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SEPARATION SCIENCE AND TECHNOLOGY
SEMIANNUAL PROGRESS REPORT

October 1991—March 1992

by

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Chemical Technology Division

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	1
I. INTRODUCTION	4
II. IMPROVEMENTS TO GENERIC TRUEX MODEL	5
III. INTEGRATION OF GENERIC TRUEX MODEL AND ASPEN PLUS SIMULATOR	10
A. The ASPEN PLUS Simulator	10
B. Available Options to Incorporate GTM into ASPEN PLUS	10
1. Use of GTM to Calculate Liquid-Liquid Extraction within ASPEN PLUS	11
2. Constant D Values	11
3. Empirical Correlations to Calculate D Values	12
4. Incorporation of SASPE into ASPEN PLUS	12
5. Creation of an ASPEN PLUS Data Bank	13
C. Recommendations	13
IV. DATA COLLECTION FOR GENERIC TRUEX MODEL	14
A. Correction of Activity Values at Ionic Strengths Higher than Experimental Data	14
B. Activity Coefficient and Osmotic Coefficient for $\text{Al}(\text{NO}_3)_3$	15
C. Chemical Properties of Bismuth	17
1. Hydrolysis Reactions	17
2. Complex Formation and Ion Exchange	18
3. Solvent Extraction	20
4. Solubility of Bi(III) Compounds	21
5. Radiochemistry of Bismuth	21
D. Concentrations of Fluoboric Acid	23
E. Cadmium Distribution Ratio	25
F. Phosphoric Acid Distribution Ratio	27
V. CENTRIFUGAL CONTACTOR DEVELOPMENT	29
A. Super High-Throughput Centrifugal Contactor	29
1. Rotor Design	29
2. Motor/Rotor Coupling	30

TABLE OF CONTENTS (contd)

	<u>Page</u>
3. Contactor Housing	30
4. Support Frame	31
5. Nuclear Criticality	33
B. Minicontactor	33
1. Factorial Test	34
2. Partial Gas Bubble Blockage	35
VI. PROCESSING OF NEW BRUNSWICK LABORATORY WASTE SOLUTION	43
A. Acidified Carbonate Waste Processing	44
1. Background	44
2. Ammonium Oxalate Stripping of Plutonium	45
3. Ammonium Oxalate Stripping of Americium	46
4. Flowsheet	47
5. Discussion of Run	48
6. Sample Analysis	53
B. Processing of Batch 2	62
1. Flowsheet Sensitivity Analysis	62
2. Preliminary Batch Tests	66
3. Flowsheet Batch Tests	68
4. Solvent Cleanup	70
5. Solids Dissolution	78
VII. DECONTAMINATION OF GROUNDWATERS CONTAINING VOLATILE ORGANIC COMPOUNDS	83
A. Analytical Procedures to Detect VOCs in Natural Oils or Water	84
B. Determination of Henry's Law Constants	85
C. Mass Transfer in a Hollow Fiber	87
D. Optimal Configurations of Hollow Fiber Modules	93
VIII. DEVELOPMENT OF ADVANCED EVAPORATOR TECHNOLOGY	94
A. Neutron Activation Analysis	94
B. Laboratory-Scale Evaporator	95
REFERENCES	99

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Back Titration of Hydrolysis Product of 30 mL of 0.076M Fluoboric Acid against Standard HCl (0.457M) in Presence of Mannitol	24
2.	Distribution Ratio of Cadmium as Function of Nitric Acid and Nitrate Salt Concentrations	25
3.	Graphical Analysis of D_{Cd} to Obtain Stability Constant and Thermodynamic Equilibrium Constant in Organic Phase	26
4.	Distribution Ratios of Phosphoric Acid as Function of Pre-equilibrated Phosphoric Acid Concentration for TRUEX-NPH Solvent at 25°C	27
5.	Distribution Ratios of Phosphoric Acid as Function of Nitric Acid and Nitrate Salt Concentrations for TRUEX-NPH Solvent at 25°C	28
6.	Potentiometric Titration Results of $[H_3PO_4]_{org}$ vs. $[H_3PO_4]_{aq}$ for 1:1 and 10:1 O/A Volume Ratios	28
7.	Three Views of Design for Two-Stage 10-cm SHTCC	32
8.	Minicontactor Setup for the 2 ⁵ Factorial Tests	34
9.	Sketch of Insert for Aqueous Inlet to 2-cm Contactor Stage	34
10.	Effect of Flow Rate on the Height of Water in the Line to the Aqueous Inlet Port	38
11.	Effect of 0.5-mL Bubble on the Transient Height of Water in the Line to the Aqueous Inlet Port for Various Water Flow Rates	39
12.	Effect of 1-mL Bubble on the Transient Height of Water in the Line to the Aqueous Inlet Port for Various Water Flow Rates	40
13.	Effect of 2-mL Bubble on the Transient Height of Water in the Line to the Aqueous Inlet Port for Various Water Flow Rates	41
14.	General Flowsheet for Processing Plutonium Waste Solutions	44
15.	Flowsheet Schematic for Acidified Carbonate Waste Processing	47
16.	Scintillation Counting Results vs. Time for DW Samples during Acidified Carbonate Waste Processing	54
17.	Scintillation Counting Results vs. Time for EW Samples during Acidified Carbonate Waste Processing	55
18.	Scintillation Counting Results vs. Time for FW Samples during Acidified Carbonate Waste Processing	55
19.	Scintillation Counting Results vs. Time for GW Samples during Acidified Carbonate Waste Processing	56

