Fig. 4. In this figure, the phosphoric acid concentration in the organic phase is plotted versus its aqueous phase concentration; the slope of the line through the data equals $D_{\text{H}_3\text{PO}_4}$. Note that $D_{\text{H}_3\text{PO}_4}$ increases with the phosphoric acid concentration. These data and radiotracer data obtained using $\text{H}_3^{32}\text{PO}_4$ under conditions where the concentrations of nitric acid, phosphoric acid, and nitrate salts were varied, permitted the derivation of a mechanistic model for the extraction of phosphoric acid.

Distribution ratios of fluoroboric acid have been measured by hydrolyzing HBF_4 with NaOH to $\text{B}(\text{OH})_4^-$ in both the aqueous and organic phases and back-titrating $\text{B}(\text{OH})_4^-$ with acid. Data are still being collected, but, based on our experience in modeling the extraction of HTcO_4 , it is likely that the shape of the curve shown in Fig. 5 can be fit by assuming a competition for CMPO and/or TBP between HBF_4 and HNO_3 . The acid dissociation constant for HBF_4 may also be important to modeling the data.

Sensitivity Analysis Using the GTM

The GTM can be used to determine the effect of variations (anticipated or due to process upset) on a specific TRUEX process flowsheet. Sensitivity analysis can define effects of:

- flow rate variations
- compositional variations
- stage loss

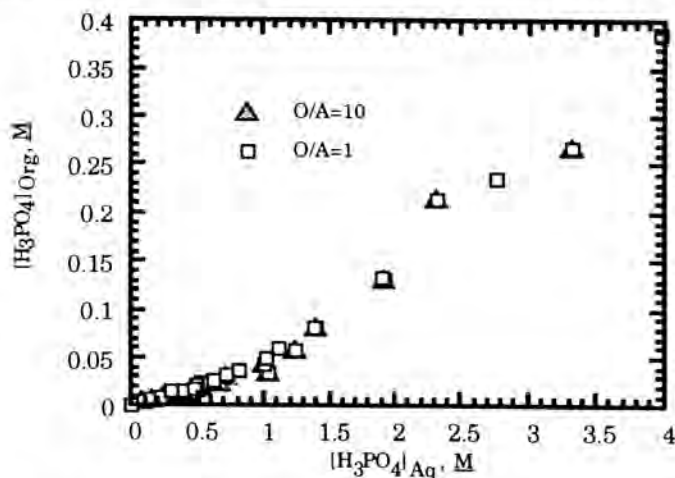


Fig. 4. Concentration of H_3PO_4 in TRUEX solvent vs. aqueous concentration of H_3PO_4 and organic-to-aqueous volume ratio (O/A).

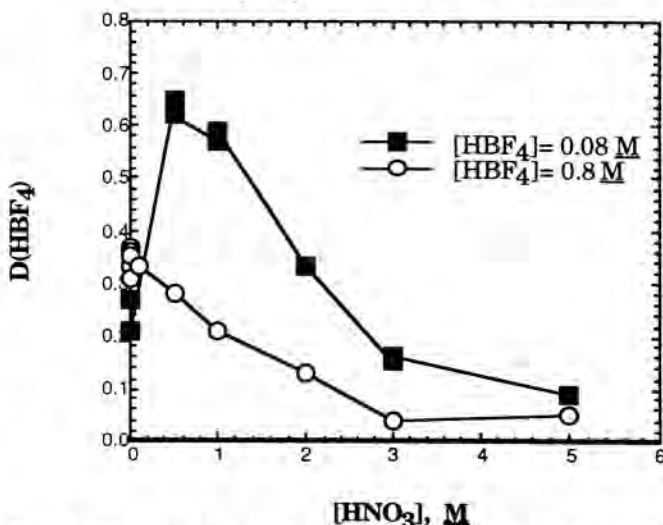


Fig. 5. Distribution of fluoroboric acid in TRUEX solvent extraction process as function of concentrations of nitric acid and fluoroboric acid before equilibration.

- other-phase carryover
- equipment type.

