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ABSTRACT

This document reports on the work done by the Separations Science and Technology Programs of the Chemical Technology Division, Argonne National Laboratory, in the period April-September 1992. This effort is mainly concerned with developing the TRUEX process for removing and concentrating actinides from acidic waste streams contaminated with transuranic (TRU) elements. The objectives of TRUEX processing are to recover valuable TRU elements and to lower disposal costs for the nonTRU waste product of the process. Two other projects are underway with the objective of developing (1) a membrane-assisted solvent extraction method for treating natural and process waters contaminated by volatile organic compounds and (2) evaporation technology for concentrating radioactive waste and product streams such as those generated by the TRUEX process.

SUMMARY

The Division's work in separation science and technology is mainly concerned with developing a technology base for the TRUEX (TRAnsUranic EXtraction) solvent extraction process. The TRUEX process extracts, separates, and recovers TRU elements from solutions containing a wide range of nitric acid and nitrate salt concentrations. The extractant found most satisfactory for the TRUEX process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is abbreviated CMPO. This extractant is combined with tributyl phosphate (TBP) and a diluent to formulate the TRUEX process solvent. The diluent is typically a normal paraffinic hydrocarbon (NPH) or a nonflammable chlorocarbon such as carbon tetrachloride (CCl_4) or tetrachloroethylene (TCE).

The objectives of TRUEX processing are to recover valuable TRU elements and to lower disposal costs for the nonTRU waste product of the process. The major thrust of the development efforts has been the Generic TRUEX Model (GTM), which is used with Macintosh or IBM-compatible computers for designing TRUEX flowsheets and estimating cost and space requirements for installing TRUEX processes for treating specific waste streams.

The GTM version 2.4.3 was distributed to Macintosh and IBM-PC users during April. Efforts continued to add features to the GTM and make it faster. One of the modules in the GTM calculates a unique solution to the mass-balance equations for $\text{CMPO}_{\text{free}}$ and TBP_{free} during HNO_3 extraction by TRUEX solvents. This module was improved by revising the equations needed to calculate $\text{CMPO}_{\text{free}}$, TBP_{free} , and HNO_3 . All upgraded equations used to calculate $\text{CMPO}_{\text{free}}$, TBP_{free} , and $[\text{HNO}_3]_{\text{org}}$ are given, as are values for extraction constants used in those equations.

The data base generated for developing the GTM contains information (from the literature and our own laboratory measurements) on the solution and extraction behavior of important feed components over a wide range of possible waste-stream and processing conditions. Our recent efforts on expanding the data base and adding extraction models have focused on zirconium, an important component in nuclear fuel cladding; H_3PO_4 , which is found in the nuclear waste storage tanks at Hanford; HBF_4 , one of

the main constituents in some of the wastes containing TRU elements at Idaho National Engineering Laboratory; and bismuth, another important constituent in the Hanford storage waste tank. As part of this effort, we developed a neutron activation analysis method for determining zirconium distribution ratios, a method for calculating water activities in phosphoric acid solution, a titrimetric method for estimating the concentration of HBF_4 in the aqueous solutions, and a method for measuring the purity of CMPO for use in the TRUEX solvent. In addition, we measured the distribution ratios for bismuth in the TRUEX-NPH system by use of ^{210}Bi as a tracer. These measurements indicate that the extraction and stripping steps in the current TRUEX process will require modification to separate plutonium (and americium) from bismuth.

We have started a project to demonstrate the new TRUEX-SREX process, which is a combination of the TRUEX process and a recently developed SREX (strontium extraction) process. In August, staff in the ANL Chemistry Division performed experiments to show that substituting diamyl(aryl) phosphonate (DA[AP]) for TBP in the TRUEX-SREX solvent could essentially eliminate third-phase formation as a problem, even at high metal loading. This is certainly an improvement, but DA[AP] is a much stronger base than TBP and extracts more acid into the organic phase. To calculate a flowsheet for using this process solvent, we needed to change the model for nitric acid extraction in the GTM. To do this, we employed the same set of equilibria equations used for the TRUEX solvent, but modified the constants related to TBP extraction to fit the solvent containing 1.2M DA[AP]. Based on limited data collected by the Chemistry Division staff, the extraction behavior of strontium and several other metal-ion nitrate salts in the TRUEX-SREX process has been modeled and incorporated into the GTM.

A flowsheet was developed to conduct cold tests of the TRUEX-SREX process with nitric acid in a minicontactor. The combined TRUEX-SREX solvent will selectively extract and partition U, Sr, Bi; the TRU elements such as Am and Pu; the lanthanides; and most of the Tc from Hanford dissolved sludge wastes. Using the GTM and, when appropriate, additional data specific to the TRUEX-SREX process, we evaluated the various sections of the flowsheet design to verify that they will meet process goals for the subsequent tests with radioactive materials. This modeling effort indicated that solvent loading of U and Bi will be important in the final process design. This loading will be important not only because of possible third-phase formation but also reduced distribution ratios for Am, Bi, and the lanthanides in the extraction section.

A 20-stage minicontactor was set up to experimentally verify the calculated nitric acid concentrations for the TRUEX-SREX flowsheet. Preliminary tests were initiated to check that this equipment will work properly when (1) the new TRUEX-SREX solvent, which has a high solvent density, is used, and (2) a new aqueous-phase sampling system is in place for selected contactor stages. The tests with the actual process solvent were postponed after the dispersion number for the solvent was measured and found to be too low. We have formulated a new solvent which appears to resolve these problems. Cold testing will begin once this new solvent is prepared.

The GTM was used to design a TRUEX flowsheet for treating plutonium-containing waste (~200 L) generated at ANL and the New Brunswick Laboratory. The plutonium product stream from Batch 1 has been evaporated and calcined. Two batches of oxide were produced from the calcination. Batch 1a weighed 6.40 g containing 6.20 g Pu, and Batch 1b weighed 21.20 g containing 3.39 g Pu. Batch 1b was also contaminated with sodium and potassium. After washing Batch 1b with water to remove sodium and potassium, the weight decreased to 5.5 g.

A second batch of waste (containing 13 g plutonium and 16 g uranium) was processed over four days. Also processed was solution containing raffinate from Batch 2 that had unacceptable high activity

levels, acidified carbonates from Batch 2, and various solutions from the glovebox. This processing took only a single day to complete.

A tear in the feed carboy caused Batch 2 to leak into a secondary container. Unfortunately, the lead shielding for this carboy was placed in between the carboy and the secondary container. The highly acidic feed dissolved some of the lead shielding. Therefore, Batch 2 and Batch 2 Waste contained lead, making these solutions mixed waste. Tests were completed to determine if the lead could be precipitated, making the supernatant liquid simply radioactive waste. The lead was not precipitated by either hydroxide or sulfate. Because Waste Management Operations at ANL picked up the waste as is, no further testing or processing was completed.

Based on an analysis of the process streams for Batch 2 and Batch 2 Waste, we completed a plutonium and uranium material balance. A total of 12.0 g of plutonium was recovered from the 12.5 g of plutonium remaining in the feed after the feed carboy leak, for a 95% total plutonium recovery. An estimated 15.3 g of uranium remained in the feed after the feed carboy leak, of which 14.5 g was recovered, for a 95% total uranium recovery.

An effort has been initiated to develop evaporator technology for concentrating radioactive waste and product streams such as those generated by the TRUEX process. A laboratory-scale evaporator fabricated by LICON Inc. was delivered and installed during this report period. Minor equipment changes were made to ensure safe operability. Documentation and data log sheets have been developed, and a safety review was undertaken. Two shakedown runs using feeds of salt solutions were completed.

Prediction of the vapor composition in equilibrium with complex aqueous solutions is an important need in designing evaporator systems for recovering nitric acid from process and product streams. According to Raoult's law, the thermodynamic activities of nitric acid and water in an aqueous solution are proportional to their partial pressures in the vapor above that solution. Work was begun in FY 1992 to extend GTM correlations that calculate activities from the present 25°C to all applicable temperatures. This approach called for adding temperature dependencies to the modified Bromley equations used in the GTM. Early results show that fitting the binary system (nitric acid/water) called for first-order temperature dependencies for three of the six constants in the modified Bromley equation. Our early work in fitting literature data for vapor compositions above ternary systems that include a nitrate salt constituent shows that determining temperature dependencies for the activities of all components may be necessary for accurate vapor-composition predictions.

Technology based on membrane-assisted solvent extraction to remove volatile organic compounds from groundwater is also under development. Experimental data required to design the system are being reviewed, and a preliminary design is discussed.

I. INTRODUCTION

(G. F. Vandegrift)

The Division's work in separation science and technology is mainly concerned with developing a technology base for the TRUEX (TRansUranic EXtraction) solvent extraction process. The TRUEX process extracts, separates, and recovers TRU elements from solutions containing a wide range of nitric acid and nitrate salt concentrations. The extractant found most satisfactory for the TRUEX process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is abbreviated CMPO. This extractant is combined with tributyl phosphate (TBP) and a diluent to formulate the TRUEX process solvent. The diluent is typically a normal paraffinic hydrocarbon (NPH) or a nonflammable chlorocarbon such as carbon tetrachloride (CCl_4) or tetrachloroethylene (TCE). The TRUEX flowsheet includes a multistage extraction/scrub section that recovers and purifies the TRU elements from the waste stream and multistage strip sections that separate TRU elements from each other and the solvent. Our current work is focused on facilitating the implementation of TRUEX processing of TRU-containing waste and high-level defense waste, where such processing can be of financial and operational advantage to the DOE community.

The major effort in TRUEX technology-base development involves developing a generic data base and modeling capability for the TRUEX process, referred to as the Generic TRUEX Model (GTM). The GTM will be directly useful for site-specific flowsheet development directed to (1) establishing a TRUEX process for specific waste streams, (2) assessing the economic and facility requirements for installing the process, and (3) improving, monitoring, and controlling on-line TRUEX processes. The GTM is composed of three sections. The heart of the model is the SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) code, which calculates multistaged, countercurrent flowsheets based on distribution ratios calculated in the SASPE (Spreadsheet Algorithm for Speciation and Partitioning Equilibria) section. The third section of the GTM, SPACE (Size of Plant and Cost Estimation), estimates the space and cost requirements for installing a specific TRUEX process in a glovebox, shielded-cell, or canyon facility. The development of centrifugal contactors for feed- and site-specific applications is also an important part of the effort.

Two other projects have recently been initiated in separation science and technology. The objectives of these projects are to develop (1) a membrane-assisted solvent extraction method for treating natural and process waters contaminated by volatile organic compounds and (2) evaporation technology for concentrating radioactive waste and product streams such as those generated by the TRUEX process.

II. GENERIC TRUEX MODEL IMPROVEMENTS

A. Enhancements to Generic TRUEX Model (J. M. Copple)

The GTM version 2.4.3 was distributed to Macintosh and IBM-PC users during April 1992. The major changes in this release are displayed in Table 1.

Table 1. Major Revisions to the Generic TRUEX Model, Version 2.4.3

-
- Additional speciation has been added to the SASPE module of the GTM: ZrF_4 , ZrF_5 , ZrF_6 , and $\text{Pu}(\text{C}_2\text{O}_4)_3$ have been added.
 - Thorium was added to the loading effect module.
 - The macro CMPOf_TBPF.XLM (CMPO_TBP on the Macintosh) has been combined with the macro DVALUES.XLM (D_Values on the Macintosh) to speed up execution of the GTM.
 - When the GTM terminates with a known error, the error is logged in a file.
 - The speciation calculations inside SASPE have been improved. New equations for initial guesses were added to the speciation calculations to help it converge faster. An error was corrected in taking the partial derivatives of hydrogen with respect to zirconium and hydrogen with respect to phosphate in the Newton-Raphson algorithm. This error did not affect the final answer but did affect the rate of convergence for the algorithm.
 - The M&S Equipment Cost Index in SPACE for the years 1989 and 1990 was changed to actual values instead of estimates.
-

The newest GTM version runs quicker due to combining two files. "D_Values," the file that calculates the distribution ratios of specified components, was combined with SASPE, the file that calculates speciation. During a typical case, 21 min was cut off the run. Although the size of the combined files takes 45K bytes more disk space than the sum of the two files, the time to calculate the results decreased since there was no longer a need to pass information between the two files. As an added bonus, the IBM-PC version requires less system resources since one less file has to be open. The combined file is called SASPE. The D_Values file will no longer be included with the GTM.

In addition, the diluent for the SREX (strontium extraction) process was added in the GTM.

B. Development of Spreadsheet Algorithms for Speciation and Partitioning Equilibria (M. C. Regalbuto and G. F. Vandegrift)

The SASPE (Spreadsheet Algorithms for Speciation and Partitioning Equilibria) section of the GTM will calculate distribution ratio (D) values for each aqueous phase composition selected from the feed menus or generated in SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction). The many modules to the SASPE section include charge-balance checks of the feed solution, estimates of densities of complex aqueous solutions, molar-to-molal activities of aqueous phase species, oxalic-acid additions to fission-product-containing waste to restrict zirconium extraction, aqueous-phase and organic-phase speciation of individual components, and individual-component distribution ratios.

Another one of these SASPE modules calculates a unique solution to the mass-balance equations for $\text{CMPO}_{\text{free}}^*$ and $\text{TBP}_{\text{free}}^*$ during HNO_3 extraction by the TRUEX solvents. This module generated a set of quadratic equations in which TBP_{free} and $\text{CMPO}_{\text{free}}$ could not be solved explicitly. A module named $\text{CMPO}_{\text{free}}\text{-TBP}_{\text{free}}$ was therefore created, and the two equations were combined to eliminate TBP_{free} so that only one equation written in terms of $\text{CMPO}_{\text{free}}$ needed to be solved. The macro used the Newton-Raphson method to obtain the molar concentration of $\text{CMPO}_{\text{free}}$. Starting with an initial guess for the concentration of $\text{CMPO}_{\text{free}}^i$, the next estimate is

$$\text{CMPO}_{\text{free}}^{i+1} = \text{CMPO}_{\text{free}}^i - \frac{f(\text{CMPO}_{\text{free}}^i)}{f'(\text{CMPO}_{\text{free}}^i)} \quad (1)$$

When a value for $\text{CMPO}_{\text{free}}^i$ concentration was obtained that satisfied the combined mass-balance equation, the molar concentration of TBP_{free} was calculated by using the converged $\text{CMPO}_{\text{free}}$. After the values for $\text{CMPO}_{\text{free}}$ and TBP_{free} were computed, the molar concentration of $[\text{HNO}_3]_{\text{org}}$ was calculated.

There were a few discrepancies in the way that the $\text{CMPO}_{\text{free}}$, TBP_{free} , and $[\text{HNO}_3]_{\text{org}}$ equations were initially programmed into SASPE. The constants used to solve for $\text{CMPO}_{\text{free}}$ and TBP_{free} differed from those used to calculate HNO_3 ; therefore, the values generated by the module were wrong. Appropriate changes were made to reflect the fact that the same constants need to be used to calculate $\text{CMPO}_{\text{free}}$, TBP_{free} , and $[\text{HNO}_3]_{\text{org}}$. The equations solved by the upgraded $\text{CMPO}_{\text{free}}\text{-TBP}_{\text{free}}$ module are as follows:

$$\text{Cm}_1 = 1 + \text{Kc}_1 \cdot a_{\text{H}} + \text{Kc}_2 \cdot a_{\text{H}}^2 + \text{Km}_1 \cdot a_{\text{H}} \cdot \text{TBP}_{\text{free}} + \text{Km}_2 \cdot \text{TBP}_{\text{free}} \quad (2)$$

$$\text{CMPO}_{\text{free}} = \frac{-(\text{Cm}_1) + \sqrt{(\text{Cm}_1)^2 + 8\text{Kc}_3 \cdot a_{\text{H}} \cdot \text{CMPO}_{\text{T}}}}{4 \text{Kc}_3 \cdot a_{\text{H}}} \quad (3)$$

$$\text{Tm}_1 = 1 + \text{Kt}_1 \cdot a_{\text{H}} + \text{Km}_1 \cdot a_{\text{H}} \cdot \text{CMPO}_{\text{free}} + \text{Km}_2 \cdot \text{CMPO}_{\text{free}} + \text{Kt}_3 \cdot a_{\text{H}}^2 \quad (4)$$

$$\text{TBP}_{\text{free}} = \frac{-(\text{Tm}_1) + \sqrt{(\text{Tm}_1)^2 + 8\text{Kt}_2 \cdot a_{\text{H}} \cdot \text{TBP}_{\text{T}}}}{4 \text{Kt}_2 \cdot a_{\text{H}}} \quad (5)$$

$$\begin{aligned} [\text{HNO}_3]_{\text{org}} = & (\text{Kc}_3 \cdot a_{\text{H}}) \text{CMPO}_{\text{free}}^2 + (\text{Kc}_1 \cdot a_{\text{H}} + 2\text{Kc}_2 \cdot a_{\text{H}}^2) \text{CMPO}_{\text{free}} \\ & + (\text{Kt}_2 \cdot a_{\text{H}}) \text{TBP}_{\text{free}}^2 + (\text{Kt}_1 \cdot a_{\text{H}} + 2\text{Kt}_3 \cdot a_{\text{H}}^2) \text{TBP}_{\text{free}} \\ & + (\text{Km}_1 \cdot a_{\text{H}} + \text{Km}_2) \text{CMPO}_{\text{free}} \text{TBP}_{\text{free}} \end{aligned} \quad (6)$$

where $\text{CMPO}_{\text{free}}$ and TBP_{free} are the concentrations of free CMPO and TBP; CMPO_{T} and TBP_{T} are the total molar concentrations of CMPO and TBP; Cm_1 and Tm_1 are variables used to simplify Eqs. 3 and 5. The variable a_{H} defines the activity of nitric acid in the aqueous phase, and Kc_1 , Kc_2 , Kc_3 , Kt_1 , Kt_2 , Kt_3 , Km_1 , and Km_2 are all extraction constants, given in Table 2.

* That is, not forming an organic-phase compound with nitric acid (e.g., $\text{TBP} \cdot \text{HNO}_3$, $\text{CMPO} \cdot 2\text{HNO}_3$).

Table 2. Extraction Constants for the HNO_3 /TRUEX System at 25°C

Constant	Diluent	
	NPH ^a	TCE ^b
Kc_1	1.89	1.6
Kc_2	0.044	0.01
Kc_3	4.63	1.66
Kt_1	0.181	0.157
Kt_2	0.356	0.203
Kt_3	0.0001	0
Km_1	1.74	1.75
Km_2	0	0

^a0.2M CMPO/1.2M TBP in a normal paraffinic diluent.

^b0.25M CMPO/0.75M TBP in tetrachloroethylene.

As a result of the above work, the $\text{CMPO}_{\text{free}}\text{-TBP}_{\text{free}}$ module in the GTM was revised. In this revision, corrections were made to the equations used to calculate $\text{CMPO}_{\text{free}}$, TBP_{free} , and HNO_3 . The corrections reflect the addition of the constant Kt_3 in the equations that calculate the concentrations of TBP_{free} and the addition of the constant Km_2 in the equations used to calculate HNO_3 concentrations.

III. DATA COLLECTION FOR GENERIC TRUEX MODEL

The mechanistic- and thermodynamic-based equations in the GTM predict the solution and extraction behavior of feed components over a wide range of possible waste-stream and processing conditions. Our recent efforts have been concentrated on adding thermodynamic extraction models for components of interest at DOE waste sites.

A. Zirconium Behavior (S. Howard and L. Nuñez)

Zirconium is an important component in nuclear fuel cladding. As the nuclear fuel is dissolved, the zirconium is present in large concentrations. To account in the GTM for the complex zirconium chemistry, a solvent extraction model must be determined on the basis of measured or calculated distribution ratios. Previously, some experimental distribution ratios were measured with zirconium radiotracer, but the zirconium chemistry at tracer level is plagued with complications such as metastability as a function of time, polymer formation, and species affinity toward glass and dust. Finally, the tracer concentrations are not realistic to existing nuclear waste. An alternative to tracer studies is neutron activation analysis (NAA), where larger concentrations of zirconium can be studied.

Neutron activation analysis allows one to measure the amount of a given element X contained in some material Y. The basic steps include irradiating Y with a source of ionizing radiation so that X changes to X*, a radioactive isotope of X. An instrumental technique can be employed to "isolate" X and X* from all other elements in Y (not necessarily totally); the activity of X* is then measured. From this point, the amount of X present can be calculated. For example, in this work, the amount of zirconium in an aqueous or organic solution will be measured. The equation for the reaction that will be occurring is:

The ZrF_4 may not be in high abundance with low zirconium concentrations (10^{-8} to 10^{-9} M). Earlier tracer studies for zirconium extraction behavior in solutions containing high fluoride concentrations have not agreed with results at Pacific Northwest Laboratories using actual waste solutions.¹ Data were needed at higher zirconium concentrations; NAA determination of distribution ratios at higher concentrations of zirconium may be used to assess the effect of fluoride ion. With many distribution ratio measurements for zirconium, the stability constants and thermodynamic equilibrium constants for organic-phase complexes can be determined. These experiments will be performed at University of Illinois (UI) facilities.

For short-lived neutron activation analysis, both thermal [1.2×10^{13} n/(cm²·s) at 1.5 MW] and epithermal cadmium-lined [1.0×10^{12} n/(cm²·s) at 1.5 MW] irradiation facilities with "rabbit" carriers are available at UI. To account for proper irradiation times, an electronic timer with measurements to one-tenth of a second is in place. For long-term irradiations, a "lazy-Susan" facility with a thermal flux of 3.3×10^{12} n/(cm²·s) at 1.5 MW is capable of irradiating up to 80 samples simultaneously. For higher neutron fluxes, an in-core facility for thermal [1.2×10^{13} n/(cm²·s) at 1.5 MW] and epithermal [1.0×10^{12} n/(cm²·s) at 1.5 MW] irradiation positions is also available.

The UI neutron activation facility is located in the Materials Research Laboratory, where the "rabbit" terminal and counting equipment are available. Three setups are present: a 19% efficient

germanium detector in conjunction with a Compton Suppression system, a 13% efficient γ -X detector capable of detecting both X- and γ -rays, and a 24% efficient germanium detector in conjunction with a sample changer. A 15% efficient germanium detector is also available for use.

Each irradiated sample will be counted on a 13% efficient γ -X germanium counter for half an hour. The resolution of this detector is 2.0 keV at the 1332 keV cobalt-60 photopeak. The resolution is defined as the ratio of the full width at half-maximum (FWHM). The detector is calibrated at 400 eV/channel, and there are 8192 channels.

An important concept in NAA is the detection limit. The detection limit (L_D) is defined as the value at which a given analytical procedure may be relied upon to lead to detection. This value, for NAA, is the minimum number of counts detected above background to be certain that a radioisotope is present:

$$L_D = 4.65 \times \sqrt{C_B} \quad (8)$$

where C_B is the average background count for a gamma peak. This count is obtained from

$$C_B = \frac{C_L + C_R}{2} \times N \quad (9a)$$

where C_L and C_R are the number of counts in the channels just left and right of the peak, and N is the number of channels that the peak spans.² It is also possible to convert the detection limit to a minimum detectable concentration (C_m),

$$C_m = \frac{L_D \times C_i}{C_N} \quad (9b)$$

where L_D is the detection limit in counts, the concentration is in ppm, C_i is the radioisotope concentration, and C_N is the net counts (total counts in the peak minus C_B).

While NAA will be used to determine the zirconium distribution ratios, the GTM will be used to calculate the concentrations of the ZrF_n species in the solution, based on current literature stability constants for six zirconium fluoride species. We assumed that the neutral ZrF_4 species could be extracted by the TRUEX solvent. Figure 1 shows the calculated effect of HNO_3 concentration on the fraction of ZrF_4 concentration to total zirconium in solution.*

* Unless stated otherwise, calculations and experiments in this report are for 25°C.

Fig. 1. Effects of HNO₃ Concentration on the Fraction of ZrF₄ to Zirconium Solution (based on GTM speciation calculations). The fluoride concentration was held at four times that of zirconium.

B. Bromley Constants for H₃PO₄
(L. Nuñez)

Previous analysis of data from tracer and potentiometric titration experiments yielded a model for the H₃PO₄ extraction. In this report period, the activities of H₃PO₄ were calculated by using the literature values from vapor-phase pressure measurements (VPM). Data on the activity of water (a_w) in a H₃PO₄-H₂O system were reported by Elmore et al.³ for molalities ranging from 0.1659 to 217.4. To incorporate these data into the GTM, we obtained the constants for the activity of water in the H₃PO₄ system from the Bromley equation:

$$\log \gamma_{ij}^{\circ} = \frac{-A Z_i Z_j \sqrt{I}}{1 + B \sqrt{I}} + \beta I + C I^2 + D I^3 + \dots \quad (10)$$

where Z_i and Z_j are the charges of the cation and anion, I is the ionic strength, A is the Debye-Hückel constant, and A , B , β , C , D ,... are constants. Figure 2a shows the calculated values for $\log \gamma_{ij}^{\circ}$ for H₃PO₄-H₂O at 25°C, and Fig. 2b shows the calculated values for a_w determined for the following constants in Eq. 10: $B = 0.028$, $\beta = 0.100$, $C = -0.001$, $D = -4.821 \times 10^{-6}$, $E = 1.2045 \times 10^{-7}$. The plot (Fig. 2b) shows an excellent correlation of the reported values³ to the calculated values. For a range of 60 molal, the largest aberration is only 6.4%.

C. Fluoboric Acid Behavior
(B. Srinivasan)

Fluoboric acid (HBF₄) is one of the main constituents in some of the wastes containing transuranic elements at Idaho National Engineering Laboratory (INEL). In the TRUEX process, the

Fig. 2a. Plot of Calculated $\log \gamma_{ij}^{\circ}$ for $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$ System at 25°C

Fig. 2b. Plot of Calculated and Reported Activities of Water in $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$ System (Elmore et al.³) at 25°C

presence of HBF_4 may alter the extraction behavior of these elements into the organic phase. Hence, it is essential to know independently about the extraction properties of HBF_4 .