LIST OF FIGURES (contd)

<u>No.</u>	<u>Title</u>	<u>Page</u>
20.	Scintillation Counting Results vs. Time for HW Samples during Acidified Carbonate Waste Processing	57
21.	Scintillation Counting Results vs. Time for HP Samples during Acidified Carbonate Waste Processing	57
22.	Magnitude Comparison of Scintillation Counting Results for DW and HP Samples during Acidified Carbonate Waste Processing	58
23.	Comparison of Scintillation Counting Results for DF, EW, FW, and HP Samples during Acidified Carbonate Waste Processing	60
24.	Comparison of Scintillation Counting Results for GW, HW, IF and HP Samples during Acidified Carbonate Waste Processing	61
25.	Base Case for GTM Modeling of Batch 2 Flowsheet	63
26.	New Base Case for GTM Modeling of Batch 2 Flowsheet	65
27.	Suggested Flowsheet for Processing NBL Batch 2	69
28.	Alumina Column Setup with Colors and Gamma Field Values for First-Pass Column of Old Solvent	76
29.	Flow Diagram of MASX/MADS Process	83
30.	Volatile Organics Detected with Electrolytic Conductivity Detector from a Sunflower Oil Sample	84
31.	Sparged Reactor for Henry's Law Experiments	85
32.	Semilog Plot of C/C_0 vs. Gas Purged at 50°C for Carbon Tetrachloride in Sunflower Oil	87
33.	Cylindrical Fluid Element in Tube with Laminar Flow Velocity Profile	88
34.	Laminar Flow Velocity Profile Inside a 200- μ m Dia Fiber	90
35.	Volume Element for Mass Transfer with Laminar Flow	90
36.	Concentration Profiles Inside a Hollow Fiber	93
37.	Flow Diagram for FRIDGEVAP FVP-C3 Evaporator	96
38.	Orientation of Hood and Evaporator	98

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Options Available in GTM 2.4.1	5
2.	File Sizes in the GTM Before and After Improvements	8
3.	Run Times for GTM 2.4.2a with Different PC Models	9
4.	Compositions of Test Solutions Used to Compare Old and Revised SASPE	14
5.	Composition Calculations by Old and Revised SASPE on Nine Test Solutions	15
6.	Ionic Strength vs. Activity Coefficient	16
7.	Critical Stability Constants (K) of Complexes of Bismuth with Inorganic Ligands	18
8.	Distribution Ratios for Bismuth in Acid Solutions for BioRad AG50W-X8 Cation Exchange Resin	20
9.	Distribution Ratios for Bismuth in Acid Solutions for Dowex-1 Anion Exchange Resin	20
10.	Solubility Products of Bismuth Compounds	22
11.	Radioactive Isotopes of Bismuth Suitable for Tracer Studies	22
12.	Determination of Fluoboric Acid Concentration by Back Titration Method.....	24
13.	Results of the 2 ⁵ Factorial Test	36
14.	Effect of Bubble Volume and Flow Rate on the Apparent Rate of Liquid Backup in the Aqueous Inlet Line.....	42
15.	Results of Ammonium Oxalate Strip of Plutonium in TRUEX-NPH	45
16.	Results of Ammonium Oxalate Strip of Americium in TRUEX-NPH.....	46
17.	Flow Rates of Feed Pumps during Acidified Carbonate Waste Processing	49
18.	Time Line of Major Events in TRUEX Processing of Acidified Carbonate Waste	50
19.	Sample Time and Liquid Scintillation Counting Results of DF and IF Samples	58
20.	Sample Time and Liquid Scintillation Counting Results of DW Raffinate Carboy Samples	61
21.	Composition of Waste Pails Constituting Batch 2.....	62
22.	Results from GTM Sensitivity Analysis for Batch 2 Flowsheet.....	64
23.	Summary of First Set of Extraction Experiments	66
24.	Summary of Second Set of Extraction Experiments.....	67