Reference 5 discusses using the GTM to do sensitivity analyses for a specific TRUEX process flowsheet that was designed in 1985 (before the GTM was available) for treating a TRU waste stream generated in Hanford's Plutonium Finishing Plant (1). This flowsheet has a 4-stage extraction section, a 4-stage scrub section, a 7-stage americium strip section, and a 4-stage plutonium strip section. The feeds to the scrub and the first strip section were both 0.04M HNO_3 , and the feed to the second strip was 0.05M HNO_3 and 0.05M HF . The GTM verified that this flowsheet would meet its process goals of 1) making the TRU concentration in the raffinate < 10 nCi/mL, 2) having < 0.3 mol % of the americium in the plutonium product (effluent from the second strip section), 3) having < 1.1 mol % of plutonium in the americium product (effluent from the first strip section), and 4) having < 0.01 mol % of the TRU not stripped from the solvent in the americium and the plutonium strip sections. However, sensitivity analysis showed that the flowsheet as designed (base case) would not

meet these goals if even minor variations occurred in the process.

Based on this sensitivity analysis, an improved flowsheet was designed that was much more robust. This new flowsheet increased the concentration of nitric acid in the scrub feed from 0.05 to 0.5M HNO₃ and added two more stages to the second strip section. Figures 6 and 7 show how the flowsheet has been made much less sensitive to solvent-flow-rate variation by these improvements. Controlling the flow rate to 0.935 - 1.01 of the base case would be difficult (old flowsheet); a range of 0.764 - 1.10 is easily achievable (new flowsheet).

Pilot-Plant Demonstration of the TRUEX Process

Approximately 200 liters of waste solution from the analysis of plutonium samples has been accumulating over the past several years at the New Brunswick Laboratory (NBL) and Argonne National Laboratory (ANL). These residues, stored in over six hundred 250-mL sample bottles, contain varying concentrations of nitric, sulfuric, phosphoric, and hydrochloric acids, as well as uranium, plutonium, neptunium, and americium. Originally destined for storage at the Idaho National Engineering Laboratory and eventual disposal at the Waste Isolation Pilot Plant (WIPP) in New Mexico, these wastes now appear to have no place that will accept them. In this project the TRUEX process is being used to convert the bulk of this waste into a nonTRU low-level waste. The goal is to reduce the TRU elements to a concentration that is less

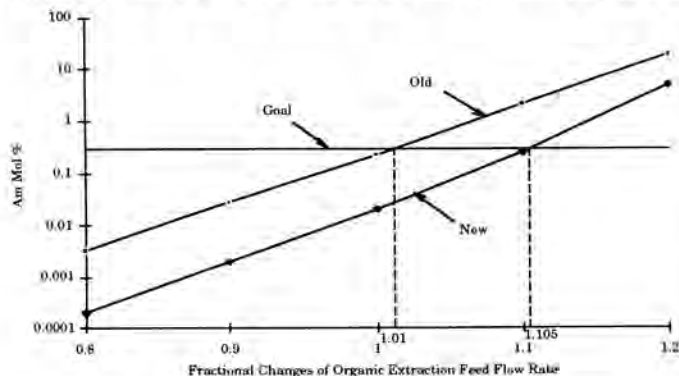


Fig. 6. Americium mole percent in second-strip effluent as function of changes in flow rate for organic extraction feed. (Flow rates are relative to the base case.)

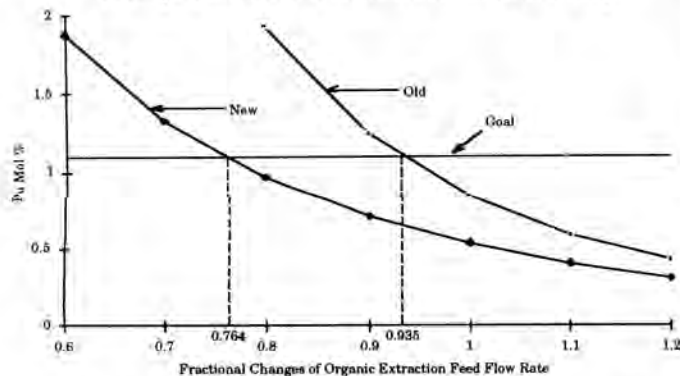


Fig. 7. Plutonium mole percent in first-strip effluent as function of changes in flow rate for organic extraction feed. (Flow rates are relative to the base case.)

than 10 nCi/mL. The 168 grams of plutonium that will be recovered by the TRUEX process will be converted to a metal and returned to NBL for storage and subsequent transport to ANL-West to be used as fuel in the EBR-II. The TRUEX solvent extraction process, used to generate the nonTRU waste stream and recover the plutonium, is being completed in a 20 stage 4-cm centrifugal contactor installed in a glovebox.