1. Quantitative Analysis of HBF_4

During this report period, a large fraction of the experimental effort was spent on establishing a reliable titrimetric method of analysis to estimate the concentration of HBF_4 in the aqueous and organic phases following extraction. Direct titration of HBF_4 against standard solution of alkali (NaOH) yields multiple end points, which proved difficult to interpret. Because HBF_4

hydrolyzes appreciably in dilute solutions, acid molecules that can react with NaOH to yield multiple endpoints are created. The hydrolysis reactions of HBF_4 are

The total concentration of HBF_4 (irrespective of the nature of the acid species) can be determined by hydrolyzing the HBF_4 completely to $\text{B}(\text{OH})_4^-$, and titrating the $\text{B}(\text{OH})_4^-$ formed against standard acid solution (HCl). The hydrolysis is carried out at elevated temperature (70 to 85°C) in the presence of excess Ca^{2+} to remove the HF formed as insoluble CaF_2 . As the hydrolysis proceeds, the solution is neutralized by the addition of alkali, and finally made alkaline ($\text{pH} > 11$) before titration with HCl. The equations governing hydrolysis are

The two equations governing titration are

The pH titration of the hydrolyzed solution results in two end points. The first end point represents the excess OH^- present in the solution, while the difference between the first and second end points represents the amount of $\text{B}(\text{OH})_3$ produced by hydrolysis and, therefore, the amount of HBF_4 in the titrated solution.

The concentrations of three different solutions of HBF_4 (approximately 0.08, 0.8, and 8M) were determined using the above procedure, and the results are shown in Table 3. Reproducible results were obtained when sufficient time was allowed for quantitative hydrolysis of HBF_4 in the samples. The kinetics of the hydrolysis reaction was not studied. However, this reaction appears to go to completion in about 3 h for all the samples studied.

The above titrimetry procedure was also used to determine the concentration of HBF_4 in solutions which are mixtures of HBF_4 and HNO_3 . In these cases, it is necessary to add enough alkali to neutralize the HNO_3 present in the samples before hydrolysis of HBF_4 . Again reproducible results were obtained (see Table 4).

2. Extraction of HBF_4

We studied the extraction of HBF_4 in aqueous solutions of pure HBF_4 (nearly 0.08M and 0.8M), as well as in mixtures of HBF_4 and HNO_3 (nearly 0.8M HBF_4 mixed with 0.1M or 0.5M

Table 3. Determination of HBF_4 Concentration in Concentrated and Dilute Solutions of HBF_4 . Analysis method involved hydrolysis followed by titration against standard HCl .

Determined Concentration of HBF_4 , M		
7.76M Sol. ^a	0.78M Sol. ^a	0.08M Sol. ^a
7.73	0.78	0.08
7.91	0.76	0.08
7.26	0.76	0.08
8.18	0.76	
7.66	0.78	
7.84	0.76	
7.85	0.81	
7.85	0.81	
7.85		
Mean: 7.79	0.78	0.08

^a Calculated from percent HBF_4 , density of stock solution, and dilution by water.

Table 4. Determination of HBF_4 Concentration in 0.76M HBF_4 ^a Mixed with Three Different Concentrations of HNO_3 . Analysis by hydrolysis followed by titration against standard HCl .

Determined Concentration of HBF_4 , M		
0.1M HNO_3 ^a	0.5M HNO_3 ^a	5M HNO_3 ^a
0.74	0.73	0.72
0.73	0.74	0.72
0.74	0.73	0.73
0.72	0.74	0.72
	0.74	0.73
	0.75	
Mean: 0.73	0.74	0.72

^a Calculated from percent HBF_4 , density of stock solution, and dilution by water.

or 5M HNO_3), by the TRUEX solvent (0.2M CMPO + 1.4M TBP in n-dodecane). The aqueous phase of the acid samples was contacted with the organic phase of the TRUEX solvent [organic-to-aqueous (O/A) volume ratio of 1:1] at 25°C. The aqueous and organic phases were separated following the contacts, and the HBF_4 concentrations in both the phases were determined by the titrimetry procedure given above. In the case of organic phases, the HBF_4 was back extracted into water, before the titrimetric analysis was initiated. Distribution ratios, defined as concentration of HBF_4 in organic phase divided by concentration of HBF_4 in aqueous phase, are given in Table 5.

It is proposed to continue determining D values for other mixtures of HBF_4 and HNO_3 as part of the ongoing effort to expand the GTM for radioactive wastes containing HBF_4 .

Table 5. Distribution Ratios for HBF_4 or Mixtures of HBF_4 and HNO_3 with the TRUEX Solvent

$[\text{HBF}_4], \text{M}$	$[\text{HNO}_3], \text{M}$	D Value
0.08		0.27
		0.21
0.78		0.36
		0.33
		0.35
		0.36
		0.37
		0.36
		0.31
		0.35
0.73	0.1	0.33
		0.33
0.74	0.5	0.28
		0.28
0.72	5	0.05
		0.05

D. Americium Behavior

(J. Sedlet and G. F. Vandegrift)

A rapid method for testing the purity of CMPO is to measure the distribution ratio of americium in dilute nitric acid solution. The impurities of concern are acidic agents that extract metal ions more efficiently at low aqueous phase acidities than the neutral CMPO, and thus give higher distribution ratios. These will be noticeable at low nitric acid concentrations when the distribution ratios are low. The distribution ratio at 0.01M HNO_3 is a measure of these impurities. Because very small concentrations of the impurities will affect the distribution ratio at this acidity, the concentrations of americium or other trivalent ions can affect the results.

A ^{241}Am stock solution was prepared in 0.01M HNO_3 . The addition of this stock solution would not change the acidity of the aqueous phase to which it is added. A small volume ($40\text{ }\mu\text{L}$) of this solution was added to 1 mL of 0.0102M HNO_3 and contacted with 1 mL of a used TRUEX solvent, which had been purified with several carbonate and water washes. The americium concentration in the aqueous phase was initially $\sim 4.0 \times 10^{-8}\text{M}$. The TRUEX solvent was pre-equilibrated by three contacts with equal volumes of 0.01M HNO_3 . This same extraction was repeated, except that the aqueous phase was made 10^{-4}M in cerium. In addition, the distribution ratios were also measured at 2M HNO_3 as a check on the laboratory procedure, since the ratio at this acidity is well known and would not be affected by the impurities. The results are shown in Table 6.

The distribution ratios at 2M HNO_3 are very similar to those found earlier, ~ 25 .⁴ At 0.01M HNO_3 , the ratio without Ce^{3+} present indicates a CMPO of satisfactory purity for a TRUEX solvent. A measure of the acidic impurity concentration is shown by the factor of two decrease in the presence of cerium ion. The cerium concentration was probably sufficient to react with all the acidic

Table 6. Distribution Ratios for ^{241}Am between Nitric Acid and TRUEX-Dodecane

$[\text{HNO}_3]$, <u>M</u>	$[\text{Am}^{3+}]$, <u>M</u>	$[\text{Ce}^{3+}]$, <u>M</u>	Dist. Ratio	Material Bal., %
0.01	4×10^{-8}	--	0.0138	100.1
0.01	4×10^{-8}	10^{-4}	0.0056	98.9
2.0	4×10^{-8}	--	24.5	100.1
2.0	4×10^{-8}	10^{-4}	25.0	104.0

impurities, but one cannot be certain without repeating the measurements at higher cerium concentrations. A reverse extraction could be performed at 0.01M HNO_3 if the americium concentration were increased by a factor of ten, and the counting were done by liquid scintillation. We suggest that these measurements be used as a test procedure for new workers to check their laboratory technique for performing distribution ratio measurements.

E. Bismuth Behavior (J. Sedlet and S. Weber)

Data on the distribution of bismuth between the organic and aqueous phases in the TRUEX process are being collected because, for the Hanford wastes now in single-shell 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, these Hanford wastes contain large amounts (of the order of grams per liter) of bismuth, which could be extracted by the TRUEX process.

A radioactive bismuth isotope, ^{210}Bi (1.16-MeV beta emitter, 5.01-day half-life), is being used to measure distribution ratios at the tracer level. The ratios will then be remeasured in the presence of low concentrations (milligrams per liter) of stable ^{209}Bi to determine the effect of solvent loading and bismuth solubility and hydrolysis. Isotopic exchange between ^{210}Bi and stable ^{209}Bi is expected to occur rapidly in moderately acidic solution ($\sim 1\text{M}$) since bismuth has only one oxidation state (3+) and is not hydrolyzed in strong acid solutions.

The Hanford wastes also contain large concentrations of sodium nitrate, since waste solutions contained nitric acid and were later neutralized to prevent corrosion of the steel tanks in which they were stored. The actinides form complexes with oxalate, fluoride, sulfate, and phosphate ions. Oxalate and fluoride may be used to strip the actinides from the solvent phase. Sulfate and phosphate may be present in the waste solution from the chemical processing. For these reasons, we also determined the distribution ratios of bismuth from aqueous solutions containing varying amounts of nitric acid with and without sodium nitrate, as well as solutions of sulfuric acid/sodium nitrate, and oxalic acid/nitric acid/sodium nitrate.

1. Analysis Methodology

Bismuth-210 is a convenient bismuth tracer since it can be repeatedly separated from its parent, ^{210}Pb , a weak beta emitter with a 22.3-yr half-life.* The ^{210}Pb is commercially available

*Bismuth-207 is preferable since it is a long-lived beta/gamma emitter, but it was not available when this work was begun.

since it is a member of the ^{238}U decay series and is a byproduct of uranium ore processing. The ^{210}Pb decay scheme is as follows:

If ^{210}Bi is separated from ^{210}Pb and from ^{210}Po , it can be used for distribution ratio measurements for about two weeks as long as sufficient radioactivity is obtained. At this time, our ^{210}Bi sample has grown back into ^{210}Pb to about 80% of its equilibrium value, and the ^{210}Bi can be separated again and used for further studies. It is important to retain all the ^{210}Pb and completely separate the ^{210}Po from the ^{210}Bi , since the measurement method to be used, liquid scintillation counting, will not distinguish the polonium alpha particle from the bismuth beta particle at high beta energies.

The separation method chosen for this work uses a crown ether, 4,4'(5')-bis-t-butylcyclohexano-18-crown-6, absorbed on a purified solid Amberlite resin and operated as a chromatographic column.⁵ The crown ether retains divalent ions very strongly, tetravalent less strongly, and trivalent ions poorly. Polonium has two oxidation states in aqueous solution, +2 and +4, and the divalent state is the most stable.

The separation procedure entails loading the column with ^{210}Pb from 1M HNO_3 , the acid concentration at which lead is most strongly absorbed, and eluting the ^{210}Bi with 1M HNO_3 to obtain a tracer solution for distribution ratio measurements. Because in practice some polonium also elutes, a second column is used to remove most of the polonium from the bismuth.

2. Measurement of ^{210}Bi - ^{210}Po Mixtures

If both ^{210}Bi and ^{210}Po are present and are counted in a liquid scintillation counter in an energy interval in which both are detected, the amounts of each can be calculated by counting at two or more different times during which appreciable decay of the ^{210}Bi occurs, since the two nuclides have different half-lives. The governing equations are

$$C(1) = B + P \quad (20)$$

$$C(2) = B \exp(-\lambda_b t) + P \exp(-\lambda_p t) + P' \quad (21)$$

$$P' = B[\lambda_p/(\lambda_p - \lambda_b)] [\exp(-\lambda_b t) - \exp(-\lambda_p t)] \quad (22)$$

where $C(1)$ and $C(2)$ are the total counting rates at the time of the first and second counts, respectively; B and P are the counting rates due to ^{210}Bi and ^{210}Po at the time of the first count, respectively; λ_b and λ_p are the decay constants of ^{210}Bi and ^{210}Po , respectively; P' is the counting rate of the ^{210}Po arising from the decay of ^{210}Bi ; and t is the time between the two counts. Substituting Eqs. 20 and 22 into 21 and solving for B yield

$$B = C(2) - C(1) \exp(-\lambda_p t)/(M + LM) \quad (23)$$

where $L = \lambda_p/(\lambda_p - \lambda_b)$ and $M = \exp(-\lambda_b t) - \exp(-\lambda_p t)$.

The decay of ^{210}Po , P , can now be calculated from Eq. 20. Equation 23 can be used for any pair of counts if the sample is counted several times, and with an electronic spreadsheet all pairs of counts can be calculated simultaneously. As indicated above, $C(1)$ and $C(2)$ should differ substantially for best results if significant ^{210}Bi is present.

3. Experimental

Small aliquots of the ^{210}Bi solution were added to the aqueous phase (nitric acid alone and with additives) in a glass culture tube, and an equal volume of solvent (TRUEX-NPH) was added. The tubes were placed in a 25°C constant temperature bath for 5 min. The phases were contacted with a vortex mixer for three 20 s intervals, followed by centrifuging for 1 min. Between each 20-s contact and before centrifugation, the tubes were replaced in the constant temperature bath. After centrifuging, the phases were separated with the use of Pasteur transfer pipettes, and aliquots of each phase were mixed with 10 mL of Packard Instrument Company Ultima Gold XR scintillation cocktail and counted for beta activity in a Packard liquid scintillation counter. This procedure produced results for the forward extraction given below. One-half of the organic phase was transferred to a second culture tube, an equal volume of fresh aqueous solution was added, and the extraction and ^{210}Bi measurement procedure described above was repeated. The results given below for the reverse extraction were obtained by this procedure.

In one series of experiments, the ^{210}Bi was added to the organic phase before the first extraction. For aqueous solutions that contained only nitric acid, the TRUEX-NPH solvent was preequilibrated with nitric acid by three contacts with equal volume portions of fresh nitric acid of the same concentration used in the ^{210}Bi extraction. For solutions containing sodium nitrate as well, preequilibration is not feasible because the distribution ratios for nitric acid are too high. Instead, the equilibrium nitric acid concentrations were calculated with the GTM.

4. Results and Discussion

The distribution ratios for ^{210}Bi in nitric acid solutions are given in Table 7. Reproducible results were generally not obtained below 1M HNO_3 . The values in parentheses in this table are the material balances, which were usually low at low acidities. This implies that the bismuth tracer may have been partially hydrolyzed and lost by concentration on the glass surface or at the liquid/glass interface. To correct for this problem, various methods for making the tracer solution were attempted, as described in the footnotes to the table. The only consistent data obtained have been for 2M HNO_3 and greater. A "solvent loaded" tracer solution was prepared by extracting the ^{210}Bi from Tracer 3 into TRUEX-NPH (pre-equilibrated with 1.0M HNO_3), and adding the "solvent loaded" tracer (Tracer 3A) to the organic phase to perform the contacts. Except at the lowest concentration, the results appear more consistent than usual, and this method of preparing the tracer will be studied further.

Distribution ratio measurements were also performed with $\text{HNO}_3/\text{NaNO}_3$ solutions since such values are needed to model bismuth behavior, and we believe that the ^{210}Bi tracer would behave reproducibly at high nitrate concentrations due to complex formation. Table 8 shows the nitric acid concentrations found by titration for the $\text{HNO}_3/\text{NaNO}_3$ solutions. The calculated equilibrium nitric acid concentrations together with the ^{210}Bi distribution ratios at those concentrations are shown in Table 9 and plotted in Figs. 3-6.

Table 7. Distribution Ratios for ^{210}Bi between Nitric Acid and TRUEX-NPH

[HNO ₃], M	Tracer 1, Run 1		Tracer 1, Run 2		Tracer 1A		Tracer 2		Tracer 2		Tracer 2A		Tracer 3		Tracer 3A	
	Forward	Reverse	Forward	Reverse	Forward	Reverse	Forward	Reverse	Forward	Reverse	Forward	Reverse	Forward	Reverse	Forward	Reverse
0.00951			0.394	4.72 (26%)			0.30 (36%)	0.68 (34%)	0.097 (109%)	0.25 (106%)	0.0101 (105%)	0.015 (97%)	0.04 (76%)	0.036 (81.9%)	0.100 (94%)	0.049 (96.69%)
0.0481	17.8	39.9 (90%)													5.88 (94%)	3.52 (96.69%)
0.0958			31.7	179 (95%)			34.8 (96%)	60.0 (100%)					2.41 (80.1%)	2.85	16.47	11.2
0.192	115	710 (74%)														
0.359			186	350 (97%)											41.4	44.4
0.986	619	1703 (86%)					80.7	106 (99%)					116.7 (81.8%)			
1.98					61.5 (89%)	60.8 (97%)										
3.99					20.0 (87%)	19.5 (96%)	18.3	16.2 (94%)	18.6 (100%)	18.9 (103%)	36 (96%)	20.7 (98%)	22.37 (86%)	20.19 (96%)	20.7 (100%)	17.9 (97%)
5.78					6.78 (86%)	6.4 (96%)										
7.69					3.42 (84%)	2.92 (89%)										

Notes: Tracer 1 = Prepared without carrier

Tracer 1A = Tracer 1 with Bi carrier added ($2.5 \times 10^{-5}\text{M Bi}^{3+}$)Tracer 2 = ^{210}Bi collected from column into $1\text{M HNO}_3 + 10^{-6}\text{M Bi}^{3+}$ solutionTracer 2A = Aqueous phase made 10^{-3}M in Bi^{3+} before Tracer 2 was addedTracer 3 = ^{210}Bi eluted from column with $1\text{M HNO}_3 + 10^{-3}\text{M Bi}^{3+}$

Tracer 3A = Tracer 3 extracted into TRUEX-NPH; aliquots of TRUEX-NPH added to organic phase

Table 8. Titrated Acid Concentrations vs. Prepared Concentrations^a

[HNO ₃], <u>M</u> Nominal	Titrated [HNO ₃], <u>M</u>			
	0.3 <u>M</u> NaNO ₃	1.0 <u>M</u> NaNO ₃	4.4 <u>M</u> NaNO ₃	7 <u>M</u> NaNO ₃
0.01	0.00996	0.00879	0.008124	0.00742
0.03	0.02809	0.02677	0.02406	0.02577
0.05	0.04705	0.0451	0.04218	0.04302
0.1	0.09371	0.08757	0.08248	0.09134
0.5		0.4681	0.4736	
1		0.9694	0.9297	
2		1.8973	1.864	
3			2.7685	
4		3.7922		

^aBase was standardized with potassium acid phthalate.Table 9. Aqueous Nitric Acid Concentrations and Bismuth Distribution Ratios for Contacts between HNO₃/NaNO₃ Salt Solutions and TRUEX-NPH Solvent. Nitric acid concentrations calculated with GTM.

[HNO ₃] Forward, <u>M</u>	Distribution Ratio	[HNO ₃] Reverse, <u>M</u>	Distribution Ratio
0.3 <u>M</u> NaNO ₃			
0.001564	14.7	0.002615	1052
0.003866	17.14	0.007357	2703
0.006986	17.9	0.01358	4385
0.01463	16.34	0.02961	2889
0.1377	989.31	0.302	409
0.4132	335.6	0.7986	115
0.9992	78.42	1.643	31.1
1.677	31.1	2.768	12.3
1.0 <u>M</u> NaNO ₃			
0.007647	27.77	0.009406	45.64
0.02142	49.03	0.02642	74.94
0.03565	16.56	0.04409	87.36
0.06999	26.93	0.08706	116.9
4.4 <u>M</u> NaNO ₃			
0.0004502	1880.7	0.0008844	5850
0.001634	2765.1	0.003333	197
0.002833	1082.5	0.005975	348
0.006701	7208.6	0.01541	8972
7 <u>M</u> NaNO ₃			
0.004746	137.37	0.006928	226.92
0.01454	268.72	0.02123	376.57
0.02458	304.21	0.03589	391.23
0.04821	348.38	0.07039	397.28
0.2746	304.06	0.3969	217.49
0.6217	191.78	0.883	139.06
1.26	91.24	1.738	61.28
2.725	26.52	3.577	15.97

Fig. 3.

Forward (▲) and Reverse (Δ)
Distribution Ratios for ^{210}Bi between
0.3M $\text{NaNO}_3/\text{HNO}_3$ Solutions and
TRUEX-NPH as a Function of
Equilibrium HNO_3 Concentrations

Fig. 4.

Forward (■) and Reverse (□)
Distribution Ratios for ^{210}Bi between
1M $\text{NaNO}_3/\text{HNO}_3$ Solutions and
TRUEX-NPH as a Function of
Equilibrium HNO_3 Concentrations

Fig. 5.

Forward (◆) and Reverse (◇)
Distribution Ratios for ^{210}Bi between
4.4M $\text{NaNO}_3/\text{HNO}_3$ Solutions and
TRUEX-NPH as a Function of
Equilibrium HNO_3 Concentrations

Fig. 6.

Forward (●) and Reverse (○)
Distribution Ratios for ^{210}Bi between
7M $\text{NaNO}_3/\text{HNO}_3$ Solutions and
TRUEX-NPH as a Function of
Equilibrium HNO_3 Concentrations

Although there is considerable scatter in the data, some general trends are apparent and are best shown by the 1M NaNO_3 solutions (Fig. 4). The distribution ratios initially increase with increasing nitric acid concentration, as is normally the situation with TRUEX solvent. However, as the nitric acid concentration in the organic phase increases, a point is reached at which the nitric acid ties up sufficient CMPO to cause the bismuth distribution ratio to decrease. This maximum bismuth extraction occurs at about 0.1M HNO_3 in 1M NaNO_3 solutions and at about 0.01M HNO_3 in 4.4M NaNO_3 . This difference is due to the increased nitric acid extraction at high salt concentrations.

Additional distribution ratios were measured for aqueous phases containing a constant nitrate ion concentration of 3.2M, plus varying amounts of nitric, oxalic, and/or sulfuric acids. The results are shown in Tables 10-12 and are plotted in Figs. 7-9. For solutions containing nitric acid and 3.2M nitrate ion (Table 10 and Fig. 7) the distribution ratios are large due to the high nitrate concentration, but again reach a maximum as the nitric acid concentration increases. Similar comments apply to the results for the sulfuric acid solutions (Table 11 and Fig. 8). The ratios are high, so sulfate does not form a strong complex with bismuth. This is not the case for oxalate ion (Table 12 and Fig. 9). The presence of 0.01M oxalic acid lowers the distribution ratio by four orders of magnitude (compare Figs. 8 and 9). This result may be the key to stopping the extraction of bismuth by the TRUEX solvent.

Table 10. Distribution Ratio for ^{210}Bi between Nitric Acid/Sodium Nitrate Solutions with a Constant Nitrate Concentration of 3.2M and TRUEX-NPH Solvent

$[\text{HNO}_3],^a$ M	$[\text{NaNO}_3],$ M	Dist. Ratio		Material Balance, %	
		Forward	Reverse	Forward	Reverse
0.01	3.19	159	1102	100.0	102
0.1	3.10	103	1432	97.1	104
0.5	2.70	641	443	99.7	98.9
1.0	2.20	263	170	101.1	100

^aConcentration before equilibration.

Table 11. Distribution Ratio for ^{210}Bi between Sulfuric Acid/Sodium Nitrate Solutions and TRUEX-NPH Solvent

$[\text{H}_2\text{SO}_4],^a$ <u>M</u>	$[\text{NaNO}_3],^a$ <u>M</u>	Dist. Ratio		Material Balance, %	
		Forward	Reverse	Forward	Reverse
0.01	3.2	675	1308	106	99.9
0.02	3.2	623	1413	103	99.7
0.03	3.2	797	1319	122	103.8
0.05	3.2	674	960	102	99.6

^aConcentration before equilibration; HNO_3 is highly extractable from these aqueous solutions.

Table 12. Distribution Ratio for ^{210}Bi between Oxalic Acid/Nitric Acid/Sodium Nitrate Solutions and TRUEX-NPH Solvent

$[\text{H}_2\text{C}_2\text{O}_4],^a$ <u>M</u>	$[\text{HNO}_3],^a$ <u>M</u>	$[\text{NaNO}_3],$ <u>M</u>	Dist. Ratio	Material Balance, %
0.01	0.02	3.18	0.00943	98.3
0.02	0.02	3.18	0.00346	100.5
0.03	0.02	3.18	0.00224	94.9
0.04	0.02	3.18	0.00158	101.8

^aConcentration before equilibration; HNO_3 is highly extractable from these aqueous solutions.

Fig. 7. Distribution Ratios for ^{210}Bi between Sodium Nitrate/Nitric Acid Solutions and TRUEX-NPH as a Function of Initial Nitric Acid Concentration. The nitrate ion concentration was kept constant at 3.2M by the addition of sodium nitrate.

Fig. 8. Distribution Ratios for ^{210}Bi between Sulfuric/ Nitric Acid Solutions and TRUEX-NPH as a Function of Sulfuric Acid Concentration in 3.2M Sodium Nitrate

Fig. 9. Distribution Ratios for ^{210}Bi between Oxalic Acid/ Nitric Acid/Sodium Nitrate Solutions as a Function of Oxalic Acid Concentration. The nitric acid and sodium nitrate concentrations were kept constant at 0.02M and 3.18M , respectively.

IV. DEMONSTRATION OF STRONTIUM EXTRACTION COMBINED WITH TRUEX

We have started a project to demonstrate the new TRUEX-SREX process, which is a combination of the TRUEX process and a recently developed SREX (strontium extraction) process. The TRUEX extractant, CMPO, selectively extracts and partitions Am, Pu, and U along with bismuth and the lanthanides. The SREX extractant, a crown ether called 4,4'(5')-di-*t*-butylcyclohexano-18-crown-6 (also referred to as D-*t*-BuCH18C6 or, simply, CE), selectively extracts and partitions strontium and, to some extent, technetium. The combined process would be the first step in the pretreatment of dissolved sludge waste from the Hanford site, so that the amount of nuclear waste that has to be vitrified is greatly reduced, with an attendant major reduction in waste disposal costs. Both processes were developed in the ANL Chemistry Division, and this demonstration project is a cooperative effort with that division. Our work includes detailed flowsheet development, solvent evaluation, and process demonstration on a laboratory scale using a centrifugal contactor.