LIST OF TABLES (contd)

<u>No.</u>	<u>Title</u>	<u>Page</u>
25.	Summary of Third Set of Extraction Experiments	67
26.	Summary of Fourth Set of Extraction Experiments.....	68
27.	Results of Distribution Ratio Measurements for NBL Waste Pre-Run Assessment	70
28.	Alpha Activity Levels and Distribution Ratios from Contacts of TRUEX Solvents with Various HEDPA Solutions	72
29.	Results from TRUEX Solvent Cleanup Using Solid Sorbents	73
30.	Additional Results from the Cleanup of the TRUEX Solvent Using Solid Sorbents and Sodium Carbonate	74
31.	Alpha Activity Level Effluents from Alumina Column Processing of TRUEX Solvents	74
32.	Liquid Scintillation Counting Results from Sodium Carbonate Contacts with TRUEX NBL Solvents	78
33.	Scintillation Results for D_{Am} Tests Using Various Solvents	79
34.	Gamma Results for D_{Am} Tests Using Various Solvents	80
35.	Henry's Law Constants at 50°C of Various Volatile Organics in Sunflower Oil	87
36.	General Specifications for FRIDGEVAP FVP-C3	97

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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 October 1991—March 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 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. 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.

Two new versions of the GTM, version 2.4.1 and 2.4.2a, were distributed during this report period. Enhancements include new equations to calculate activities at ionic strengths above those for which experimental data are available, the addition of bismuth to the possible feed components, and the ability to conduct multiple runs of the GTM without user intervention.

The ASPEN PLUS simulator is being used at Westinghouse Hanford Co. to develop flowsheets for pretreatment of single-shell and double-shell tank waste. Because the TRUEX process is an important part of pretreatment, it is essential that GTM calculations are easily translatable into a format compatible with the ASPEN PLUS simulator. Preliminary analysis on how this task can be accomplished led to five options. The first option involves the use of the GTM as a blackbox unit operation. The second option involves using constant distribution ratios (D values). The third option involves using empirical correlations to calculate D values. The fourth option involves incorporating the SASPE (Spreadsheet Algorithms for Speciation and Partitioning Equilibria) section of the GTM into the ASPEN PLUS simulator, and the fifth option is to create a data bank in ASPEN that contains the physicochemical properties of the TRUEX process. Advantages and disadvantages of all these options are presented.

The equations that are used to calculate log activity and the osmotic coefficient (ϕ) equations in SASPE have a Debye-Hückel term followed by terms in the form of a power series. When these equations are used to calculate log activities or osmotic coefficients at ionic strengths above the available

experimental data, the resultant values can be erratic. To minimize this problem, we adopted the following procedure: (1) generate curves for log activity and ϕ vs. ionic strength, (2) draw tangents to those curves just below the maximum ionic strength, and (3) use this line to extrapolate to a region of ionic strengths above the maximum.

Data collected for $\text{Al}(\text{NO}_3)_3$ electrolyte, to improve the accuracy of the activity coefficient and the osmotic coefficient, were modeled with a simple power series. For ionic strengths greater than 10.2, a tangent to the curves at this value was used to estimate the activity coefficient as well as the osmotic coefficient.

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 chemical species from (1) the nuclear waste housed in the single- and double-shell storage tanks at Hanford, Washington, and (2) waste generated by the Idaho Chemical Processing Plant (ICPP) from the reprocessing of naval nuclear reactor fuel.

Bismuth is a major component of single-shell tank waste stored at Hanford; this bismuth is there because of its use in early processing at Hanford—the bismuth phosphate process and use of bismuthate as an oxidant. A literature review was completed on the aqueous chemistry, separations behavior, and radiochemistry of bismuth. The information gathered from this review will be used in our upcoming experimental study of the TRUEX solvent behavior of $\text{Bi}(\text{III})$. Phosphate can also be found in high concentration in the single-shell tank waste at Hanford. We have determined the distribution coefficients for phosphoric acid by radiotracer and potentiometric titrations. These data were employed in the development of an extraction model for H_3PO_4 .

Fluoboric acid (HBF_4) is a major component of high-level waste generated at the ICPP. Its behavior in the TRUEX solvent extraction process is important to designing a flowsheet for treating this waste. We are therefore developing an analytical technique to measure the concentration of HBF_4 in both the organic and aqueous phases. This technique involves hydrolyzing this acid to $\text{B}(\text{OH})_4^-$ followed by titration. Early results of this study are encouraging. Another major component in the ICPP waste is cadmium. We have determined the distribution ratio of cadmium in acid and mixtures of acid and salt. The analysis of these distribution data resulted in a thermodynamic model for the extraction of cadmium nitrate.