The objectives of this demonstration are fivefold. First, the treatment of these waste solutions solves a waste treatment problem here at Argonne. Second, the lessons that we learn will benefit others contemplating the installation of a TRUEX facility. Third, this program gives us experience and evaluates the applicability of the GTM to designing flowsheets for specific feeds and process goals. Fourth, the data collected will be used to verify the Generic TRUEX Model predictions. And fifth, this demonstration will show the applicability of using the TRUEX process for treating similar wastes at Rocky Flats, Los Alamos, Oak Ridge, Hanford, and Idaho.

Figure 8 is a schematic of the TRUEX flowsheet designed by the GTM for processing the second batch of waste. The concentrations of the species in the feed box were calculated from the waste forms; the amounts of Pu, Am, and U in the effluent streams are actual results. Note that the raffinate from the extraction section has 6 nCi/mL of alpha activity, making that stream nonTRU. The GTM predicted that this stream would be lower in TRU content than was actually reached; subsequent batch contacts showed that alpha activity in that raffinate was not extractable by the TRUEX solvent--meaning that it was likely in a colloidal state, e.g., plutonium polymer. The model also predicted less carryover of the americium into the Pu/U product; it appears that the nitric acid concentration in the feed was higher than calculated from the waste forms. Future runs will add stages to the scrub or the second strip sections to decrease loss of americium to the second strip section. Note that americium was concentrated in the americium-product stream by a factor of 30 from its feed concentration. Plutonium and uranium were concentrated by a factor of 12.

Three other features of this flowsheet worth discussing are 1) the incorporation of an Al(NO₃)₃ scrub, 2) the use of ammonium oxalate as a Pu/U scrubbing agent, and 3) use of an alumina column for solvent cleanup. At the high phosphoric acid concentration in the feed (0.89M), the Pu(IV) was severely complexed, which prevented its extraction. However, with an Al(NO₃)₃ addition in this stream, distribution ratios of plutonium in the extraction section were increased, and the aluminum nitrate acted to strip phosphoric acid from the solvent before the solvent entered the americium strip section. If it were not scrubbed, plutonium and uranium would have been stripped from the solvent in the first strip, and they, with americium, may have precipitated in the contactor.

Use of (NH₄)₂C₂O₄ as a stripping agent for actinides (and plutonium, in particular) has many advantages over the use of oxalic acid: 1) oxalic acid has a distribution ratio between 1 and 3, while that of ammonium oxalate is < 0.04; 2) Pu, Am, and U are all very much more soluble in ammonium oxalate than in oxalic acid due to formation of oxalato anionic species; and 3) distribution ratios for these metals are much lower in ammonium oxalate than oxalic acid. Both solutions can be evaporated to dryness, and the oxalates can be calcined to oxides.