A. Nitric Acid Extraction (G. F. Vandegrift)

In August, Horwitz et al. (ANL Chemistry Division) performed experiments to show that substituting diamyl(amy) phosphonate (DA[AP]) for TBP in the TRUEX-SREX solvent could essentially eliminate third-phase formation as a problem, even at high metal loading. This is certainly an improvement, but DA[AP] is a much stronger base than TBP and acts to extract more acid into the organic phase. To calculate a flowsheet for using this process solvent, we needed to change the model for nitric acid extraction in the GTM. To do this, the same set of equilibria employed for the TRUEX solvent was used, but the constants related to TBP extraction were modified to fit the solvent containing 1.2M DA[AP]. Figure 10 shows the fit of the modified GTM model to the experimental data. The fit is very good except at the lowest nitric acid concentration. This may be due to experimental uncertainty or to extraction of nitric acid by a species not accounted for in the model. The equations and constants for the TBP and DA[AP] solvents are shown in Table 13. Note that CMPO-alone constants were not modified.

Table 13. The HNO₃-Extraction Constants Varied to Fit DA[AP]-Solvent Data

Constant	DA[AP]- Solvent Value ^a	TBP-Solvent Value	Species ^b	Equations
KC3	4.63	4.63	EXT•HNO ₃	KT1*{HNO ₃ }*EXT _{free}
KC1	1.89	1.89	CMPO•HNO ₃	KC1*{HNO ₃ }*CMPO _{free}
KC2	0.044	0.044	EXT ₂ •HNO ₃	KT2*{HNO ₃ }*(EXT _{free}) ²
KT2	0.7	0.356	CMPO•2HNO ₃	KC2*{HNO ₃ } ² *CMPO _{free}
KT1	0.54	0.181	CMPO ₂ •HNO ₃	KC3*{HNO ₃ }*(CMPO _{free}) ²
KM1	3.2	1.74	CMPO•HNO ₃ •EXT	KM1*{HNO ₃ }*CMPO _{free} *EXT _{free}
KT3	0.0018	0.0001	EXT•2HNO ₃	KT3*{HNO ₃ } ² *EXT _{free}

^aBolded values were varied to fit DA[AP]-solvent data.

^bEXT = TBP or DA[AP].

As seen by Fig. 11, calculations predict DA[AP] extracts higher concentrations of nitric acid at all aqueous-phase nitric acid concentrations—varying from 75% more at the lower [HNO₃]_{aq} to

Fig. 10. Experimental vs. Calculated Organic-Phase Nitric Acid Concentration for TRUEX-SREX (DA[AP]) Solvent. See Table 13.

Fig. 11.

Organic Concentration of Nitric Acid vs. Aqueous-Phase Nitric Acid Concentration for 0.2M CMPO•1.2M EXT

23% at the highest $[\text{HNO}_3]_{\text{aq}}$ measured. Figures 12 and 13 show the organic-phase concentrations of the DA[AP]- HNO_3 and CMPO- HNO_3 species vs. the activity of nitric acid in the aqueous phase. Figures 14 through 17 compare how individual DA[AP]- HNO_3 and TBP- HNO_3 species concentrations vary with aqueous nitric acid concentrations. The constants in Table 13 have been incorporated in the GTM for designing flowsheets for this solvent.

Fig. 12. Concentration of DA[AP]• HNO_3 Species in TRUEX-SREX (DA[AP]) Solvent vs. Aqueous HNO_3 Activity

Fig. 13. Concentration of CMPO Species for TRUEX-SREX (DA[AP]) Solvent vs. Aqueous HNO_3 Activity

Fig. 14.

Concentration of $\text{HNO}_3 \cdot 2\text{EXT}$
vs. Aqueous HNO_3 Concentration

Fig. 15.

Concentration of $\text{HNO}_3 \cdot \text{EXT}$ Complex
vs. Aqueous HNO_3 Concentration

Fig. 16.

Concentration of $\text{EXT} \cdot 2\text{HNO}_3$
vs. Aqueous HNO_3 Concentration

Fig. 17.

Concentration of $\text{HNO}_3 \cdot \text{EXT} \cdot \text{CMPO}$
vs. Aqueous HNO_3 Concentration

B. Fitting of TRUEX-SREX Extraction Data to Nitrate Activities
(G. F. Vandegrift)

Based on limited TRUEX-SREX extraction data collected by Horwitz et al.,⁶ the extraction behavior of strontium and several other metal-ion nitrate salts has been modeled and incorporated into the GTM.

Fig. 18. Distribution Ratios of Strontium between Nitric Acid/Nitrate Salts and the TRUEX-SREX System

The calculated D values for strontium were derived as a function of nitrate activity, $\{\text{NO}_3^-\}$, by fitting the following equation:

$$D_{\text{Sr}} = K_1 \{\text{NO}_3^-\}^2 / (1 + K_2 \{\text{NO}_3^-\}) \quad (24)$$

The criterion used to optimize the fit

$$S = \sum_i \left[\frac{D_{\text{Sr}}(\text{calc}) - D_{\text{Sr}}(\text{exp})}{D_{\text{Sr}}(\text{calc}) + D_{\text{Sr}}(\text{exp})} \right]^2 \quad (25)$$

The fit of the GTM calculations to the measured data was very good, as shown in Fig. 18. The values for K_1 and K_2 to give the fit shown in Fig. 18 are 10.1 and 3.8, respectively.

In a recent programmatic review, Horwitz et al.⁶ reported on distribution ratios measured for a series of mono-, di-, and tri-positive metal ions in a complex aqueous solution containing 1 or 3M nitric acid. The composition of these solutions and the distribution ratio of the metal ions are presented in Tables 14-16, which are taken directly from that presentation. Although only two data points were available for each constituent, a model was needed in the GTM to calculate the distribution ratios for these species. Using these data and available nitrate ion complexation constants,⁷ an equation was generated for extraction of each constituent.

Table 14. Distribution Ratios of Inert Constituents in Dissolved Sludge Waste with Solvent of 0.2M CMPO-0.2M CE-1.2M TBP-Isopar-L. Provided by Horwitz, et al.⁶

Constituent	Conc., M	Distribution Ratios	
		1M HNO ₃	3M HNO ₃
Na	0.12	3.6×10^{-2}	9.3×10^{-2}
Mg	1.2×10^{-3}	2.7×10^{-2}	2.5×10^{-2}
Al	3.2×10^{-2}	6.1×10^{-3}	8.2×10^{-3}
Ca	9.4×10^{-4}	2.0×10^{-1}	1.7×10^{-1}
Mn	3.3×10^{-3}	1.2×10^{-2}	2.4×10^{-2}
Fe	0.11	5.3×10^{-2}	1.8×10^{-1}
Ni	5.6×10^{-3}	1.8×10^{-3}	2.1×10^{-3}
Cu	1.3×10^{-3}	6.9×10^{-3}	1.1×10^{-2}

Table 15. Distribution Ratios of Fission Products in Dissolved Sludge Waste with Solvent of 0.2M CMPO-0.2M CE-1.2M TBP-Isopar-L. Provided by Horwitz, et al.⁶

Constituent	Conc., M	Distribution Ratios	
		1M HNO ₃	3M HNO ₃
Rb	2.1×10^{-4}	0.19	0.31
Sr	1.0×10^{-3}	2.9	12
U	5.5×10^{-4}	1.8	1.7
Zr	2.4×10^{-3}	2.7×10^{-2}	5.2×10^{-2}
Mo	1.3×10^{-4}	2.3×10^{-1}	2.9×10^{-1}
Tc	Trace	9.1	3.7
Ru	1.6×10^{-3}	1.7×10^{-1}	1.2×10^{-1}
Rh	4.4×10^{-4}	$<5 \times 10^{-2}$	$<5 \times 10^{-2}$
Pd	4.7×10^{-4}	1.1	6.4×10^{-1}
Cd	3.4×10^{-5}	$<5 \times 10^{-2}$	1.2×10^{-1}
Cs	1.0×10^{-3}	3.4×10^{-2}	3.9×10^{-2}
Ba	4.6×10^{-5}	1.3	2.6

Table 16. Distribution Ratios of Lanthanide Fission Products in Dissolved Sludge Waste with Solvent of 0.2M CMPO-0.2M CE-1.2M TBP-Isopar-L. Provided by Horwitz, et al.⁶

Constituent	Conc., M	Distribution Ratios	
		1M HNO ₃	3M HNO ₃
La	8.7×10^{-4}	6.4	3.2
Ce	2.0×10^{-3}	11	5.9
Pr	7.0×10^{-4}	—	11
Nd	2.4×10^{-3}	10	7.2
Sm	2.2×10^{-4}	>10	8.0
Eu	4.3×10^{-5}	16	8.3

The method used to calculate the distribution ratio of $\text{Sr}(\text{NO}_3)_2$ was described above, and the two data points for strontium extraction were included in that fit. The other cations were treated in a similar manner, assuming that the cations were extracted as the neutral salt by the crown ether in the solvent. Therefore, the D values for these cations were proportional to the nitrate activity of the solution to the power of the cationic charge (e.g., $\{\text{NO}_3\}$ to the third power for aluminum and $\{\text{NO}_3\}$ to the first power for sodium). The second assumption is that nitrate complexes are formed in the aqueous phase; in some cases, data were available for complexation constants⁷; in others they were assumed analogous to similar elements. The equations used to fit the experimental data are presented in Table 17. Table 18 shows the nitrate, hydrogen, and water activities calculated by the GTM for the solutions identified in Tables 14-16. Figures 19-28 show the calculated curves for each D value vs. nitrate activity. These calculations are now included in the GTM. When more data become available, these equations will be upgraded.

Table 17. Equations Used for Calculated Distribution Ratios of Cations in the TRUEX-SREX Solvent System^a

Metal Ion	Charge	Equation for Distribution Ratio	Notes for Nitrate Complexation Constants
Na	1	$0.426 \cdot \{\text{NO}_3\} / (1 + 10^{-0.6} \cdot \{\text{NO}_3\})$	Ref. 7
Mg	2	$0.199 \cdot \{\text{NO}_3\}^2 / (1 + 10^{0.6} \cdot \{\text{NO}_3\} + 10^{0.7} \cdot \{\text{NO}_3\}^2)$	Guess based on Ca, Sr, Ba
Al	3	$0.0448 \cdot \{\text{NO}_3\}^3 / (1 + 10^{0.6} \cdot \{\text{NO}_3\} + 10^{0.7} \cdot \{\text{NO}_3\}^2 + 10^{0.5} \cdot \{\text{NO}_3\}^3)$	Guess based on Sc
Ca	2	$0.141 \cdot \{\text{NO}_3\}^2 / (1 + 10^{0.6} \cdot \{\text{NO}_3\} + 10^{0.7} \cdot \{\text{NO}_3\}^2)$	Ref. 7
Mn	2	$0.0258 \cdot \{\text{NO}_3\}^2 / (1 + 10^{0.1} \cdot \{\text{NO}_3\} + 10^{-0.2} \cdot \{\text{NO}_3\}^2)$	Guess based on Ca, Sr, Ba
Ni	2	$0.0149 \cdot \{\text{NO}_3\}^2 / (1 + 10^{0.6} \cdot \{\text{NO}_3\} + 10^{0.7} \cdot \{\text{NO}_3\}^2)$	Guess based on Ca, Sr, Ba
Cu	2	$0.0181 \cdot \{\text{NO}_3\}^2 / (1 + 10^{0.1} \cdot \{\text{NO}_3\} + 10^{0.5} \cdot \{\text{NO}_3\}^2)$	Guess based on Ca, Sr, Ba
Rb	1	$0.219 \cdot \{\text{NO}_3\} / (1 + 10^{-0.4} \cdot \{\text{NO}_3\})$	Guess based on Na, K
Sr	2	$10.9 \cdot \{\text{NO}_3\}^2 / (1 + 3.76 \cdot \{\text{NO}_3\})$	From fit of all Sr data
Cs	1	$0.0806 \cdot \{\text{NO}_3\} / (1 + 10^{0.2} \cdot \{\text{NO}_3\})$	Guess based on Na, K

^aData from Ref. 6; nitrate complexation constants from Ref. 7.

Table 18. Activities of Nitrate Ion, Hydrogen Ion, and Water in Complex Nitrate Salt Solution vs. Nitric Acid Concentration in TRUEX-SREX System

$[\text{HNO}_3]$ in Solution	$\{\text{NO}_3\}$	$\{\text{H}_2\text{O}\}$	$\{\text{H}\}$
1.00M	1.41	0.95	0.78
3.00M	4.42	0.85	3.45

Fig. 19.

Calculated Sodium Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

Fig. 20.

Calculated Magnesium Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

Fig. 21.

Calculated Aluminum Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

Fig. 22.

Calculated Calcium Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

Fig. 23.

Calculated Manganese Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

Fig. 24.

Calculated Nickel Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

Fig. 25.

Calculated Copper Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

Fig. 26.

Calculated Rubidium Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

Fig. 27.

Calculated Strontium Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

Fig. 28.

Calculated Cesium Distribution Ratios vs. Nitrate Activity for the TRUEX-SREX System

C. Combined TRUEX-SREX Processing

(R. A. Leonard, D. B. Chamberlain, C. J. Conner, G. F. Vandegrift,
D. G. Wygmans, J. A. Dow, and S. E. Farley)

We are demonstrating the combined TRUEX-SREX process on a laboratory scale using the ANL-designed centrifugal contactor. This effort is being carried out in cooperation with Phil Horwitz, Mark Deitz, and Herb Diamond, of the ANL Chemistry Division and Robin Rogers of the Chemistry Department, Northern Illinois University. Our initial tasks are to measure dispersion numbers for the new solvent, develop a detailed flowsheet for the process, and verify the nitric acid portion of the flowsheet experimentally in a 20-stage minicontactor (2-cm centrifugal contactor). After the initial tasks have been completed, the process flowsheet will be tested in the minicontactor with radioactive materials.

1. Flowsheet Development

A flowsheet for the combined TRUEX-SREX process, shown in Fig. 29, was developed for the cold tests such that they will lead to an appropriate design for the subsequent hot tests. The cold tests (C1, C2, and C3) focus on the concentration profile of nitric acid in a 20-stage minicontactor (2-cm centrifugal contactor). Using the GTM and, when appropriate, additional data specific to the combined TRUEX-SREX process, the flowsheet design was evaluated to ensure that it will meet process goals for the subsequent tests with radioactive materials. The hot test results will be used to design a flowsheet for the combined TRUEX-SREX process as it relates to the expected range of feed compositions for dissolved sludge waste (DSW) from Hanford single-shell tanks.

a. Solvent

The combined TRUEX-SREX solvent consists of 0.2M CMPO, 0.2M crown ether [the specific crown ether is 4,4'(5')-di-t-butylcyclohexano-18-crown-6, usually referred to here as CE or D-t-BuCH18C6], and 1.2M diamyl amylphosphonate (usually written as DA[AP] or DAAP) in Isopar M (a commercial isoparaffinic solvent from Exxon). This combined solvent is referred to here as PS 9. At the start of this project, 1.2M TBP was used as the phase modifier instead of DAAP because we discovered that DAAP allows for significantly greater loading of the uranium in the solvent without a second organic phase forming.

b. Feed Composition

The composition of the various feeds for the first cold test will be HNO_3 alone except for the carbonate wash section, which would remain 0.25M Na_2CO_3 . This test (C1) will allow us to verify that the nitric acid profile is as expected for the proposed flowsheet. Knowing the nitric acid concentration in each stage is central to designing the rest of the flowsheet. Two follow-on cold tests are planned. The first follow-on test (C2) adds $\text{H}_2\text{C}_2\text{O}_4$, $\text{Fe}(\text{NO}_3)_3$, and $\text{Sm}(\text{NO}_3)_3$ to the TRU feed and $\text{Al}(\text{NO}_3)_3$ to the first scrub feed. The second follow-on test (C3) adds, in addition, tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) to the strip feed. These components will be added as shown in Fig. 29.

c. Extraction Section

In the extraction section, the desired decontamination factor (D.F.) for strontium in DSW is 33,000. The D.F. value is 550 for Pu, 107 for Am, and 2 for Tc. Considering

Shaded stages indicate where aqueous phase will be sampled from the bottom of the stage at a rate of 0.33 mL/min. The nitric acid profile obtained will be compared with that given by the GTM. To offset sampling losses, the flow at DS is 7.3 rather than 6.0 mL/min; at EF, 4.0 rather than 3.0 mL/min. Numbers in () are relative flows for operation with no stage sampling.

Before the FP effluent is reused in Tests C2 and C3, it will be washed with 0.1 M HNO₃ at an O/A ratio of 2.0.

Fig. 29. Combined TRUEX-SREX Flowsheet for Cold Tests with HNO₃ (THFTCA = tetrahydrofuran-2,3,4,5-tetracarboxylic acid)

the expected D values for these components, given below, the key for the good extraction-section operation will be to attain the desired D.F. for strontium. As shown in Fig. 29, the extraction section will have six stages, an O/A flow ratio of 0.5, and a $[\text{HNO}_3]$ in the DF feed of 3M . With these operating conditions, the D.F. for strontium will be 4,100 in the extraction section if D_{Sr} is 7.6, a worst case value. This is almost a factor of 10 less than the desired D.F. of 33,000. Because of the high aluminum concentration from the scrub feed and the higher acid concentration in every stage except stage 1, D_{Sr} will be significantly higher than 7.6. For example, if D_{Sr} is 11 in every extraction stage, then we could meet the desired D.F. goal in six stages.

In the design of an actual plant for these operating conditions and the DSW feed, three more extraction stages would be added. The one additional stage should give the desired D.F. The other two stages would give the extraction section a robust design with respect to variations in flow rates and feed concentrations. Work within the ANL Chemistry Division shows that the distribution ratio for strontium stays high no matter how low the strontium concentration drops. Thus, we should expect continuing reductions of the strontium concentration in the aqueous (DW) raffinate with each additional extraction stage.

d. Scrub Section

To keep oxalate and fluoride ions in the DF feed from entering the strip section, we decided that the scrub (DS) feed should contain enough $\text{Al}(\text{NO}_3)_3$ to complex these anions and keep them in the aqueous phase. An analysis of this scheme showed that the dissolved solids in the strip (EW) raffinate would be mostly $\text{Al}(\text{NO}_3)_3$. To limit the aluminum in the strip raffinate to 10% of the strontium, a split scrub was designed. The first strip (DS1) feed to the second strip stage will contain 2M $\text{Al}(\text{NO}_3)_3$. The second strip (DS2) feed to the last scrub stage will contain 0.04M HNO_3 , i.e., essentially water. The number of stages in the second scrub was varied from 1 to 4 by using the GTM. From this evaluation, we found that two stages would be sufficient to reach our goal for the amount of aluminum in the strip raffinate. However, to obtain a nitric acid concentration of $0.1\text{--}0.25\text{M}$ in the organic phase leaving the scrub section, we had to use three stages in the second scrub.

Using the GTM and the SASSE worksheet, we showed that as the nitric acid concentration drops below the lower limit, we pinch the strontium in the scrub section. As we raise the nitric acid concentration above the upper limit, the ability of THFTCA to strip Am, Pu, and the rare earths is reduced. The exact amount of this reduction, which is a function of both $[\text{HNO}_3]$ and $[\text{THFTCA}]$, has not been measured at HNO_3 concentrations greater than 0.2M . When the phase modifier is TBP, two stages in the second scrub were calculated to be sufficient; when DAAP, three stages. This additional second scrub stage is required as DAAP extracts HNO_3 better than TBP. The effect of modifier on HNO_3 extraction is shown in Table 19. This table compares the D_{HNO_3} values measured by Herb Diamond (ANL Chemistry Division), where 1.2M DAAP was used as the modifier, with GTM (Version 2.5a) calculations using 1.2M TBP as the modifier. This effect of DAAP on the D values for HNO_3 has now been added to the GTM.

As a part of these GTM/SASSE calculations, the effect of the O/A flow ratio (1.5, 2.0, and 4.0) in the second scrub was evaluated. We looked at both the pinching of strontium in the scrub and the ability to scrub out HNO_3 . An O/A flow ratio of 2.0 gave the best balance between a high ratio that does not scrub out enough HNO_3 and a low ratio that pinches the strontium.

Table 19. Effect of Solvent Modifier on the D Values for Nitric Acid

$[\text{HNO}_3]_{\text{aq}}, \text{ M}$	D_{HNO_3} with DAAP as Modifier	D_{HNO_3} with TBP as Modifier	$\frac{D_{\text{HNO}_3}(\text{DAAP})}{D_{\text{HNO}_3}(\text{TBP})}$
0.0112	0.1518	0.0155	9.79
0.0957	0.178	0.0988	1.80
0.505	0.438	0.291	1.50
0.974	0.482	0.342	1.41
1.99	0.431	0.333	1.29
3.01	0.384	0.307	1.25
5.04	0.330	0.268	1.23

e. Strip Section

Several strip sections were considered. One plan called for two strip sections. The first strip would have used dilute nitric acid (0.04M) to extract americium as well as the lanthanides and strontium. The second strip would have used vinylidene diphosphonic acid (VDPA) or 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) in the range from 0.1 to 0.25M to take out most of the other metals in the solvent. Of the two acids, HEDPA is a better stripping agent than VDPA, but VDPA is easier to decompose than HEDPA. Both stripping agents leave a phosphate residue that would add to the number of glass logs that need to be formed. Because of this, THFTCA was considered as an alternative stripping agent. While THFTCA is harder to decompose, it leaves no phosphate residue. A problem with THFTCA is that there is no commercial source. Another possible stripping agent for the second strip is ammonium oxalate. This has proved to be very effective in our work with New Brunswick Laboratory wastes (see Sec. V). The drawback on a plant-scale process is that significant amounts of ammonium nitrate will be formed, which can be explosive under certain circumstances. Another possible stripping agent for the second strip is oxalic acid. The problem here is that oxalic acid forms precipitates at very low concentrations with some of the metals to be stripped.

As the problem of a commercial source for the THFTCA appears to be resolved, it was chosen as the stripping agent. After consideration of two feeds and two effluents in various combinations for the strip section, the final design is a strip/scrub section which will have two feeds but only one effluent. In this design, shown in Fig. 29, the THFTCA is introduced in the strip (EF) feed. Only dilute nitric acid is introduced at the strip scrub (ES) feed, which scrubs out the THFTCA as well as the Sr, Am, and lanthanides. It is desired to have THFTCA in the solvent going to the carbonate wash section contain only 0.03M THFTCA so that all the carbonate will react with the THFTCA and still have the bicarbonate ion left. If the D value for THFTCA is 0.5, this low THFTCA concentration will be reached. It now appears that the D value for THFTCA will be 0.6 or higher. If the D value is 0.6, as is the case for the calculations shown below, the THFTCA in the solvent going to the carbonate wash section will contain 0.041M THFTCA. During the cold tests, samples will be taken to determine both the concentration of THFTCA in the solvent leaving the strip scrub section and the ability of the carbonate wash to remove this THFTCA.

In the design the strip/scrub section, we can account for the effect of the THFTCA on D_{Am} , D_{Pu} , and D_{U} for various concentrations of THFTCA and HNO_3 . The results from experimental tests (H. Diamond, CHM Division) and calculated values (GTM version 2.5a) are shown in Figs. 30-32. They show that Am and Pu will be effectively stripped out to the low concentration level required for good process operation, while most of the U will be left in the solvent, where it will

be recovered in the carbonate wash section. For the flowsheet calculations, the appropriate D values have to be added to the SASSE worksheet for Am, Pu, and THFTCA in the strip/scrub sections as neither THFTCA nor the effects of THFTCA are included in the GTM. We used the GTM to calculate most D values and then corrected or added D values as needed to the SASSE worksheet to determine the final concentration profiles for each component. This approach is referred to here as the "GTM/SASSE calculations."

Fig. 30. Effect of THFTCA and HNO₃ on the D Value for Americium

Fig. 31. Effect of THFTCA and HNO₃ on the D Value for Plutonium

Fig. 32. Effect of THFTCA and HNO_3 on the D Value for Uranium

f. Carbonate Wash

The present plans call for a one-stage carbonate wash section to remove solvent-degradation components such as dibutyl phosphoric acid. Most of the U and Tc would also be removed in this section. The aqueous (FF) feed for this section would be 0.25M sodium carbonate. Two or three stages would be used instead of the one stage shown if we were not constrained to 20 stages for this test of the combined TRUEX-SREX process.

g. Acid Rinse

Because we have only 20 process stages, we plan to rinse the liter of FP solvent with 0.1M HNO_3 in a separatory funnel at an O/A ratio of 2.0 after test C1. This will re-acidify the solvent and prepare it for use in tests C2 and C3. The carbonate wash effluent will be checked first to ensure that it is still a basic solution, i.e., that it was able to take out all the THFTCA without being neutralized. If this is not the case, the solvent will be subjected to a second carbonate wash before the acid rinse.

2. Flowsheet Calculations with GTM

The combined TRUEX-SREX flowsheet was evaluated using GTM version 2.5a, which has been updated to include strontium extraction by the crown ether and the higher nitric acid extraction because DAAP is a part of the solvent in place of TBP. However, GTM 2.5a addresses neither the concentration of the stripping agent, THFTCA, nor the effect that THFTCA has on the D value for Am and Pu. These effects were determined by manually entering the appropriate D values in the SASSE worksheet from the GTM. The process flowsheet used for the GTM/SASSE analysis is shown in Fig. 33, the feed compositions are listed in Table 20, the D values in Table 21, and the results in Table 22. Note that the D value for THFTCA is assumed to be 0.6. Some results suggest that D values for THFTCA can be as high as 1.0. More data are needed in this area since this will affect the number of stages needed in the strip/scrub section to keep significant amounts of THFTCA from ending up in the sodium carbonate wash.