The Argonne centrifugal contactor is modified as necessary to work with specific extraction processes. During this report period, work was done to show how greater than 1% aqueous phase carryover could occur in the interstage line for the organic phase of the minicontactor (2-cm contactor) under operating conditions where this would not normally be expected. A series of special tests was done to elucidate this mechanism. The results showed that, under the right conditions, a gas bubble can completely block the liquid flow through the insert (flow restrictor) in the aqueous-phase interstage line. This blockage continues until the liquid level in the interstage line becomes high enough to clear the flow restrictor. This flow blockage is most significant at low flow rates. Since, when the insert is removed, the problem goes away, the use of the insert is not recommended.

The detailed conceptual design for a super high-throughput centrifugal contactor (SHTCC) was completed. This contactor is designed to increase contactor throughput by a factor of four yet keep the unit safe with respect to nuclear criticality. Vibrational analysis of the contactor rotor showed that its

operating speed is located between its first and second natural frequencies but, as desired, not close to either frequency. Detailed drawings for the construction of a prototype SHTCC are planned.

The GTM was earlier used to design a TRUEX flowsheet for treating plutonium-containing waste (~200 L) generated at ANL and the New Brunswick Laboratory (NBL). The first batch of this waste was treated in the previous report period. Approximately 80 L of acidified carbonate waste, generated from the processing of Batch 1, was processed during this report period. A plutonium stripping agent of ammonium oxalate was used with good success. Other minor changes to the flowsheet also proved successful in solving problems encountered in earlier processing runs. The raffinate waste stream resulting from processing had an activity level of approximately 2 nCi/mL. A description of the run is reported, along with scintillation counting results of samples of the various influent and effluent streams.

Batch 2 waste solutions containing plutonium and uranium were delivered to CMT. This waste contains 13.31 g plutonium and 16.27 g uranium (of which 10.03 g is U-235). A flowsheet for processing Batch 2 was finalized. Some preliminary batch tests with the feed solution are also reported. Batch contacts were then completed to verify that the various operating steps planned in the flowsheet (extraction, scrub, americium strip, and plutonium strip) work as expected. These tests also proved successful.

A study was initiated to evaluate the use of solid sorbents for removing degradation products from TRUEX solvent. In this study, acid-washed alumina, neutral alumina, and an anion exchange resin were evaluated, and we determined that all three were effective in removing acid degradation products from TRUEX solvents. Solvent batches previously used in NBL tests were passed through neutral alumina-packed columns. Activity levels in the solvents were thereby decreased to background levels, and americium distribution ratio tests showed that the alumina processing of the solvent was effective in removing degradation products.

A membrane-assisted solvent extraction process is under development to recover dilute volatile organic compounds (VOCs) from groundwater. Analytical procedures to detect VOCs in both water and natural oil samples were developed. Henry's law constants of VOCs in water were measured at 50°C in a sparged gas reactor, and mass transfer during laminar flow in tubes was modeled. Designs of current membrane modules were reviewed, and their limitations were discussed.

A project has been initiated to develop evaporator technology for concentrating radioactive streams such as those generated by the TRUEX process. A laboratory-scale evaporator, purchased from LICON, Inc., will be used for verifying materials compatibility, gathering data on the evaporation process, and assessing solids handling and maintenance needs. This knowledge will aid in the eventual design of pilot- and plant-scale evaporators. The evaporator that was purchased, a FRIDGEVAP FVP-C3, has a capacity of about 11.5 L/h (3 gal/h). Changes were made to the design of LICON's standard laboratory-scale evaporator so that the flanges at which the evaporator and condenser heating/cooling lines connect to the respective shells can be contained within a hood. The final design and fabrication work by LICON are now underway.

To measure decontamination factors in evaporators, a method for detecting non-radioactive elements was investigated. This method, neutron activation analysis, can be used to measure the concentration of an element at low concentrations. Neutron activation is simply the creation of a radioactive element as a result of neutron interaction with a stable isotope. Based upon a review of neutron cross sections for various elements, samarium was chosen as being well suited for this work. Tests will be completed to determine the applicability of using samarium for this measurement.

I. INTRODUCTION

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. IMPROVEMENTS TO GENERIC TRUEX MODEL (J. M. Copple)

Two new versions of the GTM, versions 2.4.1 and 2.4.2a, were distributed during this period. Version 2.4.1 contains many improvements and bug fixes. Enhancements include new equations that will calculate log activities at ionic strengths higher than those employed to measure the data used to generate the equation, the addition of bismuth to the possible feed components, and the ability to complete multiple runs of the GTM without user intervention. The options available in version 2.4.1 are listed in Table 1. Version GTM 2.4.2a includes changes to the code to use less memory and the addition of distribution ratios for cadmium and phosphorus. A draft version of the GTM manual is complete and has been distributed to GTM users along with GTM 2.4.2a. Improvements made to the GTM include enhancements made to the SASPE module to make the speciation calculation converge faster, the addition of thorium to the solvent loading module, and the addition of ZrF_4 , ZrF_5 , ZrF_6 , and $\text{Pu}(\text{C}_2\text{O}_4)_3^{2-}$ speciation to SASPE. These improvements are discussed later.