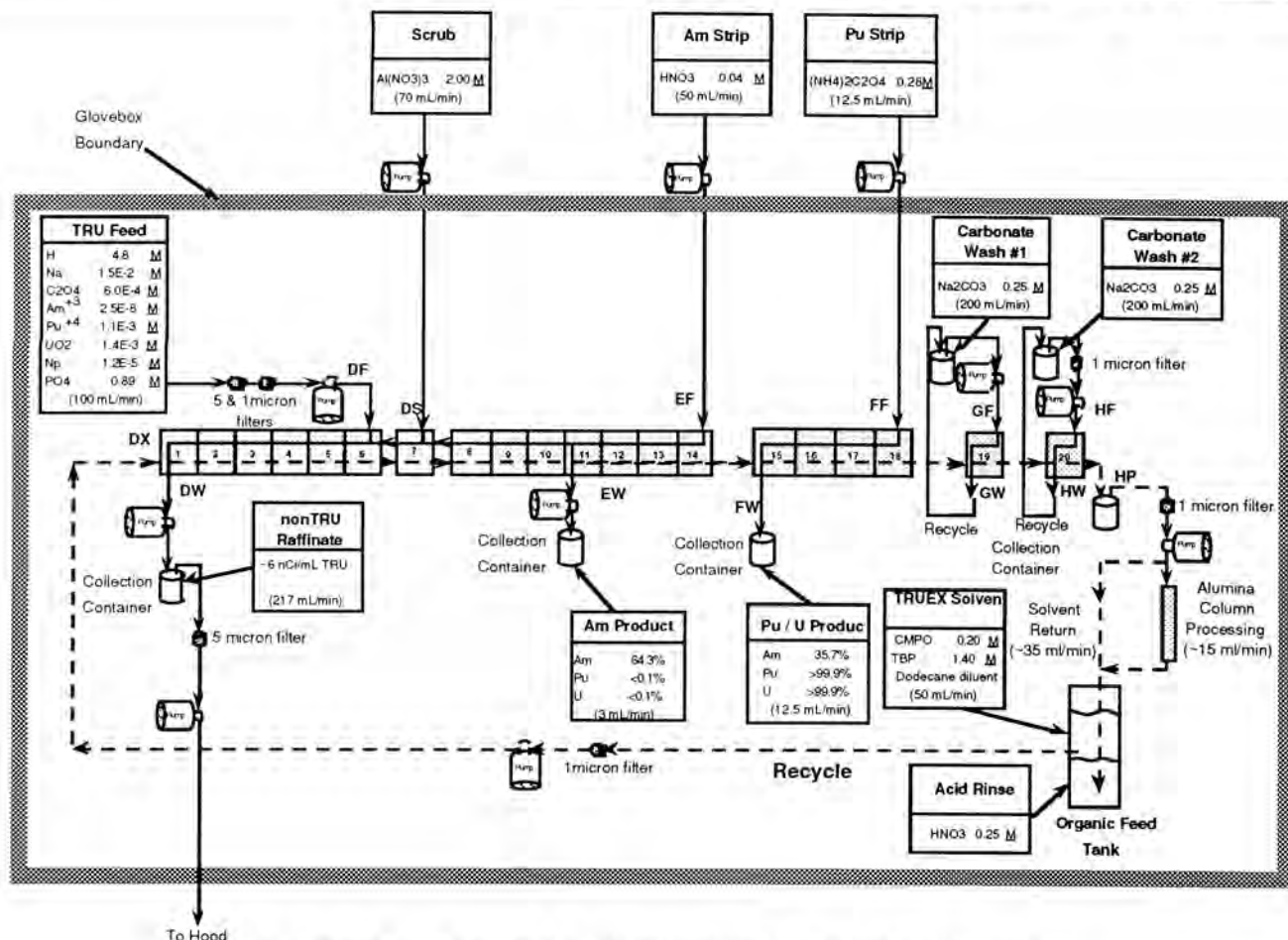


Fig. 8. Flowsheet schematic for TRUEX processing of batch 2 NBL wastes.

Two papers that describe various solvent clean-up procedures (8,9) concluded that the use of sodium carbonate as the primary clean-up method was not adequate for returning the solvent to pristine condition--additional solvent cleanup steps are necessary. In these two studies, a variety of solid sorbents were tested to determine their effectiveness in removing acidic organic degradation products from TRUEX solvents. In order to select which of these solid sorbents we would use to 1) clean up the degraded solvent on hand and 2) install in the glovebox for use during the NBL program, a study was conducted using three of these solid sorbents. Tests using the two batches of spent solvent were completed with acid-washed alumina, neutral alumina, and Amberlyst A-26 anion exchange resin. Based on these tests, activated neutral alumina was selected for use. A packed column 2.5 cm (1 in.) in diameter and 30 cm (12 in.) in length was used to successfully clean up the degraded solvent. This column was incorporated into the glove-box equipment setup for processing NBL waste.

Future Direction

New features are being added to the GTM as required. Now being added are 1) including stagewise stage efficiency to SASSE to allow more accurate calculations in mixer settlers, where stage efficiency typically varies between 60 and 90%; 2) allowing multiple solvent feeds to a flowsheet; 3) enhancing the loading module to better predict solvent loading for species that are extracted by TBP as well as CMPO (e.g., Pu, U); and 4) increasing the accuracy of SASPE Dvalue

predictions for Bi, Zr, Cr, Cd, B, and F. The TRUEX process will also be demonstrated at Oak Ridge National Laboratory by recovering Am, Cm, and Pu from irradiated target materials. Demonstration of the process on NBL wastes is continuing through 1993.

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