Fig. 33. Combined TRUOX-SREX Flowsheet Used in GTM/SASSE Calculations. Flows relative to TRU feed of 100 are shown in parentheses.

Table 20. Component Composition in Various Feed Streams for GTM/SASSE Calculations

	Component Concentration, <u>M</u>							
	Phase:	Org.	Aq.	Aq.	Aq.	Aq.	Aq.	Aq.
	Feed Code:	DX	DF	DS1	DS2	EF	ES	FF
	Feed Stage:	1	6	8	11	14	19	20
	Flow Rate, mL/min:	12	16	2	6	3	9	6
H		1E-15	3	0.01	0.04	0.01	0.01	0
Fe		1E-15	0.15	0	0	0	0	0
Bi		1E-15	0.001	0	0	0	0	0
Al		1E-15	0	2	0	0	0	0
La		1E-15	0.002	0	0	0	0	0
Tc		1E-15	0.000015	0	0	0	0	0
THFTCA		1E-15	0	0	0	1	0	0
Zr		1E-15	0.05	0	0	0	0	0
Sr		1E-15	0.0012	0	0	0	0	0
UO ₂		1E-15	0.001	0	0	0	0	0
Am		1E-15	6E-07	0	0	0	0	0
Pu ⁴⁺		1E-15	0.000017	0	0	0	0	0
F		1E-15	0.088	0	0	0	0	0
C ₂ O ₄		1E-15	0.2	0	0	0	0	0
PO ₄		1E-15	0.006	0	0	0	0	0

In using the GTM, it was necessary to revise its convergence criteria and make several other changes so that we could run at the high solvent loadings caused by high concentrations of U and Bi. With these changes, we found that, at a concentration of 0.03M for both UO₂²⁺ and Bi³⁺ in the DF feed, the solvent loading was such that most of the Am, Bi, and lanthanides came out in the DW raffinate. This was also true when both UO₂²⁺ and Bi³⁺ were 0.01M. At 0.001M for both UO₂²⁺ and Bi³⁺ in the DF feed, solvent loading was not a problem. This is the case that was used in Tables 20-22. Phil Horwitz (CHM Division) points out that UO₂²⁺ and Bi³⁺ loading of the solvent should be less severe than predicted by the GTM since, at high concentrations of UO₂²⁺ and Bi³⁺, the extraction of these nitrates can be treated as though it were done by one CMPO molecule rather than the two CMPO molecules used to calculate these loadings in the GTM. Moreover, DAAP by itself is a good extractant for uranium and is likely to be also by bismuth. More work needs to be done on solvent loading by UO₂²⁺ and Bi³⁺ since their concentrations will be high in much of the Hanford wastes. From these GTM calculations, we conclude that UO₂²⁺ and Bi³⁺ loading will start to become a problem at some point between 0.002 and 0.02M.

The calculated concentration profiles for H, Sr, Am, Pu, and Tc are given in Figs. 34 through 38, respectively, for all 20 process stages. The calculated concentration profile for THFTCA is given in Fig. 39 for the process stages in the strip/scrub section.

Table 21. Distribution Ratios for Various Components in GTM/SASSE Calculations

Section Number: Stage Number:		Distribution Ratios																				Notes	
		1	1	1	1	1	1	2	2	3	3	3	3	3	3	4	4	4	4	4	5		5
H	1	0.508	0.465	0.459	0.459	0.459	0.459	0.729	0.794	0.476	0.489	0.459	0.345	0.2	0.086	0.047	0.042	0.043	0.047	0.044	1	a	
Fe	1	0.026	0.03	0.03	0.03	0.029	0.016	0.025	0.025	0.008	0.005	0.003	0.002	6E-04	8E-04	9E-04	9E-04	9E-04	8E-04	9E-04	0.001	a	
Bi		66.77	48.7	46.4	46.05	45.59	38.79	80.59	96.66	66.62	75.83	76.38	40.9	14.83	2.77	0.978	0.811	0.835	0.639	0.563	0.001	a	
Al		0.008	0.009	0.009	0.009	0.009	0.009	0.01	0.01	0.004	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	a	
La		27.54	25.64	25.29	25.23	24.99	21.27	52.72	59.34	13.2	9.313	5.596	1.926	0.487	0.069	0.023	0.019	0.012	0.014	0.013	0.001	a	
Tc	4	2.5	2.5	2.5	2.5	2.5	2.5	6	7	6	9	12	13	10	8	7	7	7	7	7	0.001	a	
THFTCA		0	0	0	0	0	0	0	0	0	0	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0	b	
Zr		0.012	0.014	0.014	0.014	0.014	0.014	0.376	13.92	25.26	18.84	10.23	1.643	0.103	0.02	0.023	0.036	0.037	0.04	0.037	0.002	a	
Sr		6.88	9.05	9.408	9.46	9.468	9.47	11.49	10.72	2.829	1.451	0.604	0.22	0.063	0.011	0.005	0.004	0.003	0.003	0.003	0.001	a	
UO ₂		1237	1411	1435	1437	1429	1284	2109	2148	581.8	388.7	254.1	108.3	33	6.366	2.718	2.341	2.384	1.888	1.695	9E-04	a	
Am		45.91	42.73	42.16	42.05	41.66	35.45	87.86	98.9	22	15.52	9.327	3.21	0.811	0.115	0.038	0.031	0.019	0.024	0.021	7E-05	c	
Am		45.91	42.73	42.16	42.05	41.66	35.45	87.86	98.9	22	15.52	9.327	0.15	0.016	0.007	0.007	0.031	0.019	0.024	0.021	7E-05	d	
Pu ⁴⁺		1481	1900	1957	1964	1954	1754	3214	3245	2699	2053	1087	333.1	84.38	15.58	6.63	5.708	5.813	4.603	4.132	0.001	c	
Pu ⁴⁺		1481	1900	1957	1964	1954	1754	3214	3245	2699	2053	1087	0.35	0.1	0.07	0.09	0.2	0.4	0.8	4	0.001	d	
F		0.031	0.037	0.037	0.037	0.037	0.037	0.002	0.002	0.049	0.105	0.043	0.008	0.014	0.072	0.164	0.188	0.182	0.137	0.105	1E-04	a	
C ₂ O ₄		0.004	0.003	0.003	0.003	0.003	0.003	0.007	0.012	0.052	0.033	0.012	0.001	0.001	0.002	0.004	0.008	0.008	0.006	0.004	1E-04	a	
PO ₄		0.005	0.004	0.004	0.004	0.004	0.004	0.002	0.002	0.011	0.013	0.011	0.009	0.007	0.001	1E-04	9E-05	8E-05	5E-05	4E-05	1E-04	a	

^a Values calculated by the GTM and used in the SASSE worksheet.

^b Values used in SASSE worksheet. Not in the GTM.

^c Values calculated by the GTM. They were modified as noted before using in the SASSE worksheet.

^d Values used in SASSE worksheet. GTM values were corrected for the effects of the THFTCA concentration.

Table 22. Stage Composition and Effluent Flow Rates Based on GTM/SASSE Calculations

		Component Composition, M																							
Section Number:	1	1	1	1	1	1	1	1	2	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Stage Number:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Org. Eff. Flow, mL/min:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Aq. Eff. Flow, mL/min:	23.94																								
Aqueous Phase																									
H	1.895	2.376	2.449	2.459	2.46	2.461	1.383	1.194	1.468	0.971	0.519	0.25	0.098	0.03	0.013	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.1	0.102	0.102	0.102	0.102	0.102	0.003	1E-04	9E-06	2E-07	5E-09	4E-11	3E-13	2E-15	1E-17	9E-20	7E-22	6E-24	5E-26	5E-28	5E-30	5E-32	5E-34	5E-36	5E-38
Bi	9E-12	3E-10	5E-09	1E-07	2E-06	3E-05	2E-05	1E-05	2E-05	2E-05	2E-05	4E-05	2E-04	0.002	0.007	0.007	0.006	0.005	0.005	0.002	0.003	0.003	0.003	0.003	0.003
Al	0.167	0.168	0.168	0.168	0.168	0.168	0.504	0.511	0.015	3E-04	4E-06	3E-08	2E-10	9E-13	7E-15	6E-17	5E-19	4E-21	3E-23	4E-25	4E-27	4E-29	4E-31	4E-33	4E-35
La	6E-10	7E-09	9E-08	1E-06	1E-05	1E-04	5E-05	5E-05	5E-05	3E-06	3E-06	1E-06	0.003	0.005	0.003	3E-04	9E-06	3E-06	3E-06	2E-10	2E-10	2E-10	2E-10	2E-10	2E-10
Tc	6E-07	2E-06	3E-06	4E-06	6E-06	8E-06	3E-06	3E-06	3E-06	2E-06	2E-06	1E-06	2E-06	2E-06	2E-06	3E-06	3E-06	3E-06	3E-06	3E-06	3E-06	3E-06	3E-06	3E-06	3E-06
THFTCA	5E-16	1E-18	3E-21	8E-24	2E-26	5E-29	4E-31	3E-33	3E-35	3E-37	1E-39	0.225	0.361	0.444	0.326	0.23	0.153	0.091	0.041	0.049	0.049	0.049	0.049	0.049	0.049
Zr	0.033	0.033	0.034	0.034	0.034	0.034	6E-04	2E-05	9E-06	1E-05	2E-05	2E-04	4E-04	4E-05	1E-06	5E-08	3E-09	2E-10	9E-12	8E-13	8E-13	8E-13	8E-13	8E-13	8E-13
Sr	1E-07	4E-07	2E-06	9E-06	4E-05	2E-04	2E-04	2E-04	9E-04	0.002	0.003	0.002	4E-04	2E-05	5E-07	7E-09	9E-11	1E-12	1E-14	2E-16	2E-16	2E-16	2E-16	2E-16	2E-16
UO ₂	2E-16	2E-14	1E-12	1E-10	1E-08	1E-06	6E-07	6E-07	2E-06	3E-06	5E-06	1E-05	5E-05	3E-04	7E-04	8E-04	9E-04	0.001	8E-04	0.003	0.003	0.003	0.003	0.003	0.003
Am	1E-14	2E-13	4E-12	7E-11	1E-09	2E-08	9E-09	8E-09	4E-08	5E-08	9E-08	8E-07	1E-07	3E-09	4E-11	7E-13	3E-14	1E-15	4E-17	2E-18	2E-18	2E-18	2E-18	2E-18	2E-18
Pu ⁴⁺	3E-18	2E-16	2E-14	1E-12	1E-10	1E-08	7E-09	7E-09	8E-09	1E-08	2E-08	2E-05	8E-06	9E-07	8E-08	1E-08	2E-09	6E-10	1E-10	8E-10	8E-10	8E-10	8E-10	8E-10	8E-10
F	0.059	0.06	0.06	0.06	0.06	0.06	0.004	4E-05	5E-07	5E-08	1E-08	5E-10	7E-12	1E-13	1E-14	3E-15	8E-16	2E-16	3E-17	7E-18	7E-18	7E-18	7E-18	7E-18	7E-18
C ₂ O ₄	0.134	0.134	0.134	0.134	0.134	0.134	0.002	3E-05	1E-06	1E-07	8E-09	1E-10	9E-13	6E-15	5E-17	7E-19	1E-20	2E-22	3E-24	5E-26	5E-26	5E-26	5E-26	5E-26	5E-26
PO ₄	0.004	0.004	0.004	0.004	0.004	0.004	5E-05	6E-07	9E-09	3E-10	9E-12	2E-13	2E-15	3E-17	2E-19	1E-21	1E-23	7E-26	4E-28	5E-30	5E-30	5E-30	5E-30	5E-30	5E-30
Organic Phase																									
H	0.963	1.105	1.125	1.128	1.128	1.128	1.008	0.948	0.698	0.475	0.238	0.086	0.02	0.003	6E-04	4E-04	4E-04	5E-04	4E-04	1E-12	1E-12	1E-12	1E-12	1E-12	1E-12
Fe	0.003	0.003	0.003	0.003	0.003	0.002	8E-05	4E-06	7E-08	1E-09	2E-11	8E-14	2E-16	1E-18	1E-20	8E-23	6E-25	5E-27	4E-29	6E-31	6E-31	6E-31	6E-31	6E-31	6E-31
Bi	6E-10	1E-08	2E-07	4E-06	8E-05	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.004	0.006	0.006	0.006	0.005	0.003	0.001	3E-06	3E-06	3E-06	3E-06	3E-06	3E-06
Al	0.001	0.002	0.002	0.002	0.002	0.002	0.005	0.005	7E-05	6E-07	4E-09	3E-11	2E-13	9E-16	7E-18	6E-20	5E-22	4E-24	3E-26	4E-28	4E-28	4E-28	4E-28	4E-28	4E-28
La	2E-08	2E-07	2E-06	2E-05	3E-04	0.003	0.003	0.003	0.003	0.003	0.003	0.005	0.003	2E-04	6E-06	2E-07	3E-09	1E-10	2E-12	6E-15	6E-15	6E-15	6E-15	6E-15	6E-15
Tc	3E-06	5E-06	8E-06	1E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	3E-08	3E-08	3E-08	3E-08	3E-08	3E-08
THFTCA	5E-31	1E-33	3E-36	8E-39	2E-41	5E-44	4E-46	3E-48	3E-50	3E-52	8E-40	0.135	0.217	0.266	0.195	0.138	0.092	0.055	0.024	5E-17	5E-17	5E-17	5E-17	5E-17	5E-17
Zr	4E-04	5E-04	5E-04	5E-04	5E-04	5E-04	2E-04	2E-04	2E-04	2E-04	2E-04	4E-04	4E-05	8E-07	3E-08	2E-09	1E-10	6E-12	3E-13	2E-15	2E-15	2E-15	2E-15	2E-15	2E-15
Sr	7E-07	4E-06	2E-05	8E-05	4E-04	0.002	0.002	0.002	0.003	0.003	0.002	4E-04	2E-05	3E-07	3E-09	3E-11	3E-13	3E-15	3E-17	2E-19	2E-19	2E-19	2E-19	2E-19	2E-19
UO ₂	3E-13	2E-11	2E-09	2E-07	2E-05	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.001	2E-06	2E-06	2E-06	2E-06	2E-06	2E-06
Am	5E-13	1E-11	2E-10	3E-09	5E-08	8E-07	8E-07	8E-07	8E-07	8E-07	8E-07	1E-07	2E-09	2E-11	3E-13	2E-14	6E-16	3E-17	9E-19	1E-22	1E-22	1E-22	1E-22	1E-22	1E-22
Pu ⁴⁺	5E-15	3E-13	3E-11	3E-09	3E-07	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	8E-06	8E-07	6E-08	8E-09	2E-09	9E-10	5E-10	4E-10	1E-12	1E-12	1E-12	1E-12	1E-12	1E-12
F	0.002	0.002	0.002	0.002	0.002	0.002	7E-06	6E-08	3E-08	6E-09	5E-10	4E-12	1E-13	9E-15	2E-15	6E-16	1E-16	3E-17	3E-18	7E-22	7E-22	7E-22	7E-22	7E-22	7E-22
C ₂ O ₄	5E-04	4E-04	4E-04	4E-04	4E-04	4E-04	1E-05	3E-07	5E-08	4E-09	1E-10	2E-13	1E-15	1E-17	2E-19	5E-21	9E-23	1E-24	1E-26	5E-30	5E-30	5E-30	5E-30	5E-30	5E-30
PO ₄	2E-05	2E-05	2E-05	2E-05	2E-05	2E-05	1E-07	1E-09	9E-11	3E-12	1E-13	1E-15	1E-17	3E-20	3E-23	1E-25	8E-28	4E-30	2E-32	5E-34	5E-34	5E-34	5E-34	5E-34	5E-34

Fig. 34. The GTM-Calculated Concentration Profile for Nitric Acid in the Combined TRUEX-SREX Process

Fig. 35. The GTM-Calculated Concentration Profile for Strontium in the Combined TRUEX-SREX Process

Fig. 36. The GTM-Calculated Concentration Profile for Americium in the Combined TRUEX-SREX Process

Fig. 37. The GTM-Calculated Concentration Profile for Plutonium in the Combined TRUEX-SREX Process

Fig. 38. The GTM-Calculated Concentration Profile for Technetium in the Combined TRUEX-SREX Process

Fig. 39. The SASSE-Calculated Concentration Profile for THFTCA in the Strip Section

3. Preparation for Contactor Tests

A 20-stage 2-cm centrifugal contactor was set up to experimentally verify the calculated nitric acid concentrations for the combined TRUEX-SREX flowsheet. Preliminary tests are being made to ensure that this equipment works properly when (1) the new TRUEX-SREX solvent is used, and (2) a new aqueous sampling system is in place. Some notes and observations during the setup process are reported here.

a. Stand-In Solvent

A possible problem with PS 9 as the combined TRUEX-SREX solvent was identified to be its density, which is 875 g/L. By comparison, the density of TRUEX-nDD solvent is only 856 g/L. The effect of this higher solvent density on minicontactor operation was evaluated using our ROTOR model. Results indicated that contactor operation would be borderline for such a high solvent density. The problem should show up first at high O/A flow ratios in the contactor.

To explore the effect of high solvent density on minicontactor operation, tests were initiated with a stand-in solvent (TBP in nDD) at solvent densities up to 902 g/L. These tests, which are reported below, showed that the minicontactor was operable at solvent densities up to 902 g/L. Thus, the combined TRUEX-SREX solvent, which has a slightly lower density, should be free of density-related operating problems in the minicontactor.

b. Stage Sampling

The possibility of taking a continuous aqueous-phase sample from the bottom of one or more contactor stages was explored in some detail. The problem has three parts. First, we had to show that we can draw off the aqueous phase at a small flow rate without taking organic phase with it. Second, we had to design a low-volume sampling system so that the residence time in the system is relatively small, no more than 10 min. Third, we had to find a suitable pump capable of low flow and constant flow rate.

As noted on Fig. 29 (shaded boxes), we would like to take aqueous samples at eight stages, 1, 7, and 9-14 at a sampling flow rate of 0.33 mL/min. To compensate for this liquid loss due to sampling, the flow rate to the second scrub will be increased from 6.0 to 7.3 mL/min, and that to the strip feed will be increased from 3.0 to 4.0 mL/min.

(1) Aqueous Samples from Bottom of Contactor Stage

To determine the maximum rate at which aqueous samples could be drawn from the bottom of a contactor stage without organic contamination, tests were performed by cracking open the ball valve for the stage. This valve, located just below the stage, is attached to it by 1/4-in. (6.4 cm) stainless steel tubing. These tests showed that, if the sampling flow rate was kept to 0.35 mL/min or less, one sees mainly aqueous phase in the sample from the bottom of the stage.

After the special low-volume sampling system described next was in place, the bottom-flow tests were repeated. For these tests, there was 12 mL/min of organic phase (40% TBP in nDD) and a 16 mL/min of aqueous phase (0.05M nitric acid) flowing through the stage while a steady stream of solution dripped from the bottom of the stage. The bottom flow passed through a 5-cm length of Viton tubing, where a small clamp controlled its rate. Several tests at flow

rates of 0.5 mL/min showed no visible organic phase in the aqueous phase exiting from the bottom of the mixing zone. These results suggest that a bottom flow rate of 0.33 mL/min should yield solvent-free aqueous samples.

(2) Low-Volume Sampling System

Initial sampling systems included the ball valve under the stage so that we could shut off flow from the bottom of the stage to disconnect the sampling system, and later, open it up to drain the stage easily. The volume in the sampling system was about 3 mL, which yielded a solution residence time of about 10 min.

A breakthrough in the design of the sampling system allowed us to keep its volume to under 1 mL, reducing the solution residence time to about 3 min. One key in designing this low-volume sampling system was allowing the sampling pump to act as the valve for the sampling line. If the pump is turned off, the valve is closed; if the speed of the pump is turned up to its maximum rate of 6 mL/min, the contents of the stage can be drained in 2 to 3 min. The design of this system is as follows. The aqueous phase is drawn down through a 1/8 in. (3.2 mm) NPT* to 1/16 in. (1.6 mm) Swagelok reducer, which screws into the bottom of the contactor stage. The sample liquid then flows through a short (1 to 2 in. [25 to 50 mm]) length of stainless steel tubing (1/16 in. OD [1.6 mm] and 1/64 in. ID [0.04 mm]) into a 5 ft (1.5 m) length of Viton tubing. This tubing, which is size #13 (0.8 mm ID), goes from the stage to a multichannel sampling pump where the end of the tubing passes through the pump. Details of the pump are presented next.

(3) Multichannel Pump with Low Flow and Constant Flow Rate

For taking bottom samples from several stages at the same time, we tested a Masterflex variable-speed multichannel peristaltic pump. The various parts of the pump are as follows (Cole-Parmer catalog number shown in parentheses): (1) multichannel variable-occlusion pump head (L-07519-00); (2) eight small tubing cartridges (L-07519-60); (3) a variable speed driver with a ten-turn potentiometer over a 1 to 100 rpm range and a repeatability of ± 1 rpm (L-07520-35); and (4) Viton tubing with an inside diameter of 0.8 mm (L-06412-13). This multichannel Masterflex pump allows eight lines to be pumped at the same time. Each tube is mounted into a cartridge designed to hold a particular size of tubing, and then the cartridge is snapped into the pump head.

Calibration of the driver controller (a 10-turn potentiometer) showed that pump speed was directly proportional to the controller setting. At no rotation, the controller has a setting of 0.5 turns; at 100 rpm, 9.5 turns. Initial results showed that pump flow rates were generally lower than expected based on the controller setting. Some sampling lines, which had no flow, were discovered to be tangled between the finger guard and the flow-inducing rollers of the pump. Because the small-tubing cartridges completely cover the finger guard and the rollers during pump operation, these tangled sampling lines went unnoticed for a time. The problem was due to an improper setting of the tubing retainer button located on the feed side of the pump. If this setting is not right, the Viton tubing can be slowly drawn into the pump. The tubing retainer buttons (located on the front and the back of each pump cartridge) are designed to halt this creeping motion. Since one cannot ordinarily see the tubing moving into the pump, a white line was marked 5 cm from the feed side of the pump. We checked every so often to verify that this distance was maintained during

* NPT = National Pipe Thread.

pump operation. If movement occurred, the back tubing retainer button was tightened further while the pump was operating. Sometimes the movement of the tubing is so slow that it would take several hours to notice any change. Thus, it is recommended that this system be monitored regularly during pump operation.

In addition to setting the tubing retainer buttons, one also has to turn an adjustment knob located on each of the small-tubing cartridges to control the occlusion setting (which determines how tightly the pump squeezes the tube). If this control is not tight enough, the pump will act like a leaky valve. When this was observed, we found that several more clockwise turns of the adjustment knob (that is, higher tension) corrected the problem. When all of the sampling lines were adjusted to the same high occlusion setting, the flow rates of the eight sampling lines were essentially the same (for example, 0.24 ± 0.02 mL/min) and were independent of liquid height in the lines to the sampling system.

c. Minicontactor Setup and Operation

A 20-stage minicontactor (2-cm contactor) was set up as shown in Fig. 29. No provision was made to recycle any effluent. The interstage lines were fashioned out of a fairly transparent tubing made of Teflon fluorinated ethylene polypropylene (FEP), with an outside diameter of 1/2 in. (12.7 mm) and an inside diameter of 3/8 in. (9.5 mm). The system was checked for leaks by pumping water through the stages. To protect the contactor motors from possible damage caused by acid fumes, air purge lines were connected to each stage from a common 20-stem manifold that is supplied with air at 1.5 scfh (42 L/h). Thus, the average purge air flow to each stage is 35 mL/min.

(1) Normal Two-Phase Operation

To check the system for good operation during two-phase operation, we used 0.05M HNO_3 and 40% tributylphosphate (TBP) in normal dodecane (nDD), which has a density of 838 g/L. After several hours of operation, some aqueous carryover was observed in the organic interstage lines. This other-phase carryover was only seen in stages 1-6, while the remaining organic interstage lines appeared to be free of aqueous phase. The largest amount of other-phase carryover appeared to be in the interstage line between stages 2 and 3. To determine how much aqueous phase was actually present in this line, four organic samples were taken by disconnecting the organic interstage line from stage 2 to stage 3. While this sample was being collected, the aqueous feeds and the stage-to-stage flows continued. Because all of the organic phase was being drained at stage 2, the flow of organic phase through the rest of the stages stopped. The average amount of aqueous phase observed in the organic-phase effluent from stage 2 was 1.05%. Since the other organic interstage lines appeared to have less aqueous phase, we assumed that the other stages had less than 1% other-phase carryover.

The minicontactor was designed to give less than 1% other-phase carryover if the total flow rate is 40 mL/min or less. Thus, stage 2 operation was borderline as it was operating at total flow rate of 40 mL/min and an O/A flow ratio of 1.0. (Note that the flow rate and O/A flow ratio for stage 2 differ from those in Fig. 29 because an early version of the flowsheet was used in the initial setup of the minicontactor for the combined TRUEX-SREX tests.) This is apparently a subtle effect of multistage operation as subsequent single-stage tests carried out at stage 2 for three O/A ratios (0.2, 1.0, and 5) gave much better performance (Table 23). As stage 2

Table 23. Results of Single-Stage Two-Phase Tests with Solvent Density of 838 g/L

O/A Flow Ratio	Stage	Flow Rate at 1% Other-Phase Carryover, mL/min	Mode of Failure
0.2	2	63 ± 5	A in O
	6	65 ± 6	A in O
	7	77 ± 6	A in O
1.0	2	70 ± 5	A in O
	6	72 ± 8	A in O
	7	73 ± 8	A in O
5.0	2	260 ± 20	O in A
	6	240 ± 20	O in A
	7	260 ± 10	O in A

operation was not significantly out of specification and all other stages operated better, the minicontactor setup was deemed to be satisfactory.