Table 1. Options Available in GTM 2.4.1

Option 1	Calculate the complete Generic TRUEX Model for a specific feed solution.
Option 2	Calculate the charge balance, density, ionic strength, speciation, and activities (hydrogen, nitrate, and water) of an aqueous feed solution.
Option 3	Calculate oxalic-acid additions to fission-product-containing waste.
Option 4	Calculate distribution ratios for a user-specified aqueous phase, where the organic phase is assumed pre-equilibrated.
Option 5	Calculate distribution ratios for equilibration of user-specified aqueous and organic phases.
Option 6	Conduct flowsheet analysis with user-specified distribution ratios.
Option 7	Generate a TRUEX flowsheet for a specific feed solution.
Option 8	Estimate space and costs for user-specified flowsheet.
Option 9	Estimate solvent degradation for a specific TRUEX process.
Option 10	Generate reports from existing TRUEX flowsheets or space and cost calculations.
FE_Loop	Run multiple flowsheet calculations (Option 7) without using the front-end to input data.
SASPE Independently	Calculate items in Options 2 and 4 without using the front-end to input data.

Included in GTM 2.4.1 is an Excel macro developed to complete multiple runs of the GTM without user intervention. This macro is called "FE_Loop" on the Macintosh and "FE_LOOP.XLM" on the IBM-PC. This macro can be used when multiple runs of the GTM need to be completed with variations in (1) the concentrations of components in the feeds, (2) the flow rate to a section in the TRUEX flowsheet, or (3) the components present in a feed stream. Only two reports are generated when running "FE_Loop": the SASSE summary full report and the SASSE concentration profile report. In addition, the user can specify whether the SASSE file should be saved so that the entire set of reports will be generated when using Option 10 of the GTM.

Because of the addition of "FE_Loop", the status line displayed when running Options 1 and 7 of the GTM has been modified. The status display during the SASSE-SASPE calculations is:

delta D: [iter. 1 = 0.000E+0, stage 1 = 0.000E+0]

When the GTM is running "FE_Loop", the status display during the SASSE-SASPE calculations is:

delta D: [iter. 1 = 0.000E+0, stage 1 = 0.000E+0] Run:1

The "Run" number corresponds to the file being run, i.e., "Test1" would be "Run:1" and "Test23" would be "Run:23". This modification enables the user to see how far along the GTM is when completing multiple runs.

Distribution ratio (D) equations for cadmium and phosphorous were added to the D_Values macro of version 2.4.2a. For cadmium the D value equation is

$$((K_0 * \text{actNO}_3^2 * \text{CMPOf}) / (1 + \text{beta1} * \text{actNO}_3)) / (\text{Cd_free} / \text{Cd_conc})$$

where $K_0 = 1.3599$
 actNO_3 = nitrate activity
 CMPOf = free CMPO concentration
 $\text{beta1} = 1.8437$
 Cd_free = free cadmium concentration
 Cd_conc = total cadmium concentration

For phosphorus the D value equation is

$$((\text{CMPOf} * \text{TBPf}) / \text{actH}_2\text{O}) * (K_1 * \text{actH} * \text{actNO}_3 + K_2 * \text{H}_3\text{PO}_4\text{_conc}) * (\text{H}_3\text{PO}_4\text{_conc} / \text{PO}_4\text{_total})$$

where CMPOf = free CMPO concentration
 TBPf = free TBP concentration
 actH_2O = water activity
 $K_1 = 1.36$
 actH = H activity
 actNO_3 = nitrate activity
 $K_2 = 0.117$
 $\text{H}_3\text{PO}_4\text{_conc}$ = H_3PO_4 concentration
 $\text{PO}_4\text{_total}$ = Total phosphate concentration in solution

The addition of cadmium free concentration and cadmium total concentration to the equation required changes in the SASPE macro as well. These values had to be passed into the D_value macro.

As the complexity of the GTM increases, several options of the model cannot be run on some IBM-PC configurations because of memory problems. The problem is that the computer is running out of system resources, which have to be located in the 640K of conventional memory. The following suggestions are also offered as a way to get the most out of the conventional memory:

1. Have as few groups as possible in the program manager.
2. Turn off wallpaper.
3. Turn off the toolbar.
4. Start Excel fresh by shutting down Windows and starting again.
5. Turn off Print Manager in the Control Panel.