For the single-stage tests at stage 2, both the aqueous (0.05M HNO_3) and organic (40% TBP in nDD) phases were fed directly into the stage. Then, to measure other-phase carryover easily, 100-mL samples were taken of the effluent from each exit port. As appropriate, either the top or bottom of each phase would be poured into a 15-mL centrifuge tube marked at 0.1-mL intervals to look for the presence of the other phase. This allowed values of O in A and A in O to be determined to within 0.1%. In these tests, stage failure was defined as more than 1% of the other phase in the organic or aqueous effluent. This is the basis for the mode-of-failure column in Table 23.

Following the same procedure as used for the stage 2 tests, stages 6 and 7 were evaluated. The results, also listed in Table 23, show that stage 2 is a very typical stage. These results also suggest that multistage operation can sometimes be slightly degraded relative to single-stage operation.

(2) Two-Phase Operation for High Solvent Density

All 20 minicontactor stages were tested individually at an O/A flow ratio of 5. At this ratio, the rotor model specifications stated the units would fail first for a higher density solvent. The solvent used was 68.6% TBP in nDD, which has a density of 902 ± 7 g/L and corresponds to 2.51M TBP in the solvent. This high density solvent was used so that the test conditions would be even tougher than those that will be experienced with the TRUEX-SREX solvent. The results, given in Table 24, show that, in all cases, the maximum throughput stayed above the design value of 40 mL/min. As expected, the maximum throughput at an O/A flow ratio of 5 dropped relative to values obtained for this O/A flow ratio at a lower solvent density (see Table 23), and the mode of failure was O in A for all cases.

After the individual tests of the 20 minicontactor stages at an O/A flow ratio of 5, three stages were chosen to investigate operation for O/A ratios over a range from 0.2 to 5. These stages were picked so that we had stages that gave a typical maximum throughput at an O/A of 5.0 (stage 2), a high maximum throughput (stage 7), and a low maximum throughput (stage 11).

Table 24. Results of Single-Stage Two-Phase Tests with Solvent Density of 902 g/L and O/A Flow Ratio of 5.0

Stage Number	Mode of Failure	Max. Throughput, mL/min
1	O in A	118 ± 9
2	O in A	114 ± 12
3	O in A	139 ± 6
4	O in A	165 ± 20
5	O in A	139 ± 6
6	O in A	117 ± 17
7	O in A	166 ± 18
8	O in A	139 ± 6
9	O in A	139 ± 6
10	O in A	163 ± 19
11	O in A	70 ± 7
12	O in A	124 ± 15
13	O in A	162 ± 18
14	O in A	162 ± 18
15	O in A	122 ± 11
16	O in A	122 ± 12
17	O in A	139 ± 6
18	O in A	139 ± 6
19	O in A	122 ± 11
20	O in A	122 ± 11

The results, given in Table 25, show that, as expected, the largest drop in maximum throughput was at an O/A flow ratio of 5. Maximum throughputs at lower O/A flow ratios are essentially unchanged. In all cases, the maximum throughput is well above the design throughput for the minicontactor of 40 mL/min. Thus, the minicontactor will be suitable for tests with solvents which have a high density as high as that for the combined TRUEX-SREX solvent.

Table 25. Results of Single-Stage Two-Phase Tests with Solvent Density of 902 g/L

O/A Flow Ratio	Stage	Flow Rate at 1% Other-Phase Carryover, mL/min	Mode of Failure
0.2	2	91 ± 20	A in O
	7	96 ± 6	A in O
	11	75 ± 6	A in O
1.0	2	90 ± 10	Both
	7	78 ± 3	A in O
	11	90 ± 10	A in O
5.0	2	114 ± 12	O in A
	7	166 ± 18	O in A
	11	70 ± 7	O in A

d. Test Plan

In making detailed test plans, we prepared three Excel worksheets. The first worksheet calculates the volume of each feed stock that will be required and the amount of each chemical needed based on available materials. The second worksheet gives a step-by-step procedure for carrying out test C1, the cold test with only HNO_3 and Na_2CO_3 present. The third worksheet gives a step-by-step procedure for carrying out tests C2 and C3, the cold tests with HNO_3 and Na_2CO_3 plus oxalate, Fe, Sm, and Al present. In addition, test C3 will introduce THFTCA into the strip section. The worksheets allow us to estimate the materials that we will need during the tests. They also provide a list of crucial operations and the time that they should be carried out during the test. After the preliminary test discussed next was completed, the worksheets were reviewed and revised. They are now ready for tests C1 through C3.

4. Preliminary Test

A preliminary test was performed using the 20-stage minicontactor set up as shown in Fig. 29 for the combined TRUEX-SREX flowsheet. The purpose of this test was to (1) check for leaks, (2) determine if the test procedure is workable, and (3) test the sampling pump system. In this test, the organic phase was 40% TBP in nDD, and the aqueous phase was 0.01M nitric acid.

The results of the preliminary test showed no leaks in the system. The pump for bottom sampling of the aqueous phase at eight stages, as shown in Fig. 29, gave an average sampling rate of 0.28 mL/min. Large amounts of organic phase were discovered in the aqueous samples taken from stages 1 and 12, $50 \pm 10\%$ and $78 \pm 6\%$, respectively. Note that stage 1 was used in the exploratory tests reported above without significant organic phase appearing in the sampling flow. Thus, we did not expect to find solvent in the bottom stage samples. None of the other stage samples showed a measurable amount of organic phase in the aqueous phase.

After the test, we observed that the Viton tubing was slightly swollen at the end connected to the stainless steel capillary tube for stages 1 and 12. It is not clear whether the swollen tubing was the cause or the result of measurable organic phase in the aqueous phase. At any rate, swollen portions were removed by cutting off about 5 cm of tubing. With this modification, the sampling operation will be used for the cold tests.

The three 20-stage cold tests (C1, C2, and C3) will be done as soon as an appropriate solvent is identified. The evaluation process to select an appropriate solvent is discussed next.

5. Solvent Evaluation

When the PS 9 solvent was prepared (Sec. IV.C.1.a), its density was measured. In addition, the effect of HNO_3 and Na_2CO_3 on its density was determined. The results, given in Table 26, show how density changed by alternating contacts between 0.1M HNO_3 and 0.25M Na_2CO_3 . The nitric acid increased the density by 0.0044 g/mL, the sodium carbonate by 0.0036 g/mL.

After the density of solvent PS 9 was determined, the value of its dispersion number (N_{Di}) was measured. The results, given in Table 27, show that N_{Di} was low, and the maximum amount of A in O was high. The N_{Di} values were as low as 2.5×10^{-4} for nitric acid at O/A = 1.0. Since design calculations are based on an N_{Di} value of 8×10^{-4} , and maximum throughput (both phases) is

Table 26. Effect of Contact with Various Aqueous Phases on Solvent Density

Liquid	Solution Contacted with Liquid	Density		Apparent Density Gain	
		Measured, g/mL	Reference, ^a g/mL	g/mL	%
Water	(none)	0.9947	0.9955 ^b	--	--
PS 9	(none)	0.8751	0.875 ^c	--	--
	0.1M HNO ₃	0.8797	0.875	0.0047	0.54
	0.25M Na ₂ CO ₃	0.8787	0.875	0.0037	0.43
	0.1M HNO ₃	0.8791	0.875	0.0041	0.47
	0.25M Na ₂ CO ₃	0.8785	0.875	0.0035	0.40

^a Except as noted, reference case is solvent that has never been in contact with an aqueous phase.^b See Ref. 8.^c Measured by Herb Diamond (ANL Chemistry Division).

Table 27. Effect of Various Aqueous Phases on the Dispersion Number for Three Solvents

Solvent Name	Aqueous Phase	O/A = 0.33		O/A = 1.0		O/A = 3.0		Notes
		N(Di) x10 ⁴	Max. A in O, %	N(Di) x10 ⁴	Max. A in O, %	N(Di) x10 ⁴	Max. A in O, %	
PS 9	0.25M Na ₂ CO ₃	8.1	5	6.3	5	1.5	10	
	0.01M HNO ₃	8.3	4	4.3	4	4.0	6	
	0.1M HNO ₃	9.3	8	2.5	7	1.6	7	a
	0.1M HNO ₃	7.4	9	2.7	3	2.6	4	
	0.1M HNO ₃	12.4	3	9.2	1	3.6	1	b
	3.0M HNO ₃	7.0	3	4.3	4	2.9	5	
	0.2M THFTCA	5.0	1 ^c	3.5	4	4.0	6	
PS 10								
w/o CE	0.25M Na ₂ CO ₃	9.9	2	7.4	3	8.7	3	
	0.1M HNO ₃	7.9	1	7.1	1	7.1	1	
PS 10	0.25M Na ₂ CO ₃	7.1	4	6.5	4	4.2	4	
	0.1M HNO ₃	13.2	0.4	5.1	1	4.6	2	

^a The solvent was not contacted with sodium carbonate solution before this test.^b These dispersion tests were done at 48 ± 5°C. All others were done at 24.3 ± 0.8°C.^c For this case, max. O in A is reported. Max. A in O was less. Aqueous phase was the continuous phase.

proportional to N_{Di} , the total throughput for stages containing nitric acid would be reduced to about 30% of the nominal 40 mL/min for the 2-cm contactor, that is, to about 12 mL/min. For stages containing sodium carbonate, this reduction would be to about 20% of the nominal 40 mL/min for the 2-cm contactor, that is, to about 8 mL/min. Even with these reductions, the amount of A in O could still be as high as 10%. Note that, except where indicated for THFTCA, the amount of O in A was well below 1% for all cases. Overall, then, PS 9 is not a satisfactory solvent.

One test of PS 9, also shown in Table 27, was made at an elevated temperature, 48 ± 5°C rather than 24.3 ± 0.8°C. This test showed that PS 9 had improved processing properties based on higher N_{Di} values and lower A in O values. Since elevated temperatures reduce solvent viscosity, this suggested that we might be able to improve the solvent by decreasing its viscosity.

Thus, the PS 9 solvent was reformulated using Norpar-12 (a commercial normal paraffinic solvent from Exxon) in place of Isopar M for the diluent. This new solvent, named PS 10, was first tested without the crown ether because crown ether was in short supply. Without crown ether, the solvent name is PS 10 w/o CE. The results for both new solvents, also given in Table 27, show a much improved solvent, which is borderline acceptable for the combined TRUEX-SREX process. When a new shipment of crown ether arrives, we plan to prepare one liter of PS 10 and make the three cold tests C1 through C3.

The N_{Di} was measured using a 100-mL cylinder. In this measurement, the position of the aqueous-organic interface was noted relative to the interface position when the two phases were completely separated, that is, before shaking the cylinder containing the two phases. When the movement of the interface between the two coalescing phases has essentially stopped, that is, no movement is seen after successive 2 or 3 min intervals, the position of the interface relative to the position before shaking was used to determine the amount, if any, of A in O or O in A. The time to reach this position was used to determine the N_{Di} value. The amount of A in O or O in A allowed us to estimate the amount of other-phase carryover that we would expect to see during contactor processing.

V. VERIFICATION TESTS

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Laboratory verification tests of the TRUEX process are being carried out to (1) develop a better understanding of the chemistry of the TRUEX process, (2) test and verify process modifications, and (3) verify the computer model being developed for predicting species extraction behavior and calculating flowsheets.

Current verification tests are being completed using plutonium-residue solutions generated by the New Brunswick Laboratory (NBL). These solutions, generated from the analysis of plutonium samples, have been accumulating over the past several years at the New Brunswick Laboratory (NBL) and Argonne National Laboratory (ANL). These residues contain varying concentrations of nitric, sulfuric, phosphoric, and hydrochloric acids, plus U, Pu, Np, and Am. The TRUEX solvent extraction process, used to generate the nonTRU waste stream and recover the plutonium from the NBL waste, will be completed in a 20-stage centrifugal contactor installed in a glovebox. The organic solvent is TRUEX-nDD.

A. Continued Processing of Batch 1

The plutonium product stream generated during the processing of Batch 1 (ANL-93/38, p. 43) has been evaporated and calcined. Two batches of oxide were produced from the calcination. Batch 1a oxide weighed 6.40 g and contained 6.20 g Pu. Batch 1b oxide weighed 21.20 g and contained 3.39 g Pu. Plutonium content was determined by inductively coupled plasma (ICP)/atomic emission spectroscopy (AES). Further ICP/AES analysis indicated that batch 1b was contaminated with Na and K. Because Na and K will affect the reduction of plutonium oxide to metal, they had to be removed before the reduction process. Since sodium and potassium oxides are very water soluble, while plutonium oxide is not, we decided to wash batch 1b oxide with water.

Batch 1b oxide was placed in a beaker with ~300 mL of H₂O and stirred for several hours. The solution was filtered to remove the solids, and the pH of the filtrate measured. The pH was >10, indicating that sodium and potassium oxides had been washed out of the solids (group IA oxides form hydroxides in water). Scintillation counting of the filtrate showed 2760 cpm/ μ L, indicating that some plutonium had been dissolved but not a great deal. The solids were washed again. The pH of the filtrate was checked and found to be >10, indicating that more Na and K had been removed. The solids were washed a third time. When the pH of the filtrate was measured this time, it was ~7, indicating that no more Na or K was removed. Batch 1b oxide was then dried and reweighed. The new weight was 5.5 g. The nearly 16 g reduction in mass indicates that the sodium and potassium oxides were washed out by the water. An assay by ICP/AES will be performed on the new oxide to determine its plutonium content.

The filtrates from the three washings were combined and sampled. Scintillation counting indicated that the combined filtrate contained 490 cpm/ μ L. To determine if the filtrate could be acidified and added to the next feed, distribution ratios (D) of the acidified filtrate were checked. To check D values, 800 μ L of 2M HNO₃ and 200 μ L of filtrate were mixed, and the pH determined. The pH equaled 1, indicating that the filtrate had been acidified. Next, 1 mL of TRUEX-nDD was added to the acidified filtrate sample, and the resulting solution mixed. The phases were separated, sampled, and scintillation counted. A 900 μ L sample of the aqueous phase was then contacted with 900 μ L of fresh TRUEX-nDD. The phases were again separated, sampled, and scintillation counted. Finally, 800 μ L of the aqueous phase was contacted with 800 μ L of fresh TRUEX-nDD. The phases were

again separated, sampled, and scintillation counted. Distribution ratios for the three contacts were 34, 1.0, and 0.4, respectively (see Table 28). The D value for the third contact is very low, but the scintillation counting of the aqueous phase showed that it was 0.47 cpm/ μ L, which is well below raffinate that we have produced in the past. We concluded that the filtrate can be acidified and added to the feed tank of the next batch.

Table 28. Distribution Ratios for Acidified Filtrate

Contact No.	Scint. Count, cpm/ μ L		Dist. Ratio
	Aq.	Org.	
1	2.1	72.1	34
2	0.73	0.73	1.0
3	0.47	0.20	0.4

B. Processing of Batch 2

1. Flowsheet Development

Batch 2, the second batch of waste received from NBL, contained approximately 13 g of plutonium and 16 g of uranium. Preparations for Batch 2 were completed during the last reporting period. Processing Batch 2 was accomplished over four days of operation (March 27, March 31, April 6, and April 9, 1992). The base flowsheet for processing is shown in Fig. 40. Changes in flow rates for some feed streams were made during processing, and these changes are noted in the discussion of the run (Sec. V.B.2).

One change in the flowsheet for this batch worthy of note here is the inclusion of an alumina column to aid in solvent cleanup. Based upon batch tests, the solvent quality is greatly improved when passed through an alumina column. The alumina helps remove degradation products and reduces the TRU activity in the solvent. Because the alumina column could only handle 30% of the organic flow rate, valves were installed on the HP pump so that we could switch between the alumina column or bypass the alumina column and return the solvent to the DX feed tank (Fig. 40).

2. Discussion of Run

Three problems occurred during the first day of operation. After 23 min of operation, the level in the DX tank had dropped below the pump pickup tube, stopping organic flow. The organic effluent (HP) pump had a valve attached to it that was used to direct flow either to the alumina column or to the DX tank. The HP flow had been directed to the column, and the low level in the DX tank was solved by directing the HP flow into that tank.

After operating for 50 min, the level in the scrub feed tank dropped below the pump suction line. The length of time that we lost the scrub flow is not known, but based upon a flow rate of 70 mL/min, the feed solution would have lasted about 43 min. This means that we may have operated for 7 min without scrub flow.

The third problem was with the americium strip product flow. For this stream, we take a small flow from the interstage line exiting stage 11. Although this takeoff worked correctly in previous runs, we could not remove aqueous phase at 3 mL/min. Therefore, we shut down for

Fig. 40. Flowsheet for NBL Batch 2 Processing

approximately 1.5 h so that we could replace this connection with a larger diameter fitting. After restart, we had no further trouble with this flow.

During the shutdown between the first and second days of processing, pump flow rates were checked. The DS and EF solutions collected (about 900 mL of solution) during these calibration checks were added to the DF tank. Also during this shutdown, the flow rates for DX, DF, DS, and FF streams were changed.

Neutralization of the DW raffinate in the carboys during the first day had been a very time-consuming process. This neutralization was accomplished by adding about 2.5 L of 10M NaOH to about 7.5 L of raffinate. Phenolphthalein was used as a color indicator to aid in the process. Problems encountered in this process were brought about by the formation of solids, presumably $\text{Al}(\text{OH})_3$, in the solution as the NaOH was added. These solids not only turned the solution into a very thick, viscous mixture, but also made the color change in the phenolphthalein almost indistinguishable. It was thus difficult to visually tell when a neutral solution had been reached. Therefore, we decided to leave the raffinate in an acidic condition but allow room in each carboy so that we could neutralize at a later date.

On March 31, 1992, the second day of processing, two abnormalities were encountered. About 90 min after startup, the plutonium product (FW) collection container was changed. We noticed two phases in the full container. About 500 mL of solvent was present in the

2-L container, although the presence of two phases had not been noted when the container was put in place upon startup that day.

The reason for the presence of this organic phase in the aqueous stream was not determined, nor was there a recurrence of the problem throughout the rest of the processing. After processing for this day was halted, the plutonium strip stages were drained to determine if any solids were present. White crystals were seen in the aqueous-phase drainage from stages 16 and 18. These crystals had the same appearance as ammonium oxalate crystals.

Slow phase separation from certain stages during drainage led to questions about the dispersion number in the plutonium strip section. Therefore, after the drainage from all four stages was combined, the two-phase mixture was shaken, and the time needed for the dispersion to separate was measured as 37 s. The aqueous-phase drainage was then contacted with solvent that had been processed through the alumina column, and the time needed for the dispersion to separate was measured as 48 s. The increased time needed for separation in the presence of "clean" solvent is hard to explain. However, the other-phase carryover does not appear to be related to a problem in the dispersion number.

The second problem encountered on the second processing day was the presence of foam in certain stages. Because of the foaming, the DF feed was shut off, while the other pumps were left running, to determine if this would stop the foaming. Other problems in the laboratory, however, interrupted the experimenters, and the rest of the system was shut down before the foaming problem could be thoroughly investigated.

During shutdown, the carbonate wash feeds as well as the acid rinse solution in the DX tank were replaced with fresh solutions. Also, all of the solvent in the DX tank was passed through the alumina column during this shutdown.

Upon startup of the "cold" feed pumps on April 6, 1992 (the third day of processing), foaming was again observed in the organic and aqueous effluents from certain stages. In looking for a cause, we noticed that the DW raffinate pump was pumping too slowly to remove the aqueous effluent from stage 1. Thus, the aqueous phase was backing up in the extraction section. In an attempt to remedy this problem, the pump head for this DW pump was adjusted. Shortly thereafter, the pump head was swung in the wrong direction, causing it to pump the DW raffinate into the aqueous-exit port for stage 1. After this pump problem was fixed, the foam quickly dissipated. This suggests that the "foaming" noticed on both the second and third days was not truly foaming at all, but, instead, flooding of the stages with aqueous phase, causing two-phase flow out of the stage exits.

The normal startup procedure was modified slightly on the third day, whereby the flow rate for the DF feed was increased from zero to full flow (100 mL/min) in four equal increments over about 30 min. This was done in an attempt to lessen the spike in activity in the DW raffinate stream following initiation of DF flow. This spike in DW activity had been encountered on the previous two days of processing this batch, as well as in previous processing runs.

Well into the processing run on the third day, the DW flow rate was measured at 184 mL/min. Given the changes to the flow rates at the end of the first day of processing, this flow rate should have been 207 mL/min. A quick check of the feed left in the carboy showed that the DF flow was too slow, so the DF pump was adjusted for a faster flow.

After 209 min of processing on the third day, we ran out of DS scrub solution. Since the order for aluminum nitrate had not yet arrived, shutdown procedures were begun. However, the wrong pump was inadvertently shut off. The DW pump was unplugged in place of the DF pump, while all other pumps were left running. About a minute later, this mistake was noticed and corrected, i.e., the DF pump was shut off and the DW pump was restarted. Shutdown was completed about four minutes later with the shutdown of all pumps. During shutdown, flow rate checks were made on a number of pumps, and the DS flow rate was decreased.

Startup procedures were again modified for the beginning of processing on the fourth day, April 9, 1992. A "cold" DF feed solution of 500 mL of 3M HNO_3 , flowing at about 50 mL/min, was started when the other feed pumps were started. Once this "cold" feed was passed, the real DF feed solution was started at 50 mL/min. After 15 min, the DF feed flow was increased to its normal value of 103 mL/min.

About two hours after startup, the DF feed flow rate, given the carboy volume, was calculated to be lower than expected. The pump was adjusted to a setting which was calculated to give 100 mL/min.

Also on the fourth day, we noted that the GF flow was intermittent because the level in the GF tank was below the pump pickup tube. The time that this condition lasted was not determined. Addition of about 500 mL of fresh carbonate to this tank solved the problem.

Processing of this batch of waste was completed when the DF feed tank was emptied on the fourth day, after 805 min of run time. The shutdown of the system included a long flushing time, during which all pumps except DF continued to run for about another 50 min.

3. Sample Analysis during Processing

The samples taken during processing were counted on scintillation and gamma counters in an isolation room. The DW samples were taken in a hood, and scintillation counted for one minute immediately to ensure that the DW raffinate was within acceptable activity limits. Samples were taken of the DW product carboys after each carboy was full and mixed well but before the carboy was removed from the hood. All other sample collected from the various streams during the run had to be bagged out of the glovebox, and this was usually done at the end of the day. At that time, all scintillation cocktails and gamma tubes prepared that day were set up to count overnight. All scintillation samples were made with 10 mL of Ultima Gold in 20-mL plastic scintillation vials. Gamma samples were diluted as necessary to make up a 1-mL solution for consistency in counting geometry.

Counting results for the DF samples are given in Table 29. The DF feed tank was not mixed during the run, because of the presence of solids in the DF carboy. These solids had precipitated out and would have plugged up the filters on the DF feed line. Even so, Table 29 shows that the activity in the DF feed remained fairly constant over the run.

During processing, samples of the DW raffinate were taken about every 30 min. The DW raffinate was pumped out of stage 1 into a 4-L container. A transfer pump then pumped this raffinate through a 1- μm filter over to the hood, where it fell into a carboy. Samples were taken in the hood at the line entering the carboy. The transfer pump was usually running, which kept the 4-L container basically empty. However, when solution in the carboy reached 7-8 L, the transfer pump was shut off to allow replacement of the carboy. Since the collection point of DW samples was

Table 29. Sample Time and Average Scintillation and Gamma Counting Results for DF Samples

Sample Name	Sample Time, min	Average Scintillation Counts, cpm/ μ L	Avg. Gamma Counts @ 59.5 keV, cps/ μ L
DF-1	0	46,951	17.0
DF-2	48	51,102	17.0
DF-3	488 ^a	44,422	16.8
DF-4	793	45,600	12.0

^aExact sample time not noted. Estimated value is given.

downstream of the 4-L container, they are not instantaneous samples, but an average sample over a short period of time.

The DW raffinate activity levels for the complete processing run are reported in Table 30. Average activities are listed, since two scintillation cocktails and two gamma tubes were prepared for each sample. Gamma activity at 59.5 keV is listed because this is the most abundant gamma signal for ^{241}Am .

The alpha activity, as determined by scintillation counting, is the most important parameter for the DW stream, since this value determines whether the stream is to be considered TRU or non-TRU waste. A plot of alpha activity vs. time for the DW samples is given in Fig. 41. (Note in Fig. 41, the x-axis is not to scale because of the bar chart format.) The arrow on the activity spike at 641 min of running time indicates that the actual value is off the chart. This spike resulted from the wrong pump being shut off at the end of processing for the third day. As seen from Fig. 41, the processing goal of 0.22 dpm/ μ L (corresponding to 0.1 nCi/mL) in the DW raffinate was not met. However, the raffinate activity in the carboys is acceptable to ANL's Waste Management Operations for disposal.

The peaks and valleys seen in Fig. 41 can best be understood when the DW activity vs. time chart is broken up into segments representing the individual processing days. The charts of DW alpha activity vs. time for each of the four days of processing are shown in Figs. 42 through 45.