Tests were conducted on ways to decrease the size of the files in the GTM. The following changes were made to the GTM files to see what the effect would be:

1. Format all the cells the same:

Number	General
Alignment	General
Font	Normal Font
Borders	None
Row Height	Standard Height
Column Width	Standard Width

2. Make sure the "last cell" is the last cell in the sheet.
3. Remove comments.
4. Remove defined name designations.
5. Remove all notes.

Table 2 is a list of the files in the GTM and information on how applying the above steps affects memory allocation. All tests were done on the Macintosh GTM version. For SASPE and Front_End_Routines, further information has been included. This table shows that the formatting information included in a file takes up much memory. Some files could not be changed in any way because their formatting is needed for display purposes. Cards_2 could be made smaller because the code has a bug that increases its file size each time the GTM is run.

Timing tests were made on GTM 2.4.2a with several different models of Macintosh and IBM PCs. Table 3 shows the results of these runs (the options defined in Table 1). From these initial runs, it appears that the Gateway 486 PC is by far the fastest machine. One surprising result was that the Macintosh IIci was not much faster than the Macintosh IICx. After further testing, we concluded that the time is much faster if the built-in video port is not used. The Macintosh IIci can run a monitor without a video card, but that requires the main processor to perform the screen functions, slowing down the machine considerably.

Table 2. File Sizes in the GTM Before and After Improvements (kilobyte units)

File Name	Before	After	Difference	Format	Comments	Defined Names
SASPE	306	255	51	33	9	9
Front_End_Routines	248	179	69	33	26	10
SPACE_PC	155	155	0			
SPACE_MS	147	147	0			
SPACE_CC	134	134	0			
Report_Generator	111	81	30			
SASSE_Generator	98	71	27			
Cards_2	93	86	7			
Front_End_Driver	89	68	21			
Transfer_File	81	78	3			
GTM_Driver	75	54	21			
Cards_3	57	57	0			
Cards_1	53	53	0			
GTM_Help	45	41	4			
D_Values	41	33	8			
Loading_Effect	36	21	15			
Cards_6	33	33	0			
Begin_GTM	32	23	9			
GTM_Message	32	24	8			
SPACE_Generator	21	15	6			
Solvent_Degradation	17	11	6			
Cards_4	12	12	0			
CMPOf_TBPf	12	9	3			
Timer	8	8	0			
FE_Loop	6	6	0			
GTM_Filenames	6	6	0			
Info_Sheet	6	6	0			
SPACE_CC_Summary	5	5	0			
SPACE_MS_Summary	5	5	0			
SPACE_PC_Summary	5	5	0			
Comment_Card	2	2	0			
GTM_Banner	2	2	0			
Totals	1973	1685	288			

Table 3. Run Times (minutes:seconds) for GTM 2.4.2a with Different PC Models

PC Model ^a	Run Type ^{b,c}	Option 1	Option 2	Option 3	Option 4	Option 5	Option 7	Option 8	Option 9	Option 10
Mac II										
sys 6/3MB/256 Color	Manual Example		4:30	10:58	4:03	20:05				
sys 6/3MB/2 Color	Manual Example		4:10							
Mac IIcx										
sys 7/3MB/256 Color	Manual Example		4:47	13:45	4:35	22:35	8:34:14		5:40	
sys 7/3MB/256 Color/no extensions	Manual Example		3:42							
sys 7/3MB/256 Color	1M HNO ₃	8:50	1:51	9:25	1:45	3:03	05:14	2:04	2:42	
sys 7/3MB/256 Color/no ext./shrunk	1M HNO ₃	6:22								
sys 7/3MB/256 Color/no extensions	1M HNO ₃	6:18								
Mac IIcx										
sys 6/3MB/256 Color	Manual Example		4	9:30	3:35	18:30			4:00	
sys 6/3MB/256 Color	1M HNO ₃		1:35	13:58	1:30	2:35			3:50	
sys 6/3MB/256 Color	Feed #1		1:50							
Mac IIci										
sys 7/3MB/256 Color	Manual Example		5:05	12:42	4:35	24:30				
sys 7/3MB/B & W	Manual Example		3:35							
sys 7/3MB/256 Color/Restart Excel	Manual Example		5:03							
sys 7/3MB/256 Color/Reboot Machine	Manual Example		3:35							
Gateway 386										
	Manual Example		1:18	2:15	1:15	5:25			1:25	
Gateway 486										
	Manual Example		0:37	1:20	0:35	out of memory	44:58		0:45	
	1M HNO ₃	1:28	0:19	0:26	0:23	0:24	1:15	1:36	0:18	

^aDefinitions of terms:

sys 6 = Macintosh System 6.0.5.

sys 7 = Macintosh System 7.0.1.