Fig. 41. Scintillation Counting Results vs. Time for DW Samples during NBL Batch 2 Processing

Table 30. Sample Time and Average Scintillation and Gamma Counting Results for DW Samples

Sample Name	Sample Time, min	Average Scintillation Counts, cpm/ μ L	Avg. Gamma Counts @ 59.5 keV, cps/ μ L
DW-1	13	1.00	2.05E-03
DW-2	33	41.5	1.30E-02
DW-3	43	52.9	5.91E-03
DW-4	66	11.3	1.03E-03
DW-5	85	11.4	1.01E-03
DW-6	141	16.5	6.25E-04
DW-7	151	8.8	2.40E-04
DW-8	173	7.2	2.21E-04
DW-9	211	7.4	2.92E-04
DW-10	221	7.19	1.75E-04
DW-11	274	81.7	1.85E-03
DW-12	304	3.66	a
DW-13	326	87.2	5.24E-03
DW-14	331	48.9	1.80E-03
DW-15	336	23.2	6.55E-04
DW-16	349	17.6	2.53E-04
DW-17	356	13.3	3.08E-04
DW-18	374	12.0	6.46E-04
DW-19	384	15.9	8.87E-04
DW-20	436	2.55	5.62E-05
DW-21	454	1.65	a
DW-22	461	2.21	1.11E-04
DW-23	467	15.5	7.24E-04
DW-24	470	18.4	6.94E-04
DW-25	478	14.7	5.88E-04
DW-26	478	11.4	3.99E-04
DW-27	501	12.0	4.28E-04
DW-28	531	8.87	2.02E-04
DW-29	556	7.76	2.41E-04
DW-30	576	7.28	2.48E-04
DW-31	606	6.44	1.92E-04
DW-32	632	6.24	1.61E-04
DW-33	641	530	1.46E-02
DW-34	647	20.8	5.69E-04
DW-35	649	11.6	3.53E-04
DW-36	653	8.56	8.28E-05
DW-37	657	10.7	2.87E-04
DW-38	665	7.70	2.84E-04
DW-39	668	7.20	1.87E-04
DW-40	675	6.38	2.23E-04
DW-41	691	4.62	1.34E-04
DW-42	720	3.79	8.26E-05
DW-43	742	3.39	8.74E-04
DW-44	760	3.19	9.76E-05
DW-45	793	2.91	8.43E-05
DW-46	814	3.33	6.85E-05
DW-47	843	3.09	6.55E-05
DW-48	880	3.12	9.61E-05
DW-49	901	2.69	4.57E-05

^aNot detected in this sample.

Fig. 42. Scintillation Counting Results vs. Time for DW Samples during Day 1 of NBL Batch 2 Processing

Fig. 43. Scintillation Counting Results vs. Time for DW Samples during Day 2 of NBL Batch 2 Processing

Fig. 44. Scintillation Counting Results vs. Time for DW Samples during Day 3 of NBL Batch 2 Processing

Fig. 45. Scintillation Counting Results vs. Time for DW Samples during Day 4 of NBL Batch 2 Processing

As seen in these figures, the peaks in DW activity for days 1 and 3 are associated with startup of the system for that day. The first few DW samples for the day had very low activity levels associated with the cold startup procedure, during which all pumps except DF were running. This low-activity period is then followed by a spike in activity, which came immediately after the start of the DF feed. After the spike, the activity in the DW samples tapered off slowly, finally reaching a steady state.

In contrast to days 1 and 3, the first samples taken on days 2 and 4 showed high activity levels. The reason for the high activity level of the first sample on day 2 (274 min) is not clear. No unusual events were recorded for the end of day 1 or the beginning of day 2 that could account for this spike. However, the remaining DW samples for day 2 follow the general pattern stated above. The high activity level of the first sample on day 4 (641 min) resulted from the mistake made in the shutdown procedure at the end of day 3. As can be seen in Fig. 45, this high activity was quickly flushed out of the system, and by the time the hot DF feed flow was started (at 649 min), the activity in the DW stream was below 12 dpm/ μ L.

As stated above, the startup procedure for the system was altered during the processing of this batch. This was done to decrease the spike in DW activity that occurred when the DF feed was introduced upon startup. Figures 44 and 45 indicate that the startup procedures used on days 3 and 4 did, indeed, decrease the magnitude of this spike in DW activity.

The activity for the samples of the carboys into which the DW raffinate was pumped is given in Table 31. Carboys 1-5 were filled on the first day of processing and were neutralized after the sample had been drawn for analysis. Because of high alpha activity levels, carboys 6, 7, and 13 were set aside for recycle to the system for further processing as part of the feed for Batch 2 Waste (Sec. V.C). The contents of carboy 1 had already been neutralized by the time we had decided to recycle the carboys; otherwise, carboy 1 would have also been recycled.

Table 31. Sample Time and Average Scintillation and Gamma Counting Results for Carboy Samples

Sample Name	Sample Time, min	Average Scintillation Counts, cpm/ μ L	Avg. Gamma Counts @ 59.5 keV, cps/ μ L
C-1	68	49.28	3.75E-03
C-2	98	13.76	5.17E-04
C-3	151	26.99	8.55E-04
C-4	190	7.65	3.64E-04
C-5	231	7.44	3.50E-04
C-6	321	78.00	2.24E-03
C-7	367	19.52	1.01E-03
C-9	503	11.20	4.41E-04
C-10	541	10.24	3.36E-04
C-11	586	7.38	a
C-12	638	6.57	2.44E-04
C-13	685	38.24	1.32E-03
C-14	731	4.39	1.30E-04
C-15	785	3.26	1.23E-04
C-16	831	3.13	7.66E-05
C-17	877	3.11	5.92E-05

^aNot detected in this sample.

Scintillation and gamma counting results for the rest of the process streams (DX, EW, FW, GW, HW, HP, and acid rinse) are given in Figs. 46-51 and Tables 32 and 33.

Analysis of the organic feed samples (DX) shows an increase in both the gamma and alpha activity at about 350 min into the run (Fig. 46). This corresponds to startup on day two. During startup, the solvent was contaminated, and more than 400 min was required to remove this activity from the solvent. The activity in the solvent also increases after 800 min. This could be due to increased activity in the carbonate washes and/or to more of the solvent bypassing the alumina column.

Counting results for the americium product samples are reported in Fig. 47. These data show a decrease in activity over the first 500 min of the run, followed by an increase in activity over the next 300 min. This is probably due to the problem we had at the beginning of the run with the EW effluent flow. For the first 90 min of the run, this flow was not being removed from stage 11 because the line size was too small. Because this stream was not removed, more americium was recycled back into the extraction section, thereby allowing the americium to build up in the system. Once this flow was fixed by replacing the fitting with a larger diameter fitting, the americium apparently dropped in concentration as it was bled out of the system at 3 mL/min. This appears to be what we see in Fig. 47.

Sample analysis of the plutonium strip solution (FW) is reported in Fig. 48. The cause for the decrease in activity during day 3 of the run (300-600 min) is not known for sure, but could be the decrease in the feed flow rate that was noted earlier. The decrease in the gamma counts after 600 min is probably related to the increase in americium removed by the EW raffinate stream (Fig. 47). With more americium being removed in the americium product stream, less americium would end up in the plutonium strip solution.

Sample analyses of the carbonate washes are shown in Figs. 49 and 50. Both show the general trend of increasing activity, with a drop in activity at the 500-min mark. At that time, both carbonate solutions were replaced with fresh solutions. The decrease in the gamma counts in the first carbonate wash (GW, Fig. 49) after the 600-700 min mark is again probably related to the increase in americium removed by the EW raffinate stream (Fig. 47).

Sample analysis of the acid rinse solution is shown in Fig. 51. The counting trend for this solution is downward, with spikes at shutdown on day 3 (600 min) and day 4 (800 min). Data for the organic solvent stream leaving stage 20 (HP) and the solvent exiting the bottom of the alumina column (BC) are reported in Tables 32 and 33. These data generally show low levels of activity in both streams, with the solvent exiting the alumina column being two or three times lower. The large spike in activity seen in sample HP-3 is probably related to the startup problems on day 2.

C. Processing of Batch 2 Waste

1. Flowsheet Development

Approximately 46 L of waste was collected from three carboys that had unacceptable high activity levels during the processing of Batch 2, acidified carbonate waste from Batch 2, old samples, and various other solutions that have been collecting in the glovebox. This waste was designated as NBL Batch 2 Waste. We employed the GTM to generate a flowsheet for processing this waste, using Fig. 40 as a starting point. The feed composition was estimated as shown in Table 34.

Fig. 46.

Average Scintillation and Gamma Counting Results for DX Samples

Fig. 47.

Average Scintillation and Gamma Counting Results for EW Samples

Fig. 48.

Average Scintillation and Gamma Counting Results for FW Samples

Fig. 49.
Average Scintillation and Gamma
Counting Results for GW Samples

Fig. 50.

Average Scintillation and Gamma
Counting Results for HW Samples

Fig. 51.

Average Scintillation and Gamma
Counting Results for Acid Rinse (IF)
Samples

Table 32. Sample Time and Average Scintillation and Gamma Counting Results for HP Samples

Sample Name	Sample Time, min	Average Scintillation Counts, cpm/ μ L	Avg. Gamma Counts @ 59.5 keV, cps/ μ L
HP-1	199	6.10	a
HP-2	241	7.69	1.70E-04
HP-3	361	246	a
HP-6	491	5.54	a
HP-7	559	3.86	a
HP-8	618	1.64	3.04E-04
HP-9	708	2.91	a
HP-10	780	2.94	a
HP-11	843	3.08	a

^aNot detected in this sample.

Table 33. Sample Time and Average Scintillation and Gamma Counting Results for Bottom-of-Column (BC) Samples

Sample Name	Sample Time, min	Average Scintillation Counts, cpm/ μ L	Avg. Gamma Counts @ 59.5 keV, cps/ μ L
BC-1	166	3.95	7.24E-04
BC-2	241	1.10	9.23E-04
BC-3	361	3.60	a
BC-6	568	8.71	a
BC-8	618	3.92	a
BC-9	708	1.04	a
BC-10	780	1.12	a
BC-11	843	0.8	a
BC-12	910	0.9	a

^aNot detected in this sample.

Table 34. Estimated Feed Composition of NBL Batch 2 Waste

Component	Conc., <u>M</u>
H ⁺	3.00
Al ³⁺	0.2
Na ⁺	0.05
Am ³⁺	1.6E-7
Pu ⁴⁺	2.6E-5
F ⁻	0.1
PO ₄ ³⁻	0.2

Modifications made to the Batch 2 flowsheet (Fig. 52) include decreased flow rates for the scrub, americium strip, and plutonium strip; a lower concentration of ammonium oxalate for the plutonium strip; and a lower concentration of aluminum nitrate for the scrub solution. Finally, the feed flow rate was increased.

The ammonium oxalate concentration was lowered to decrease the amount of solids produced when this stream is evaporated to dryness. The stoichiometric amount of ammonium

Fig. 52. Flowsheet for NBL Batch 2 Waste

oxalate needed to strip the plutonium present in the organic flowing into the plutonium strip section is $\sim 0.001M$. The concentration used in the strip feed will be $0.05M$, which is 20 times greater than needed but considerably less than the $0.28M$ used in Batch 2. The flow rate on this stream was reduced to decrease the volume of solution to be evaporated.

The aluminum concentration in the scrub was lowered from 2 to $0.1M$ because the feed does not contain as much phosphate or oxalate, which complexes Pu(IV). The americium strip and scrub flow rates were decreased to reduce the amount of the DW raffinate produced during the run.

The feed flow rate was increased from 100 to 200 mL/min. This will allow all of the solution in the feed carboy to be processed in one day. The plutonium and americium

concentrations are so low that the increased flow rate will not significantly affect the extraction section because of the decreased O/A.

Stages 1-14 were modeled using the GTM (version 2.5). The plutonium strip section could not be modeled because ammonium oxalate is not included in the model. Results from the recommended flowsheet are shown in Table 35. The model predicts that the DW raffinate should contain $<10^{-12}\text{M}$ Am³⁺ and Pu⁴⁺. This is well below the concentrations needed to satisfy the 0.1 nCi/g limit set by WMO.

Table 35. Predictions of GTM for Specified Flowsheet

Stream Identity	Flow Rate, mL/min	Component Conc., M						
		H	Al	Na	Am	Pu ⁴⁺	F	PO ₄
DX	50	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15
DF	200	3.00E+00	2.00E-01	5.00E-02	1.60E-07	2.60E-05	1.00E-01	2.00E-01
DS	20	5.00E-02	1.00E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
EF	37	4.00E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
DW	253.9797	2.37E+00	1.65E-01	3.93E-02	2.10E-13	3.69E-14	7.87E-02	1.57E-01
EW	3.020455	7.73E-02	2.11E-10	1.22E-12	9.90E-06	3.88E-06	2.43E-05	1.19E-09
EP ^a	49.99999	2.25E-03	1.12E-19	6.56E-22	4.19E-08	1.03E-04	3.25E-06	9.45E-19

^aBecause the plutonium strip section cannot be modeled in the GTM, the organic leaving the americium strip section was labeled EP and reported by the GTM.

2. Discussion of Run

Only two major problems occurred during the run: (1) the DX feed pump was not calibrated before the run, and (2) the flow rate of the DF feed pump steadily decreased during the initial stages of the run until the cause was identified and corrected.

Foaming was observed in the organic interstage lines of the extraction section during the first 10 min of the run. After this was discovered, we determined that the DX feed pump had not been calibrated before the run. The flow rate was then measured as 59 mL/min. After decreasing the flow rate to 50 mL/min, the foaming problem disappeared.

The problem with the DF feed pump was slightly more difficult to fix. A 5- μm and a 1- μm filter are located on the suction side of the DF pump. These filters remove any solids present in the feed tank. Evidently, this feed had a significant amount of particulate matter in it. After 150 min of processing, the DW raffinate flow rate was measured and found to be only 150 mL/min, when it should have been 250 mL/min. The DF feed tank level was measured, and based on tank depletion, the DF feed rate was calculated to be only 88 mL/min. The feed pump flow rate was increased, but the flow rate quickly dropped. After trying unsuccessfully to adjust the DF flow rate several times, we turned off the DF pump and replaced the 5- μm filter with a new filter. The DF pump was turned back on a couple of minutes later. However, changing the 5- μm filter did not seem to help. Therefore, the 1- μm filter was also changed. When this did not help either, the 1- μm filter was removed from the system, after which the DF pumped at an estimated 370 mL/min for 10 min. The pump was adjusted to the correct flow rate. After that, the flow rate decreased only slightly throughout the rest of the run. The 1- μm filter evidently plugged rapidly, creating a large pressure drop across the filter. The DF pump was unable to provide enough suction to overcome the pressure drop and the flow rate decreased.

3. Sample Analysis

Samples collected during the processing of Batch 2 Waste were both scintillation and gamma counted to determine the Pu and Am concentrations in the various streams. Samples were taken of the hot feeds in the glovebox before processing started. The Pu and Am concentrations in the hot feeds are shown in Table 36.

Table 36. Plutonium and Americium Concentrations in the TRUEX Solvent and the Aqueous Feed Solution for NBL Batch 2 Waste

Sample ID	Conc., g/L		Total α , cpm/ μ L	59.5 keV Gamma Count Rate, cps/ μ L
	Pu	Am		
DX #1	1.88E-04	3.59E-07 ^a	3,470	6.1E-03
DF #1	5.15E-03	3.39E-05 ^a	11,300	0.57
DF #2	4.53E-03	2.96E-05 ^b	9,950	0.50

^aInitial sample.

^bThis sample taken 124 min into the run.

The DW raffinate exited stage 1, where it was pumped to a 4-L surge tank located in the contactor glovebox. The raffinate was then pumped from the surge tank into a carboy, where DW raffinate samples were taken about every 20 min.

Figure 53 shows the Am and Pu concentrations in the DW raffinate. The initial (0 min) high concentrations of both Am and Pu probably result from contamination in the raffinate lines and surge tank, but raffinate from the cold feed washed the contamination out, and the concentrations quickly dropped. A small activity spike was seen when the hot feed was started. This activity spike had been seen in previous runs, but the use of a cold feed reduced the spike. The DW raffinate was not affected by the DF feed pump fluctuations because the extraction section contained more stages than necessary to reduce the raffinate to its minimum achievable activity.

Fig. 53. Americium and Plutonium Concentrations in the DW Raffinate

The DW raffinate averaged about 20 cpm/ μ L on the scintillation counter; <0.5 cpm/ μ L was expected. A batch test done with the raffinate during the run showed that the activity could not be significantly lowered by further contacts with the TRUEX solvent. The D value for the raffinate and fresh solvent was 0.22, indicating that the raffinate contained some unextractable species. The 20 cpm/ μ L in the raffinate corresponds to 9.1 nCi/ μ L, which is greater than the 0.1 nCi/g limit set by ANL's Waste Management Operations (WMO), but much less than the 100 nCi/g TRU limit. Since we could not obtain the 0.1 nCi/g limit, we neutralized the raffinate for transport to WMO.

The sample of DW raffinate at 110 min was lost before it could be analyzed, and the last DW sample was counted by liquid scintillation once before this sample was lost. The plutonium concentration in this sample has not been corrected for americium decay since no sample was available for gamma counting.

The DW raffinate was collected in 10 L carboys in a hood next to the glovebox. The carboys were filled to approximately 7.5 L. After being filled, they were mixed and a sample was scintillation counted. If the activity was approximately 20 cpm/ μ L, the carboy was neutralized with 10M NaOH. As the NaOH was added, the pH was checked using pH paper. Aluminum present in the raffinate precipitated as the NaOH was added, forming a slurry. When the pH of this slurry reached 7, the bottle was capped and removed from the hood.

The EW raffinate is the americium product stream. This stream is taken as a portion of the aqueous phase flowing from stage 11 to stage 10. Table 37 reports the Am and Pu concentration in the EW raffinate samples. Some of the plutonium concentrations were calculated to be negative because the plutonium concentration was calculated by subtracting the americium α -activity. Since the americium concentration is based on gamma counting, the plutonium concentration is strongly dependent on americium concentration. This is especially true when [Am] is equal to or greater than [Pu]. Such is the case in the EW raffinate. Therefore, plutonium concentrations are not reliable for this stream.

Batch 2 had a much higher americium concentration than Batch 2 Waste. Since the stages were never drained between runs, the americium was being washed out of the americium strip/scrub section, as seen by the high initial concentration quickly dropping.

Table 37. Concentration of Americium and Plutonium in the EW Samples

Sample	Time, min	Conc., mg/L		Total α , cpm/ μ L
		Pu	Am	
EW #1	47	<0 ^a	2.9	21700
EW #2	109	2	1.7	13200
EW #3	169	6	1.7	12400
EW #4	229	<0 ^a	1.8	13400
EW #5	294	5	1.4	11900
EW #6	364	<0 ^a	1.6	12200

^a Corrected plutonium concentrations were <0, which is obviously impossible. See text.

The FW raffinate is the plutonium product stream, and the majority of the plutonium is recovered here. This stream is aqueous raffinate that exits stage 15. Figure 54 shows the concentration of Am and Pu in the FW raffinate. The plutonium decreased steadily for the first half of the run. Because the feed pump flow rate was decreasing, less plutonium was entering the system, thereby decreasing plutonium concentration in the plutonium product stream. When the feed flow

Fig. 54. Americium and Plutonium Concentrations in the FW Raffinate

rate was increased, the plutonium concentration increased (between 200 and 300 min). The americium concentration should follow the same trend as the plutonium concentrations, i.e., decrease steadily and then rise between 200 and 300 min. However, the concentration dropped steadily throughout the entire run.

The GW raffinate is the raffinate from the first carbonate wash stage. This stream is recycled to the feed tank, which holds approximately 1.5 L. Figure 55 shows the Am and Pu concentrations in the GW raffinate. The concentrations remained fairly constant throughout the run. Most of the activity should have been removed from the organic phase before it reached this stage, but a small variation in concentration would be difficult to detect because of the initially high activity level in the GF feed. The GF had initially high activity levels because the feed carbonate was used to calibrate the carbonate feed pumps.

Fig. 55. Americium and Plutonium Concentrations in the GW Raffinate

The HW raffinate is the raffinate from the second carbonate wash stage and is also recycled to a 1.5-L feed tank. Figure 56 shows Am and Pu concentrations in the HW raffinate. The concentrations are fairly constant throughout the run, rising only slightly toward the end.

Fig. 56. Americium and Plutonium Concentrations in the HW Raffinate

The HP product stream is the organic that leaves stage 20. It is either pumped to the top of the alumina column or into the solvent reservoir, where it bubbles through 0.1M HNO_3 . Figure 57 shows Am and Pu concentrations in the HP product. The concentrations of Am and Pu decreased slightly throughout the run.

Fig. 57. Americium and Plutonium Concentrations in the HP Product

The column samples are taken as the solvent leaves the alumina column. Solvent from the HP product is pumped to the alumina column, where it travels through the alumina bed, is pumped into the solvent reservoir tank, and bubbles through 0.1M HNO_3 to reacidify the solvent

before being fed to stage 1. The alumina column is a solvent polishing step to remove any solvent degradation products that the carbonate washes are unable to remove. Because the stages were not drained between the running of Batch 2 and Batch 2 Waste, the solvent remaining in the contactors was not cleaned with solvent in the reservoir before the run. Therefore, the solvent that exited the contactors during the first part of the run was pumped directly into the alumina column reservoir. This solvent probably had an initially high activity level; however, as this solvent is washed through the column and diluted with the cleaned solvent the activity level should decrease. The slight rise in americium concentration in the middle of the run, shown in Fig. 58, cannot be explained at this time.

Fig. 58. Americium and Plutonium Concentrations in the Organic Phase Leaving the Column

The tank samples are taken from the organic solvent held in the solvent reservoir. This reservoir contains solvent that has been processed through the alumina column and solvent that bypasses the column. All of the solvent bubbles through 0.1M HNO_3 to reacidify before being fed to stage 1. Figure 59 shows the concentrations of Am and Pu in the solvent reservoir. The Am and Pu concentrations decrease throughout the run. The initial activity level was much higher in the solvent reservoir than in the HP product. The activity of the solvent in the reservoir decreased as it was diluted with solvent of lower activity from the contactors.

Samples were also taken from the acid rinse (initially 0.1M HNO_3) that the organic phase bubbles through as it enters the solvent reservoir. The acid rinse reacidifies the organic phase before it is fed back to the contactors. Figure 60 shows the concentrations of Am and Pu in the acid rinse. The concentrations in the second sample are much lower than in the first and third samples. This difference cannot be explained.

D. Material Balance

Solutions generated during the processing of Batch 2 and Batch 2 Waste have been analyzed to determine Pu and U concentrations of the various streams. Based on the analysis of these streams, a Pu and U material balance was completed.

Fig. 59. Americium and Plutonium Concentrations in the Organic Reservoir

Fig. 60. Americium and Plutonium Concentrations in the Acid Rinse

1. Plutonium

Plutonium concentrations were calculated in several ways. The first involved scintillation counting to find total alpha activity, then subtracting alpha activity due to americium decay as calculated by the 59.5 keV gamma ray. The remaining alpha activity is assumed to be caused by decay of plutonium. (This method is denoted " α - γ analysis.") The next was scintillation counting to determine total alpha activity, followed by alpha spectroscopy to determine the percentage of alpha activity from each isotope (this method is denoted " α -spec analysis"). The final method was direct measurement of Am and Pu gamma rays (this method is denoted " γ analysis").

Batch 2 feed consisted of 53.9 L of solution. Feed samples were analyzed by α - γ analysis and γ analysis; the results are reported in Table 38. Isotopic composition of the feed was assumed to be 90.3% Pu-239, 8.96% Pu-240, and 0.8% Pu-241 based on isotope information

Table 38. Composition of the Feed for Batch 2^a

Method	Pu Conc., g/L	Total Pu in Feed, g
α - γ analysis	2.31E-01	12.5 $\pm$ 0.1
γ analysis	2.28E-01 ^b	12.3 $\pm$ 0.7

^aFeed samples were taken after tear occurred in the feed carboy and the resulting cleanup operations.

^bPlutonium concentrations corrected for γ -ray self-absorption estimated at 20% and for isotopic composition (only the Pu-239 concentration is measured directly). The Pu-240 and Pu-241 concentrations must be added in using the estimated isotopic ratios.

provided by the NBL on their waste disposal forms, which report a total of 13.3 g of plutonium in Batch 2. Assuming 12.5 g Pu in the feed, 800 mg Pu was lost in the cleaning operations following a tear in the feed carboy.

Plutonium was recovered in the plutonium product stream, a total of 14.5 L of solution. A representative sample was taken of this stream and analyzed using all three methods (Table 39). The isotopic composition was assumed to be the same as the feed.

Table 39. Composition of the Plutonium Product Stream for Batch 2

Method	Pu Conc., g/L	Total Pu in Product, g
α - γ analysis	9.04E-01	13.1 $\pm$ 0.2
γ analysis	7.61E-01 ^a	11.0 $\pm$ 1.3
α -spec analysis	8.21E-01 ^b	11.9 $\pm$ 0.2

^aPlutonium concentrations corrected for γ -ray self-absorption estimated at 20% and for isotopic composition (only the Pu-239 concentration is measured directly). The Pu-240 and Pu-241 concentrations must be added in using the estimated isotopic ratios.

^bThe α -spec analysis only measures Pu-239 and Pu-240. To obtain the total plutonium concentration, the amount of Pu-241 must be added in using the estimated isotopic ratios.

An additional 105 mg of plutonium, which is not included in Table 39, was accounted for in the raffinates and in samples collected during the run. All these analyses were done by the α - γ method.

The α -spec analysis should yield the best result because the fewest assumptions were made in calculating the concentration. Therefore, we assume that 11.9 g of plutonium was recovered in the plutonium product.

The most suspect assumption made in the γ -analysis is that of 20% self-shielding. Work is underway to better estimate the amount of self-shielding.

In α - γ analysis, the assumption that any remaining activity is due only to plutonium after americium α -activity has been subtracted could be a source of error. However, for the specific activities and concentrations of other materials that decay by α -particles, such as uranium, the assumption that any residual is due entirely to plutonium should be valid. But α -activity from other nuclides would explain why the plutonium concentration in the product is so much higher than when

calculated by the other methods. One such isotope is Pu-238. Since Pu-238 has such a short half-life (87.7 yr) compared to the other plutonium isotopes, very little would be required to increase the total α -activity. This analysis assumes that α -activity is only from the decay of Pu-239, Pu-240, and Am-241.