256 Color = 256 colors selected for the Monitor in the Control Panel.

no extensions = all system extensions are turned off.

Restart Excel = Excel was closed down and reopened to run this option.

Reboot Machine = machine was rebooted before running this option.

^bManual Example = the input values correspond to the example contained in the manual for the option.^cFor HNO₃ runs of option 3, the Zr concentration was set to .0001.

III. INTEGRATION OF GENERIC TRUEX MODEL AND ASPEN PLUS SIMULATOR

(M. C. Regalbuto and G. F. Vandegrift)

The ASPEN (Advance System for Process Engineering) PLUS simulator is being used at Westinghouse Hanford Co. to develop flowsheets for pretreatment of single-shell and double-shell tank waste. Because the TRUEX process is an important part of pretreatment, it is essential that results of the GTM calculations are easily translatable into a format compatible with the ASPEN PLUS simulator. We have completed a preliminary analysis on how this task can be accomplished.

We visualize that the task of integrating GTM calculations into ASPEN PLUS can be accomplished in five different ways. The first option involves the use of the GTM as a blackbox unit operation. In this mode, input flows and concentrations will be fed to the GTM; output flows and concentrations will be calculated and entered into ASPEN PLUS. Entry in the simplest form would be by the user. This entry could be made automatic by writing interface codes between the GTM and ASPEN PLUS. The second option involves using constant D values. The third option involves using empirical correlations to calculate D values. The fourth option involves incorporating the SASPE section of the GTM into the ASPEN PLUS simulator, and the fifth option is to create a data bank in ASPEN that contains the physicochemical properties of the TRUEX process. All of these options present advantages and disadvantages. Before going into detail on how these five options can be used, we will briefly describe how the GTM and the ASPEN PLUS simulator work.

A. The ASPEN PLUS Simulator

Information regarding the ASPEN PLUS simulator was obtained by three approaches: (1) conducting a library search, (2) calling Aspen Tech, and (3) calling the National Energy Software Center. The most beneficial was direct contact with Aspen Tech. Our knowledge of this simulator is limited by the fact that we are not registered ASPEN PLUS users.

The ASPEN program was developed at the Massachusetts Institute of Technology (MIT) during 1976-1981 under the sponsorship of the Department of Energy and 55 industrial participants. The ASPEN simulator became commercially available during 1981. Two companies were formed: Aspen Tech, a privately owned firm headquartered in Cambridge, Massachusetts, which distributes the ASPEN PLUS simulator, and GSD, which distributed the ASPEN/SP simulator but is no longer in business.

The ASPEN PLUS is a process-simulator and economic-evaluation package designed to model processes in the chemical and petrochemical industries. It can be used for process design and development, and for handling of plant information. Input to the model consists of information normally contained in the process flowsheet. Output from the model is (1) a complete representation of the performance of the plant, including the compositions, flows, and properties of all intermediate and product streams, and (2) the performance of the process units.

B. Available Options to Incorporate GTM into ASPEN PLUS

To model the TRUEX process using ASPEN PLUS, one must employ the unit operation model EXTRACT, which simulates liquid-liquid extraction. Distribution ratios may be calculated by an activity coefficient model, by an equation of state capable of representing two liquid phases, or by a user-supplied FORTRAN subroutine. To our knowledge ASPEN PLUS does not contain the information necessary to calculate D values for the TRUEX process; therefore, the only option left is

to create the user-supplied FORTRAN subroutine needed to calculate D values. This subroutine has the name KLL in ASPEN PLUS.

The first option involves using the GTM to simulate liquid-liquid extraction instead of the model EXTRACT in ASPEN PLUS. The next three options involve the use of the GTM to create the user-supplied subroutine KLL in EXTRACT to calculate the D values for the TRUEX process not available in ASPEN. The last option involves creating a data bank for the TRUEX process and seems to be much more complicated than the first four.

1. Use of GTM to Calculate Liquid-Liquid Extraction within ASPEN PLUS

The GTM can be used by ASPEN PLUS instead of the unit operation model EXTRACT. Input feeds (flows and concentrations) from a previous unit operation can be fed to the GTM. The GTM, in turn, will calculate output concentrations and flow rates to be used by the next unit operation processes.

Advantages: This calculation method is very simple to do with user intervention. The ASPEN PLUS user will have the ability to calculate accurate D values based on different feed compositions. Variations due to solvent loading will be present. Also a superior model to calculate mass balances for liquid-liquid solvent extraction (SASSE) will be available to the ASPEN PLUS user.