In conclusion, 12.0 g of plutonium was recovered from 12.5 g of plutonium remaining in the feed after the feed spill for a 95% total plutonium recovery.

2. Uranium

The waste forms reported 16.3 g of uranium. If the same percentage of uranium was lost as plutonium (approximately 6%), 15.3 g of uranium remained in Batch 2 feed after the spill. The ICP/AES analysis, done on the plutonium product stream, determined that it contained 1.0 g/L uranium. Thus, in the 14.5 L of plutonium product solution, 14.5 g of uranium was recovered, for a 95% total uranium recovery.

3. Lead in the Raffinate

A tear in the feed carboy caused Batch 2 to leak into a secondary container. Unfortunately, the lead shielding for this carboy was placed between the carboy and the secondary container. The highly acidic feed dissolved some of the lead. The lead from the feed is now in the raffinate from Batch 2, most of which was neutralized. When this neutralized raffinate was analyzed, it contained 958 ppm lead. Batch 2 raffinate that contained excessive levels of α -decay was not neutralized and was recycled as the feed for Batch 2 Waste. Therefore, the raffinate from this feed also contains lead. A sample of Batch 2 Waste raffinate was analyzed before being neutralized and contained 984 ppm lead. This waste was then neutralized. Batch 2 and Batch 2 Waste are mixed wastes because of the high lead content.

Several experiments were run to determine if the lead could be precipitated, making the supernatant liquid simply radioactive waste instead of mixed waste. Two different methods were tried--(1) raising the pH to 11 to precipitate lead hydroxide and (2) adding sulfuric acid to precipitate lead sulfate. A sample of the raffinate was drawn and centrifuged to remove any solids. Two 500 μ L aliquots were drawn from the centrifuged sample, and a 2 μ L spike of Pb-210 stock solution was added to each sample. The samples were then gamma counted to determine the initial activity of Pb-210. After the initial counting, five drops of 10M NaOH were added to one sample, and five drops of 7.5% sulfuric acid were added to the other. The samples were centrifuged again, and a 300 μ L aliquot was gamma counted from each sample. For both samples nearly all of the lead stayed in solution, as determined by the activity of the Pb-210, indicating that raising the pH or adding sulfuric acid does not effectively precipitate the lead in this solution. It was suggested to co-precipitate the lead with barium sulfate. Therefore, ten drops of a barium nitrate solution were added, and a white precipitate formed immediately. The sample was then centrifuged and all of the supernatant liquid drawn off. The liquid and the solids were gamma counted and no Pb-210 was detected in the supernatant liquid. Nearly all of the activity was recovered in the precipitate, indicating that the Pb-210 had been precipitated. Because WMO picked up the waste as-is, no further testing or processing was completed.

E. Processing of Batch 3

The next NBL waste batch to be processed, Batch 3, contains approximately 28 g of plutonium and 29 g of uranium. Also, an estimated 300 mg of americium was assumed to be present in the feed. The estimated feed composition for Batch 3 is shown in Table 40.

Table 40. Feed Composition for Batch 3

Component	Conc., <u>M</u>
H ⁺	5.59
UO ₂ ²⁺	0.00242
Pu ⁴⁺	0.00235
Am ³⁺	2.49E-05
PO ₄ ³⁻	0.53
NO ₃ ⁻	4.01

To develop a flowsheet for processing Batch 3, the flowsheet for processing Batch 2 was used as a starting point. Three modifications were made:

1. The scrub flow rate was reduced from 70 to 30 mL/min.
2. The plutonium strip flow rate was reduced from 12 to 8 mL/min.
3. The feed flow was increased from 100 to 120 mL/min.

The feed does not contain as much phosphate as Batch 2. Therefore, the scrub flow rate was decreased because not as much aluminum is needed to complex the phosphate. Decreasing the scrub flow rate also reduces the amount of raffinate generated.

The plutonium strip flow rate was decreased from 12 to 8 mL/min to shorten the product treatment time following the TRUEX run. Evaporating this stream to dryness has proven to be the most time-consuming step in the process. Therefore, with this decrease in the flow rate, the volume of solution to be evaporated is reduced, and the time taken to evaporate solutions should correspondingly decrease.

The feed flow rate was increased slightly to reduce the amount of raffinate generated and to speed up processing time.

Stages 1-14 were modeled using the GTM (version 2.5). The strip section could not be modeled because ammonium oxalate is not included in the model. Results from the recommended flowsheet are shown in Table 41. The model predicts that the DW raffinate should contain $<5 \times 10^{-12}$ M Am, Pu, and U. This is well below the concentrations needed to satisfy the 0.1 nCi/g limit set by WMO. The flowsheet that will be used to process Batch 3 is shown in Figure 61. All preparations for processing Batch 3 have been completed. Batch 3 material can be received for TRUEX processing as soon as Batch 2 plutonium product stream has been evaporated, calcined, reduced to metal, and shipped out of the building.

Table 41. Predictions by GTM for Batch 3 Flowsheet

Stream Identity	Flow Rate, mL/min	Component Concentration, M					
		H	Al	UO ₂	Am	Pu ⁴⁺	PO ₄
DX	50	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15
DF	120	5.59E+00	0.00E+00	2.42E-03	2.49E-05	2.35E-03	5.30E-01
DS	30	1.00E-02	2.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
EF	50	4.00E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
DW	197	3.42E+00	3.05E-01	1.46E-14	1.86E-12	3.55E-14	3.23E-01
Am Prod	3	6.89E-02	1.23E-09	4.43E-04	9.83E-04	1.59E-04	5.70E-11
EP ^a	50	2.38E-03	2.69E-19	5.78E-03	4.91E-07	5.63E-03	7.96E-23

^aBecause the plutonium strip section cannot be modeled in the GTM, the organic leaving the americium strip section was labeled EP and reported by the GTM.

Fig. 61. Flowsheet for Processing Batch 3

VI. ADVANCED EVAPORATOR TECHNOLOGY

(D. B. Chamberlain, S. Betts, L. Nuñez, D. G. Wygmans, and G. F. Vandegrift)

The purpose of this program is to develop evaporator technology for concentrating process radioactive waste and product streams such as those generated by the TRUEX process. Minimizing waste generation requires that equipment be installed for concentrating both radioactive waste streams and recycling the decontaminated condensates. A technology that shows a great deal of potential for this application is an evaporator being developed by LICON Inc. (Pensacola, Florida).

Initial studies will evaluate this technology for concentrating specific process streams in terms of (1) economic and institutional benefits and/or detriments, (2) effectiveness of this technology in terms of concentrating radioactive product and waste streams and decontamination factors for radionuclides in the overheads, and (3) the effects of concentration on plant operations. LICON and Argonne will work together to (1) design an evaporator specifically for remote operation and (2) in a hot facility at Argonne, test the remote operability and maintenance of this evaporator and other equipment in glovebox, shielded-cell, and canyon facilities. In later stages of the program, this equipment will be installed in a DOE processing/production plant for actual in-plant demonstration.

A portion of this program initially focused on completing a literature survey, where past data on mixed phase equilibria (vapor/liquid and vapor/liquid/solid) of aqueous solutions of HNO_3 in the presence of metal nitrate salts were collected, evaluated, and summarized. Information was collected on water and nitric acid concentrations in the liquid and vapor phases as a function of temperature, pressure, and composition of the aqueous solution (e.g., effects of metal nitrate salts on the volatilities of water and nitric acid). Further, solubility data as a function of solution composition were collected and summarized. These data are important in designing an evaporator for a specific stream, setting conditions of pressure and temperature, predicting effluent rates and compositions for the condensate and the bottoms, and knowing to what degree a stream can be concentrated. The literature survey is also critical to the design and interpretation of our own experiments to collect data not available in the literature.

A. Testing of Laboratory-Scale Evaporator

1. Preparations for Experimental Work

A laboratory-scale evaporator, a model FVP-C3 manufactured by LICON, was delivered to ANL in late July. Installation and connection to the hood were completed in early August. The floor plan for the area where the evaporator has been installed is shown in Fig. 62, which indicates the footprint of the evaporator and hood.

Because acid fumes cannot be introduced into the laboratory ventilation system, we analyzed ways of eliminating these vapors at the ventilation hood to which the evaporator is connected. We decided on the use of chemically treated filters, which contain particles on which vapors are sorbed. These filters are used on vent-less fume hoods available from many manufacturers. Three such sorptive filters were purchased from Heat Systems, Inc. (Farmingdale, NY). A filter housing is being fabricated to house these filters at the hood top. A temporary ventilation connection was made to the hood to allow operation of the evaporator using water and salt solutions as feed. Once the filter housing is installed, a permanent connection will be needed.

Fig. 62. Floor Plan for Test of Laboratory-Scale Evaporator

A safety review was completed for the first phase of the experimental work. This safety review covered the equipment setup of the evaporator and support equipment and the initial runs of the evaporator, during which water was evaporated. Those initial runs were made (1) to confirm that the evaporator is operating correctly and (2) to train ANL personnel in the operating and maintenance procedures for the evaporator. The safety review did not cover subsequent use of the evaporator to process liquids other than water, although equipment needs were anticipated for those subsequent processing runs. Most of the changes to the equipment and test plan specified in the safety review were minor. A second safety review will be undertaken once the final ventilation system is in place. This subsequent safety review will cover evaporation of acid solutions.

Shielding of certain parts of the evaporator was a major requirement specified by the safety review. As a result of those specifications, the bottom, framed-in section of the evaporator has been enclosed using Plexiglas panels. The distillate lines which are routed above this section were individually shielded to protect experimenters from spray should a leak in one of these pressurized lines develop. The distillate lines needed special attention since they can carry pressurized salt and acid solutions. All pressurized piping for the concentrate is contained within the bottom, Plexiglas-enclosed section. Figure 63 is a photograph of the unit.

The operation and maintenance manual for the evaporator, supplied by LICON, was modified to include the following items: (1) explanation of, and instructions for, the various items on the control panel, (2) explanation of, and testing procedures for, the automatic shutdown systems, (3) data entry logs for evaporator runs, and (4) instructions for using the electric heaters.

2. Experimental Runs Using Salt-Solution Feeds

Two evaporator runs using salt-solution feeds were completed. The first run employed a dilute $\text{Sm}(\text{NO}_3)_3$ feed solution and was performed to measure the decontamination factor (DF) that might be expected in this system. The second run used a feed solution of $\text{Al}(\text{NO}_3)_3$ and $\text{Sm}(\text{NO}_3)_3$. Concentration of the $\text{Al}(\text{NO}_3)_3$ was allowed to approach the solubility limit at the end of the run in order to estimate the boiling point elevations that can be expected in a high-salt solution.

Fig. 63.

Photograph of the Laboratory-Scale
LICON Evaporator

Both tests started with 45 L of feed and stopped when about 10 L of concentrate was left. No concentrate product was drawn off during either run. In both runs, electric heaters were used as the heat source. The temperature of the water in the heating loop was 71°C (160°F).

A schematic of the evaporator, giving the location of the conductivity elements (CE), pressure gauges (PI), thermocouples (TC), and flow meters (FI), is shown in Fig. 64. The numbering system for the sensors shown in Fig. 64 will be used in the text explaining the test runs.

a. Feed Solution of $\text{Sm}(\text{NO}_3)_3$

The feed for the first experimental run was $6.7 \times 10^{-4}\text{M}$ $\text{Sm}(\text{NO}_3)_3$. This concentration was chosen assuming a DF of 10^6 and a detection limit of 10^{-4} ppm samarium. Since the actual detection limit for samarium following neutron activation is about 10^{-5} ppm, we have a safety factor of 10 to ensure that samarium would be detectable in the distillate.

The test run took 2 h and 44 min from start-up to shut-down. Over that time, the 45 L of feed was evaporated down to about 8 L of concentrate, for a volume reduction of 5.6:1. Assuming total recovery of $\text{Sm}(\text{NO}_3)_3$ in the concentrate, the final concentration of $\text{Sm}(\text{NO}_3)_3$ in the concentrate should be about $3.77 \times 10^{-3}\text{M}$. About 34 L of distillate was produced during the run.

Fig. 64. Schematic of Laboratory-Scale Evaporator, Including Location of Sensors

Operational and process data were taken every 30 min, and samples of the concentrate and distillate were taken immediately following the recording of the data. Process data taken during the run are given in Table 42. Because of a problem with the vacuum gauge, the accuracy of the vacuum data listed in Table 42 should be regarded as around ± 102 mm Hg. Some samples taken during the run were sent out for neutron activation analysis. Analysis of those samples is underway.

The evaporator-feed flow rate (as measured by FI-605) was adjusted a few times throughout the test to keep the evaporator shell about half full of liquid. This flow rate was set at 4.2 L/min at the beginning of the run, where it stayed until toward the end of the run, when it slowly decreased to 3.8 L/min.

Table 42. Data from Evaporator Test Using a Feed of $6.7 \times 10^{-4}M$ $Sm(NO_3)_3$

Elapsed Time, min	Temp., °C				Vacuum, mm Hg	Distillate Conductivity, $\mu S/cm$	Distillate Production, ^a L/min	Evaporation Rate, ^b L/min
	Dist., TC-5	Vapor, TC-6	Conc., TC-7	Feed, TC-10				
0	22	21	21	21	560	12		
51	48	52	53	48	580	8	0.20	0.26
75	49	53	53	53	580	6	0.19	0.15
106	48	52	53	52	580	4	0.23	0.21
140	49	52	53	53	560	3	0.19	0.22
164	48	53	53	53	560	2	0.17	0.19

^aDistillate production measured by recording level increase in distillate tank.

^bEvaporation rate measured by level decrease in concentrate tank.

An important parameter in the evaporation process using salt-solution feeds is boiling-point elevation (BPE). As the concentration of dissolved solids in the boiling liquid increases, the boiling temperature of the liquid increases. The BPE is seen as a difference between the temperature of the boiling liquid (the concentrate) and the temperature of the vapor being driven off. Thus, for the laboratory-scale evaporator, BPE is the difference between the temperatures at TC-7 and TC-6. During this test the BPE was about 1°C (2°F) when the test started and fluctuated between 0.5 and 1°C (1 and 2°F) throughout. This fluctuation is probably not real but more likely due to the thermocouple indicator, which reads in 0.5°C (1°F) increments. No BPE was expected during this test because of the dilute feed. It is possible that the difference in the two temperatures does not represent the BPE but inaccuracies associated with measuring the temperature of the vapor. That the temperature difference is not a BPE is supported by the finding that it did not rise over the length of the run, as would be expected when concentration occurs.

As seen in Table 42, the conductivity of the distillate dropped from 12 $\mu S/cm$ at the beginning of the run to a final value of 2 $\mu S/cm$. We have not yet studied the correlation between the conductivity of the distillate and the amount of dissolved solids present. The only deduction that can be drawn from these data is that the distillate contained fewer dissolved solids than the distilled water from the laboratory spigot, with which the distillate tank had been filled before the run started.

Distillate production and the evaporation rates reported in Table 42 are based upon tank level changes. Both rates should be the same; some differences can be expected but these rates should agree over long periods of time.

b. Feed Solution of $Al(NO_3)_3$ and $Sm(NO_3)_3$

The feed for the second experimental run was 0.5M $Al(NO_3)_3$, plus $6.7 \times 10^{-3}M$ $Sm(NO_3)_3$. As before, we assumed DF of 10^6 with a detection limit of 10^{-3} ppm samarium. This implies that the samarium detection limit with other metals present is an order of magnitude higher than when no other metals are present. Once again a safety factor of 10 was employed to allow detection of samarium in the distillate, since the actual detection limit is 10^{-4} ppm. The aluminum nitrate concentration in the feed was chosen so that the aluminum concentration in the concentrate at the end of the run would be about 2M.

The test run spanned 3 h, 33 min of evaporator running time, although the system was shut down for about 30 min shortly after startup because a concentrate pump fuse had failed. During the test run, the 45 L of feed was evaporated down to about 10 L of concentrate, for a volume reduction of 4.5:1. Assuming total recovery of salts in the concentrate, the final concentration of $\text{Al}(\text{NO}_3)_3$ in the concentrate should be about 2.25M , and the final concentration of $\text{Sm}(\text{NO}_3)_3$ should be about $3.0 \times 10^{-2}\text{M}$. Before the run, a concentration vs. density correlation for an $\text{Al}(\text{NO}_3)_3$ solution at 35°C had been derived by using densities of prepared aluminum nitrate solutions. A density meter measured the density of samples during and after the run, and the concentration of these samples was calculated from the correlation. By this method, the concentrate at the end of the run was calculated to be 2.12M in $\text{Al}(\text{NO}_3)_3$. About 34 L of distillate was produced during the run.

Operational and process data were recorded every 30 min, and samples of the concentrate and distillate were taken immediately following the recording of the data. Process data obtained during the run are given in Table 43. Again, the accuracy of the vacuum data listed in Table 43 should be regarded as around ± 102 mm Hg. Some of the samples were sent out for neutron activation analysis, which is underway.

Table 43. Data from Evaporator Test Using a Feed of 0.5M $\text{Al}(\text{NO}_3)_3$ and $6.7 \times 10^{-3}\text{M}$ $\text{Sm}(\text{NO}_3)_3$

Elapsed Time, min	Temperatures, $^\circ\text{C}$					Distillate Conductivity, $\mu\text{S}/\text{cm}$	Distillate Production, ^a L/min	Evaporation Rate, ^b L/min
	Dist., TC-5	Vapor, TC-6	Conc., TC-7	Feed, TC-10	Vacuum, mm Hg			
0	49	53	54	52	580	2.3		
31	50	52	55	54	580	2.0	0.18	0.16
65	49	51.5	56	55	580	6.5	0.21	0.21
95	48	51	54	53	580	8.0	0.18	0.22
125	48	50	54	53	580	8.0	0.18	0.13
155	47	48	55	55	580	8.0	0.15	0.17

^aDistillate production measured by recording level increase in distillate tank.

^bEvaporation rate measured by level decrease in concentrate tank.

The calculated BPE (TC-7 minus TC-6) for this test was about 1°C (2°F) when the test started and rose to 7°C (13°F) at the end of the run. The greatest rise in the BPE occurred during the last 30 min of the test, when the BPE rose 3°C (5°F). This is because, prior to that time, the concentrate was periodically being diluted by new feed coming in to fill the concentrate tank as concentration occurred. Thus, during the final 30 min, after all of the feed had been added to the concentrate tank, the greatest amount of concentration occurred, leading to the sharpest rise in the BPE.

Interestingly, the rise in BPE did not correspond to a gradual rise in concentrate temperature as expected. Instead, this calculated rise in BPE corresponded to a drop in vapor temperature (at TC-6) from 53° (127°F) to 48° (118°F), although the system pressure appeared to remain constant. This finding is puzzling and needs to be studied further. It is possible, given a problem with the vacuum-gauge readings, that the system pressure did not remain constant, as indicated by the vacuum gauge.

The drop in vapor temperature throughout the run was also accompanied by a drop in cooling water temperature (at TC-1 and TC-2) and distillate temperature (at TC-5). The exact relationship between the drop in vapor and cooling water temperatures is not immediately clear.

The flow rate for evaporator feed (at FI-605) increased from 4.9 L/min (1.3 gpm) to 5.7 L/min (1.5 gpm) through the run. However, the flow meter FI-605 is calibrated for water at 21°C (70°F), and the viscosity of the concentrate flowing through the flow meter changed considerably as the test progressed. Therefore, the evaporator feed flow rate for this or any test should be used with caution.

The rise in conductivity over the run, as seen in Table 43, indicates that, as expected, complete decontamination was not attained.

Following the test run, the concentrate tank was drained. To flush the system, about 14 L of distillate was poured into the concentrate tank, and the evaporator was run for about 45 min using the same temperature and flow settings as used during the test. About 2 L was evaporated from the concentrate during this operation. After the flushing, the concentrate tank was drained again, and a density test on the recovered liquid suggested that this concentrate is 0.13M in $\text{Al}(\text{NO}_3)_3$. Further work is needed to establish an appropriate method of flushing the system after each run.

B. Solubility and Vapor-Liquid Equilibrium Data

To design an effective method for concentrating process streams, both solubility and vapor/liquid equilibrium data are needed. Solubility data are needed to determine the amount of solution concentration that can be achieved without precipitating components from solution. Vapor/liquid equilibrium data are needed to predict the vapor-phase concentrations for the various solution compositions that will be processed. Literature surveys were completed on both topics.

The conditions at which solids precipitate from mixed acid/metal-salt solutions as a function of temperature, pressure, and composition were obtained from these surveys. Solubility data were collected for nitrate salts of Al, Ca, Fe, La, Ni, Sm, and Na and for uranyl nitrates as a function of acid concentration at various temperatures. From these data we determined that aluminum nitrate had the lowest solubility of the nitrate salts studied. We also concluded that reducing the pressure decreases the boiling point of the system but has little effect on the vapor phase compositions. The presence of salts, with the exception of potassium nitrate, tends to salt out the nitric acid into the vapor phase, thus enriching the vapor phase in nitric acid. The solution boiling point also tends to increase as the salt concentration increases. Results from this survey will be published in a separate ANL report.

C. Modeling of Nitric Acid/Nitrate Salt Vapor Pressures (D. A. Johnson)

The GTM was used to calculate the activities of nitric acid and water in solutions from an evaporator process. These activities will be used to determine the composition of vapors in equilibrium with the solutions. This information will provide the best operating conditions for the LICON evaporator.

1. Calculation of Nitric Acid and Water Activities

Vapor-liquid equilibria and activity coefficient data were collected from literature reporting relevant data on systems containing nitric acid, water, and metal nitrates. A plot of the vapor-liquid equilibria data obtained for the nitric acid-water system is given in Fig. 65.

Fig. 65. Boiling Temperature for Nitric Acid-Water System. Based on information in Ref. 9.

The data of Davis and DeBruin⁹ were analyzed to ensure that we adequately understood the principles of vapor-liquid equilibria as applied to the nitric acid-water system at 25°C. The calculated nitric acid concentrations of Davis and DeBruin were compared with our calculations. An important part of the calculations involved choosing the appropriate standard reference state. In general, for water (the solvent), the activity coefficient $\gamma \rightarrow 1$ as the concentration of water approaches the pure liquid state. In the case of nitric acid, the standard state was chosen so $\gamma \rightarrow 1$ as the concentration or molality of nitric acid goes to zero or infinite dilution. Our calculations now agree with Davis and DeBruin.

The GTM equations for the activity coefficients and activities of nitric acid and water were examined with respect to making calculations at temperatures other than 25°C.

The stoichiometric mean activity coefficients (γ_{12}°) in mixed electrolyte solutions are calculated in the GTM using Bromley's equations.¹⁰ The γ_{ij}° values were obtained from literature and fitted with the following equation:

$$\log \gamma_{ij}^\circ = \frac{-A_\gamma z_i + z_j \sqrt{I}}{1 + B\sqrt{I}} + \beta I + C I^2 + D I^3 + E I^4 \quad (26)$$

where A_γ is the Debye-Hückel constant; B , β , C , D , and E are constants in Bromley's equations; z_i and z_j represent the absolute value of ionic charge; and the ionic strength I is calculated assuming

complete dissociation. Since A_γ , the Debye-Hückel constant, is temperature dependent, we used the values given by Pitzer¹¹ and determined that

$$A_\gamma = 0.635295 - 0.00171517T + 4.34221 \times 10^{-6}T^2 \quad (27)$$

The fit of this equation to the data is shown in Fig. 66.

Fig. 66. Debye-Hückel Constant as a Function of Temperature (triangles show Pitzer data¹¹ and curve is from Eq. 27)

Our work has centered on three areas crucial to using the GTM to calculate activities necessary to determine the composition of the vapor in equilibrium with TRUEX processed solutions. These areas are (1) finding appropriate vapor-liquid data for the nitric acid-water system at temperatures other than 25°C, (2) determining the exact temperature dependence of $\log \gamma_{\text{HNO}_3}$, (3) determining the activities of nitric acid, nitrates, and water in ternary mixtures at 25°C using the GTM, and (4) calculating the pressures of H₂O and HNO₃ above the mixtures.

There are several ways of defining activity coefficients depending on the standard state selected, the concentration scale used, and knowledge of whether ion pairing or incomplete dissociation of the electrolyte occurs. For strong electrolytes, the mean activity coefficient ($\gamma_{\pm}$) is commonly calculated. To calculate $\gamma_{\pm}$ values, it is necessary to know the degree of dissociation at all concentrations and temperatures. To avoid this requirement, the stoichiometric activity coefficient (γ_s) is calculated. The GTM uses γ_s as a basis for calculating activities. Figure 67 shows a plot of the activity coefficients of nitric acid at 25°C based on data from several sources. The Davis data⁹

represent mean activity coefficient data on the molar scale (M). The data of Hamer and Wu,¹² on the other hand, represent the mean activity coefficient data based on the molal (m) scale. The GTM meanwhile uses as the data base stoichiometric activity coefficients.

Fig. 67. Calculated and Measured Activity Coefficient Data for Nitric Acid as Function of Molal Concentrations

Lemire and coworkers carried out extensive studies of the vapor-liquid equilibrium of nitric acid-water systems at 50°C.^{13,14} In order to use the latter data for temperature studies, we determined whether the activity coefficients calculated by Lemire were stoichiometric activity coefficients (γ_s) or mean activity coefficients ($\gamma_{\pm}$). Lemire calculated stoichiometric activity coefficients on the molar scale from Davis' data at 25°C and used similar calculations for activity coefficients at 50°C. Figure 68 shows a plot of the various values of γ , i.e., γ_s or $\gamma_{\pm}$, at 25 and 50°C. Comparison of activity coefficients generated by the GTM (which are γ_s values) demonstrates that the data of Lemire are stoichiometric activity coefficients.

Fig. 68. Experimental and Calculated Stoichiometric Activity Coefficients of Nitric Acid at 25 and 50°C

To determine the temperature dependence of $\log \gamma$, we used Lemire's stoichiometric activity coefficient data at 25 and 50°C. The GTM was used to fit an equation of the form recommended by Hamer and Wu¹²:

$$\log \gamma_{\text{HNO}_3}^\circ = \frac{-A\sqrt{m}}{1 + \beta\sqrt{m}} + Bm + Cm^2 + Dm^3 + Em^4 \quad (28)$$

where m is the molal concentration.

In Eq. 28, A , B , β , C , D , and E are potentially functions of temperature. We already determined A as a function of T (Eq. 27), and B represents the distance of closest approach of ions and should not be greatly affected by a temperature increase. $\log \gamma_{\text{HNO}_3}^\circ$ data were plotted versus $\sqrt{m}$ starting with the first term on the right-hand side of Eq. 28 and successively adding terms. These plots clearly showed that the β and C coefficients are temperature sensitive. Therefore, it was assumed that

$$\beta = \beta_0 + \beta_1(T - 298.15\text{K}) + \beta_2(T - 298.15\text{K})^2 \quad (29)$$

$$C = C_0 + C_1(T - 298.15\text{K}) + C_2(T - 298.15\text{K})^2 \quad (30)$$

The data were fitted to the above equations using least-squares minimization techniques. The results of the fits are shown in Fig. 69, and the fitting parameters are given in Table 44. As seen in this figure, the calculated and experimental activity coefficients agree very well up to ~49 molal.

Fig. 69. Experimental and Calculated Activity Coefficients as a Function of Temperature

Table 44. Results of Eqs. 28-30 to Fit Experimental Data

$$\begin{aligned}
 A &= 0.63529 - 0.0017152T + 4.3422 \times 10^{-6} T^2 \\
 B &= 1.1376 \\
 \beta &= 0.1024 - 0.0008484 (T - 298.15K) + 1.5894 \times 10^{-5} (T - 298.15K)^2 \\
 C &= -4.77 \times 10^{-3} - 0.0004196 (T - 298.15K) + 1.5773 \times 10^{-5} (T - 298.15K)^2 \\
 D &= 1.0364 \times 10^{-4} \\
 E &= -8.35 \times 10^{-7}
 \end{aligned}$$

2. Calculation of Vapor Pressures

The following equations were used to calculate the vapor pressures for nitric acid and water:

$$P_{\text{HNO}_3} = \frac{P_{\text{HNO}_3}^{\circ} (a_{\text{HNO}_3})^2}{(\gamma \cdot m)^2} \quad (31)$$

$$P_{\text{H}_2\text{O}} = a_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\circ} \quad (32)$$

where a is the activity.

In Eqs. 31 and 32, $P_{\text{HNO}_3}^{\circ}$ and $P_{\text{H}_2\text{O}}^{\circ}$ represent the vapor pressures of pure nitric acid and pure water at the experimental temperature, and $\gamma \cdot m = 4.95$ at 25°C.

The calculated partial pressures for $\text{HNO}_3 = 8.864$ and 19.79M are shown in Table 45 and are compared to experimental data.^{15,16} The pressure of 0.030 torr (4.00 Pa) at 8.864M HNO_3 is subject to considerable experimental error and should be used with discretion. The fact that the GTM calculation is of the same order of magnitude is significant. The match for $P_{\text{H}_2\text{O}}$ values is much better.

Table 45. Calculated and Experimental P_{HNO_3} and $P_{\text{H}_2\text{O}}$ at 25°C.
Units are torr.

[HNO_3], <u>M</u>	Experimental ^{15,16}		Calculated	
	P_{HNO_3}	$P_{\text{H}_2\text{O}}$	P_{HNO_3}	$P_{\text{H}_2\text{O}}$
8.864	0.030	14.80	0.061	15.03
19.79	0.70	8.10	0.644	8.81

The above discussion presents a temperature-dependent model of nitric acid activities for a nitric acid-water system. This model uses the temperature dependence of the Debye-Hückel constant and the Bromley terms (Eq. 26) for nitric acid to account for the temperature dependence on the activities. But this approach is difficult to apply to high-level waste due to the lack of known temperature dependence on activities for all the available species. Currently, we are pursuing other empirical methods to solve this problem. Regardless of the method in which the activities of water and nitric acid are determined, the vapor-liquid equilibrium available from the literature data must be converted to activity to compare with any model-generated activities. There are substantial vapor-liquid equilibrium data in which the activity of various salts can be extracted as a function of temperature. One example is the vapor phase equilibrium of sodium nitrate and nitric acid, where

extensive data are available for various sodium nitrate concentrations at different pressures. In Table 46, the data are given in units of mole percent nitric acid in the vapor and liquid phases at a constant total pressure, 130 mm Hg. To obtain γ , the initial step is to convert the molarity

Table 46. Vapor-Liquid Equilibrium Data for NaNO_3 and HNO_3 System at 130 mm Hg Total Pressure

Temp., °C	Liquid [HNO_3], M	Liquid [NaNO_3], M	Liquid [H_2O], M	Liquid [HNO_3], m	Liquid [NaNO_3], m	Vapor [HNO_3], M	Vapor [HNO_3], M	P_{sat} , mmHg	P_{tot} , mmHg	γ
59.8	0.03	0.03	0.94	1.77E-03	1.77E-03	0.07	0.03	319.73	130	0.94873
61.8	0.06	0.03	0.91	3.66E-03	1.83E-03	0.2	0.06	346.89	130	1.2492
63.6	0.09	0.03	0.88	5.68E-03	1.89E-03	0.55	0.09	372.93	130	2.1303
65.7	0.12	0.03	0.85	7.84E-03	1.96E-03	1.09	0.12	405.34	130	2.9132
67.7	0.15	0.03	0.82	1.02E-02	2.03E-03	2.05	0.15	438.32	130	4.0533
69.8	0.18	0.03	0.79	1.27E-02	2.11E-03	4.07	0.18	475.29	130	6.1845
71.9	0.21	0.03	0.76	1.54E-02	2.19E-03	6.62	0.21	514.79	130	7.9608
73.5	0.24	0.03	0.73	1.83E-02	2.28E-03	10.05	0.24	546.65	130	9.9585
75.2	0.27	0.03	0.7	2.14E-02	2.38E-03	14.2	0.27	582.25	130	11.743
76.2	0.3	0.03	0.67	2.49E-02	2.49E-03	21.33	0.3	604.06	130	15.302
59.4	0	0.06	0.94	0.00E+00	3.55E-03	0	0	314.51	130	3.40E+38
61.3	0.03	0.06	0.91	1.83E-03	3.66E-03	0.11	0.03	339.92	130	1.4023
63.4	0.06	0.06	0.88	3.79E-03	3.79E-03	0.35	0.06	369.96	130	2.0498
65.3	0.09	0.06	0.85	5.88E-03	3.92E-03	0.78	0.09	398.99	130	2.8238
67.4	0.12	0.06	0.82	8.13E-03	4.07E-03	1.69	0.12	433.24	130	4.2259
69.1	0.15	0.06	0.79	1.05E-02	4.22E-03	3.05	0.15	462.7	130	5.7129
71.2	0.18	0.06	0.76	1.32E-02	4.39E-03	5.23	0.18	501.33	130	7.5343
73.2	0.21	0.06	0.73	1.60E-02	4.57E-03	8.67	0.21	540.55	130	9.929
	0.24	0.06	0.7	1.90E-02	4.76E-03		0.24		130	
	0.27	0.06	0.67	2.24E-02	4.98E-03		0.27		130	
	0.3	0.06	0.64	2.60E-02	5.21E-03		0.3		130	
60.7	0	0.09	0.91	0.00E+00	5.49E-03	0	0	331.72	130	3.40E+38
62.8	0.03	0.09	0.88	1.89E-03	5.68E-03	0.2	0.03	361.17	130	2.3996
64.7	0.06	0.09	0.85	3.92E-03	5.88E-03	0.56	0.06	389.63	130	3.1141
67	0.09	0.09	0.82	6.10E-03	6.10E-03	1.08	0.09	426.54	130	3.6574
68.8	0.12	0.09	0.79	8.44E-03	6.33E-03	2.24	0.12	457.38	130	5.3056
70.8	0.15	0.09	0.76	1.10E-02	6.58E-03	4.17	0.15	493.78	130	7.3191
	0.18	0.09	0.73	1.37E-02	6.85E-03		0.18		130	
	0.21	0.09	0.7	1.67E-02	7.14E-03		0.21		130	
	0.24	0.09	0.67	1.99E-02	7.46E-03		0.24		130	
	0.27	0.09	0.64	2.34E-02	7.81E-03		0.27		130	
	0.3	0.09	0.61	2.73E-02	8.20E-03		0.3		130	
62.1	0	0.12	0.88	0.00E+00	7.58E-03	0	0	351.12	130	3.40E+38
64.2	0.03	0.12	0.85	1.96E-03	7.84E-03	0.26	0.03	381.97	130	2.9496
66.3	0.06	0.12	0.82	4.07E-03	8.13E-03	0.72	0.06	415.01	130	3.7589
68.3	0.09	0.12	0.79	6.33E-03	8.44E-03	1.58	0.09	448.63	130	5.0871

to molality, then, for a given temperature, to calculate the saturated partial pressure of the nitric acid by its temperature dependence:

$$\log P_{\text{sat}} = 7.5119 - 1406/(T + 221.0) \quad (33)$$

It is then possible to calculate the activity of the acid using Raoult's law:

$$y_{\text{HNO}_3} P_{\text{tot}} = a_{\text{HNO}_3} P_{\text{sat}} \quad (34)$$

where y_{HNO_3} is the mole fraction of the vapor, and a_{HNO_3} is the activity of nitric acid in solution. Table 46 shows the raw data in terms of the temperature and mole fraction in the liquid and vapor phase, along with the calculated values of activity coefficients. A similar approach can be applied to obtain activity for water.

From the many salt compositions and temperatures, these nitric acid and water activities can help to develop an empirical model, analogous to the Bromley model, to determine vapor-liquid equilibrium in the evaporator.

D. Neutron Activation Analysis

Radioactive tracers would appear to be well suited for measuring decontamination factors (DFs). Detection limits for tracers are typically very low; DFs of 10^5 to 10^7 are easily measured. The problem with tracers, however, is that the equipment would be contaminated from their use. This complicates work on the evaporator and increases the cost associated with further tests. In addition, use of radioactivity at LICON (Pensacola, Florida) is prohibited. Therefore, an element that is not radioactive but can be detected at low concentrations is needed. An analytical procedure called neutron activation analysis (NAA) is one method that can be used to measure the concentration of the element at low concentrations.

To be certain that the desired DFs can be determined for the evaporator, we had to assess the detection limits of our NAA procedure. According to Currie,¹⁷ the detection limit is the minimum value at which a given analytical procedure may be relied upon to lead to detection. This detection limit is defined as

$$L_D = 2.71 + 4.65\sqrt{\mu_B} \quad (35)$$

where μ_B is the average background counts. For NAA, this value corresponds to the minimum number of counts recorded at which a given analysis may be relied upon to lead to detection. Detection limits may also be related to physical quantities. For example, L_D may be related to the minimum detectable concentration by means of

$$L_D = KC_D \quad (36)$$

where K represents an overall calibration factor relating the detector response to the concentration present, and C_D represents the minimum detectable concentration. For NAA, the K factor would be equal to the number of counts per concentration (counts/ppm). If a reference standard with a known

concentration is irradiated with the samples of unknown concentration, then the K factor is obtained from the counting data and known concentration of this reference standard. Once the detection limit, L_D , and K have been determined, the minimum detectable concentration (C_D) may be obtained from Eq. 36.

Experiments were conducted to determine the minimum detectable concentration of samarium in solution. Solutions containing 10, 0.001, and 0.0000001 ppm samarium in nitric acid and water were prepared from a samarium standard. The standard used was a samarium atomic absorption standard consisting of 995 $\mu\text{g/mL}$ samarium in 1 wt % HNO_3 , purchased from Aldrich Chemical Company. In NAA, one normally compares a known reference standard to samples of unknown concentration. In this case, one of the 10 ppm solutions was considered the reference standard. The concentration of the other samples was then calculated from the experimental data. The results of the calculations are given in Table 47. The results are good for the 10 and 0.001 ppm solutions. The other sample may have been contaminated during sample preparation or handling. Using Eq. 36, the minimum detectable concentration was found to be 2×10^{-5} ppm. The K factor was determined from the 10 ppm solution since it was used as the reference standard.

Table 47. Calculated and Actual Concentrations of Samarium Standards

Conc., ppm		
Actual	Calc.	Percent Error
10	9.9497	0.5
0.001	0.00107	7.0
0.001	0.00106	6.0
0.0000001	0.000020	—
0.0000001	0.000023	—

To verify that the data can be reproduced, the experiment was conducted a second time. In the second experiment, samarium solutions of 10, 0.1, 0.001, and 0.00001 ppm were prepared. The results of the calculations are given in Table 48. The results are good for the 10, 0.1, and 0.001 ppm solutions. The 30% error in the 0.00001 ppm solution indicates that this concentration is not detectable. From Eq. 36, the minimum detectable concentration was calculated to be 2×10^{-5} ppm. This result agrees with the first run. The results indicate that a concentration of 0.001 ppm can be detected, while 0.0001 ppm solution could probably be detected. Note, however, that these results are only good for the samarium-nitrate/nitric acid/water system. If other salts or impurities are introduced, the minimum detectable concentration will likely increase.

Table 48. Calculated and Actual Concentrations of Samarium Standards for Second Run

Conc., ppm		
Actual	Calc.	Percent Error
10	9.8257	1.74
0.1	0.1013	1.27
0.1	0.0992	0.78
0.001	0.001052	5.20
0.001	0.000985	1.50
0.0000001	0.000031	30.0

E. General Evaporator Design

Criticality safety and materials of construction need to be considered in designing an evaporator operated in a radioactive environment. Based upon a preliminary analysis, nuclear criticality safety can be achieved by geometry control if the maximum diameter of the evaporator body is 15 cm (6 in.). Because of the low concentration of fissile nuclides in many nuclear wastes, administration control may be an alternative control method in some cases. (For this type of control, procedures are put into place that limit the amount of fissile material that can be in the system at any one time.)

Self-heating of concentrate solutions caused by radioactive decay of typical fission-product (strontium and/or cesium and their short-lived daughters) or TRU-product solutions from Hanford tank waste can be accounted for but should not be of great significance to evaporator operation. Generally, the 0.1-30 W/L self-heating will be negligible compared to supplied heat input.

The materials selected for construction of a pilot-scale evaporator are important since a common problem with nuclear-waste evaporators is mechanical failure due to corrosion. A preliminary screening of materials was made using published handbooks and reports. The most common material used in construction of such evaporators is 304 stainless steel (SS). Potentially useful materials need to be screened by immersion or electrochemical-corrosion tests. The DOE has considerable experience in adjusting the chemistry of waste solutions and in heat treatment and manufacturing practices to minimize corrosion, especially in 304 SS vessels. In the future, more exotic materials than 304 SS may be available, for example, titanium or Hastelloy G-30. Work is still active in researching this problem.

F. Evaporator Upgrade

The scope of the evaporator development program was increased this year to incorporate a project initiated by Argonne's Waste Management Operations (WMO). Waste Management has been funded to replace two low-level waste evaporators that have been in operation at Argonne for over 30 years. Two LICON-designed evaporators will replace these evaporators. These two new evaporators, now scheduled for design, purchase, and installation in FY 1993, will provide a platform for collecting operating data on the processing of actual waste solutions. Tasks associated with the replacement of these evaporators will be finalized in the near future.

VII. DECONTAMINATION OF GROUNDWATERS CONTAINING VOLATILE ORGANICS

(J. C. Hutter, L. Nuñez, D. Redfield, and G. F. Vandegrift)

A membrane-based solvent extraction process is under development to recover dilute (ppb) volatile organic compounds (VOCs) from water and air streams. The VOCs studied include chlorocarbons and hydrocarbons specific to waste minimization and remediation needs of the Department of Energy (DOE) and U.S. Air Force (USAF). The process uses two unit operations, membrane-assisted solvent extraction (MASX) and membrane-assisted distillation stripping (MADS). The MASX process extracts dilute VOCs from water using a natural oil solvent such as sunflower oil. The MADS process recovers the natural oil solvent and concentrates the VOCs for destruction or reuse. Thermodynamic data are being collected to define the operating conditions of this process. In conjunction with Hoechst Celanese, prototype radial cross-flow modules will be developed and tested for the MASX/MADS application. A field demonstration at Argonne to test the MASX/MADS is being planned in the future.

The MASX/MADS system (Fig. 70) consists of two modular hollow fiber units. In the MASX, the organic phase and aqueous or gas phase are separated by the membrane fiber walls. The contaminated water or air is contacted with the nonvolatile organic solvent. As the solvent passes through the module, it contacts the feed and continuously removes the VOCs from the air/water stream by partitioning them to the solvent. The degree of decontamination can be large, up to 1000, and easily achieved by staging the extraction units in series with countercurrent flow. Large throughputs can be achieved by staging the units in parallel. In the MADS unit, the VOC-loaded solvent is regenerated for recycle to the MASX unit by vaporization of the VOCs.

Fig. 70. Flow Diagram of MASX/MADS Process

As shown in Fig. 70, contaminated groundwater is fed to the extraction modules where it is contacted with a nonvolatile solvent. Due to the high distribution ratio of the VOCs in the solvent, the flow rate of the solvent can typically be 10-20 times lower than the flow rate of the groundwater. The

groundwater leaves the extraction unit decontaminated. The VOC-loaded solvent is fed to the MADS unit, where water dissolved by the solvent, a small amount of the solvent, and most of the VOCs are vaporized. The VOC-rich vapor is then recovered by a condenser, at which point the VOCs can be destroyed or recycled. The stripping gas is recirculated to the stripping modules. The stripping gas flow is minimized to reduce the energy consumption of the chiller and the blowers. The VOC stripped nonvolatile solvent is then recycled to the MASX to be contacted with more contaminated groundwater, and the process is repeated.

The MASX/MADS units may also be placed in the air exhaust of a plant where VOCs are released. In this way the MASX/MADS process can be used to eliminate pollution caused by atmospheric releases of VOCs.

Experimental data are being collected to design a pilot-scale MASX/MADS unit. The design of the MADS required measuring Henry's law constants for VOCs in various candidate natural oils. These data were collected using a sparged gas reactor, depicted in Fig. 71. The reactor is made out of glass and has dimensions of 6.35-cm ID and 63.5-cm long. The reactor holds 1.70 L of liquid when full. Nitrogen gas is sparged into the reactor by a sintered glass diffuser. The gas flow rate is measured by a factory calibrated Cole-Palmer rotameter Model N112-02. In the present experiments, gas flow rates were varied from 0.5 to 3.5 mL/s. Temperature was controlled by circulating water through an external heating jacket. The heat transfer water was circulated to a temperature-controlled bath. The reactor temperature itself was monitored by a thermocouple. Samples of the liquid were withdrawn from the reactor using a syringe with an extended needle. A mixer was installed inside the reactor to improve the mixing of the high viscosity oil and ensure a completely mixed liquid phase. The entire reactor was placed inside a fume hood.

Fig. 71.

Sparged Gas Reactor Used in the Henry's Law Experiments

The mass transfer of a sparingly soluble component in a liquid phase to gas phase is a liquid-phase-controlled process. For a fine bubble diffuser system, fine bubbles rapidly approach equilibrium with a sparingly soluble substance in the liquid phase within the first 15 cm of the

disengagement of the bubbles from the diffusers. This phenomenon has been successfully applied to measure the Henry's law constants for various VOCs in water.¹⁸ The technique requires accurate concentration vs. time data for desorption of a VOC from a sparged reactor. A material balance on the reactor allows one to calculate the Henry's law constant from the concentration-vs.-time data.

The material balance must include subsurface mass transfer between the dispersed gas and the bulk liquid, as well as mass transfer at the turbulent liquid surface in contact with an infinite sink of gas.^{19,20} The Henry's law constant is determined from the portion of the mass transfer due to the subsurface effects. The subsurface gas dispersion exits the reactor in equilibrium with the completely mixed liquid phase. A material balance for each VOC component is given by

$$V_L \frac{dC_{oi}}{dt} = -G \frac{H_i R T C_{oi}}{P} - K_{LS} a_S (C_{oi} - C_{oi}^*) \quad (37)$$

where V_L = volume of reactor, L
 C_{oi} = VOC concentration, mol/L
 t = time, s
 G = gas rate, mol/s
 H_i = dimensionless Henry's law constant
 R = universal gas constant, L·atm/mol·K
 T = temperature, K
 P = pressure, atm
 $K_{LS} a_S$ = mass transfer coefficient, s⁻¹
 C_{oi}^* = equilibrium oil concentration, mol/L

The reactor was installed in a fume hood continuously purged with clean air. As the sparge gas exits the reactor, it is rapidly entrained by the large gas flow and sent to the building ventilation system. Owing to the high volumetric flow of the fume hood gas, the gas above the reactor's turbulent liquid surface does not contain any VOCs, and C_{oi}^* is zero. Equation 37 can be integrated with the initial condition, $C_{oi} = C_{oi}^0$ at $t = 0$. Thus,

$$\log \frac{C_{oi}}{C_{oi}^0} = - \left(\frac{G H_i R T}{P} + K_{LS} a_S \right) \frac{t}{V_L} \quad (38)$$

The sparged reactor was initially filled with 1000 ppb of each VOC listed in Table 49. Grab samples were taken from the reactor, and the concentration-vs.-time results were collected for each VOC. Experiments in the sparged reactor were evaluated with Eq. 38. For $G = 0$, $K_{LS} a_S$ was measured. For the experiments with gas flow, this value of $K_{LS} a_S$ was used to calculate the Henry's law constants (Eq. 38). A plot of typical experimental data is shown in Fig. 72. As predicted by Eq. 38, a plot of $\log C_{oi}/C_{oi}^0$ vs. t is a straight line. The least squares fit of the slope was used in the analysis.

The line for $G = 0$ in Fig. 72 is for the component methylene chloride. Since all the components were desorbed at almost the same rate, the $G = 0$ values of $K_{LS} a_S$ were within about 10% of each other for all the VOCs. This is expected since all these components have about the same diffusivity in the sunflower oil, and the mass transfer coefficient is directly proportional to the diffusivity according to film theory.²¹ Methylene chloride had the highest estimated diffusivity in sunflower oil, and thus it showed the most rapid loss from the sparged reactor in the $G = 0$ tests.

Fig. 72. Experimental Data from the Sparged Gas Reactor for Three VOCs and Zero Gas Flow

The Henry's law constants for the VOCs in sunflower oil are summarized in Table 49. The Henry's law constants in sunflower oil can be correlated with the pure component boiling points of each VOC, as given in Table 49. The data indicate that the Henry's law constants decrease as the boiling point increases. Also, because the VOCs are in vapor-liquid equilibrium in a capillary column GC, the retention time is directly related to the partial pressures of the components above the stationary phase. In the table, the components are listed in the order that they elute from the GC.

Table 49. Boiling Points and Henry's Law Constants of VOCs at 1000 ppb in Sunflower Oil

Component	Boiling Pt., °C (1 atm)	Retention Time, min	Henry's Law Constant		
			50°C	70°C	90°C
Methylene Chloride	40.0	10.5	0.021	0.029	0.071
Trans-1,2-Dichloroethylene	47.0	12.0	0.018	0.025	0.071
Cis-1,2-Dichloroethylene	60.0	21.9	0.012	0.020	0.036
Chloroform	61.7	24.0	0.0099	0.015	0.037
1,1,1-Trichloroethane	74.1	28.8	0.010	0.015	0.034
Carbon Tetrachloride	76.6	32.0	0.0099	0.017	0.031
Benzene	80.0	35.6	0.010	0.017	0.028
Trichloroethylene	87.0	39.1	0.0062	0.011	0.019

The Henry's law constants can also be determined from

$$\ln H_i = \frac{\Delta H_{i,diss}}{RT} + \frac{\Delta S_{i,diss}}{R} \quad (39)$$

Figure 73 shows a plot of $\ln H_i$ vs. $1/T$ typical for the VOCs we studied. The thermodynamic quantities obtained from these plots are listed in Table 50. The values of $\Delta H_{i,diss}$ agree well with the published values of ΔH_{vap} for the pure components at their boiling points.²² As shown in the table, the pure-component enthalpies are smaller than the enthalpies of dissolution from sunflower oil. Thus, more energy is needed to vaporize the VOCs from the sunflower oil as compared to the pure components, and the sunflower oil has a high affinity for the VOCs. We have extrapolated our experimental Henry's law constant data over a wide range of temperatures (50-90°C), which will be useful in optimizing the MADS unit.

Fig. 73. Thermodynamic Plots Used to Correlate the Henry's Law Constants for Three VOCs in Sunflower Oil

Table 50. Thermodynamic Quantities of Various VOCs in Sunflower Oil

Component	$\Delta H_{i,diss}$, kJ/mol	$\Delta H_{i,vap}$, kJ/mol	$\Delta S_{i,diss}$, J/mol·K
Methylene Chloride	43	28.1	96
Trans-1,2-Dichloroethylene	42	-	94
Cis-1,2-Dichloroethylene	34	-	65
Chloroform	41	29.2	86
1,1,1-Trichloroethane	38	29.9	78
Carbon Tetrachloride	40	29.8	83
Benzene	39	30.8	79
Trichloroethylene	38	31.4	71

The experimental data along with previously published mass transfer data were used to develop a preliminary design of the MASX/MADS. Future work will concentrate on testing prototype MASX/MADS components in the laboratory to evaluate the technical feasibility of this technology.

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