Disadvantages: This calculational method will increase computational time for the ASPEN PLUS simulator since (1) separate GTM runs followed by user input of its results are needed or (2) the GTM must be run inside of ASPEN PLUS. The GTM-ASPEN PLUS interface needs to be developed to carry out these tasks automatically. Development of the interface between ASPEN PLUS, which is written in FORTRAN, and the GTM, which is written in EXCEL, will be a major task.

2. Constant D Values

Given a user-specified flowsheet and feed compositions, Option 7 (Table 1) of the GTM can be used to calculate D values for every component present in the feeds for every single stage in the TRUEX process. These values can be entered by the user and employed by ASPEN PLUS via the KLL subroutine in EXTRACT to calculate component concentrations.

Advantages: This method is very simple to do. The user will run the GTM, obtain the D values needed, put them in the KLL subroutine in EXTRACT, and run the ASPEN PLUS simulator as usual.

Disadvantages: Since the D values used in the KLL subroutine are constant, we will lose the ability to calculate D values in ASPEN PLUS because feed compositions vary due to recycle or changes in other unit operations in the plant. The D value for each component is a complex function of aqueous phase composition, and in a multistage process, these compositions are far from being constants. Also changes in the D values due to variation in solvent loading will not be present. When the number of stages or number of sections in the TRUEX flowsheet is varied (usually the case when doing simulations), the GTM will have to be rerun, and the ASPEN PLUS KLL subroutine will need to be updated for every simulation tested.

3. Empirical Correlations to Calculate D Values

Given several user-specified feed compositions, we can use Option 5 of the GTM (calculate D values for equilibration of user-specified aqueous and organic phase) to generate a family of curves for the D value of each component versus aqueous phase composition. For example, a plot for D values for americium as a function of the concentrations of americium, nitric acid, nitrate salts, and oxalic acid can be generated. Once all the values necessary for the plot in a given composition range are generated, the points in the plot can be fit by a simple empirical correlation. This empirical correlation can then be used by the KLL subroutine in EXTRACT. Correlations can be obtained for any given component at any given range of compositions.

Advantages: The ASPEN PLUS user will have the ability to calculate D values based on different aqueous phase compositions. The KLL subroutine will be very easy to write once all the empirical correlations are obtained.

Disadvantages: The initial effort of determining the correlations needed to obtain the D values will require some time. Distribution ratio calculations will be far less accurate than those calculated in the GTM. Also, if any feed composition falls outside the given composition range, the correlation will no longer be valid.

4. Incorporation of SASPE into ASPEN PLUS

The SASPE is used to calculate distribution ratios for each aqueous-phase composition from user-specified feed or from stage compositions generated by SASSE. The SASSE is used to calculate the compositions in the organic and aqueous phase in each stage of the solvent extraction process at steady state, based on the D values generated by SASPE. Since the ASPEN PLUS simulator provides a model for doing liquid-liquid extraction in the unit operation model EXTRACT, it will not be necessary to export SASSE to ASPEN PLUS. Note that SASSE and EXTRACT are different models for doing mass balance for liquid-liquid solvent extraction. They both offer different features that will not be addressed in detail at this point. It is possible that SASPE and EXTRACT could interact via the KLL subroutine. The KLL subroutine can be written so that all the information now available in the GTM via SASPE is accessible to the ASPEN PLUS simulator to calculate D values for all components present in the TRUEX process.

Advantages: The ASPEN PLUS user will have the ability to calculate accurate D values based on different feed compositions. Variations in the D values due to solvent loading will be present.

Disadvantages: This change will increase the computation time for the ASPEN PLUS simulator since KLL (SASPE) and EXTRACT will interact until D values for all components for every given stage converge. This change will require customizing SASPE so that it could be used by the ASPEN PLUS simulator. At present, SASPE is written in Microsoft EXCEL and will need to be translated to FORTRAN. This should require about 3-4 months of work. Since we are not a licensed user of ASPEN PLUS, we will need to establish a contact person with a good knowledge of the ASPEN PLUS simulator that will interact with us. This person will let us know what are the present needs at Westinghouse Hanford and will assist in the testing of the KLL-SASPE routine in ASPEN PLUS.

5. Creation of an ASPEN PLUS Data Bank

Aspen Tech has indicated that it is possible to create a data bank in which all physico-chemical properties of the TRUEX process are included. We have very little information about this possibility. Because we are not registered users of ASPEN PLUS and have limited knowledge of the simulator, we do not know the advantages or disadvantages of this option.

C. Recommendations

Options one (using the GTM to calculate liquid-liquid extraction externally or within ASPEN PLUS) and four (incorporate SASPE into ASPEN PLUS) offer the best choices for integrating the GTM with ASPEN PLUS. Option one should be the easier and faster alternative, provided the interface problem is solved. In the event that the interface problem is not solved or in the case that Westinghouse Hanford would wish to use only ASPEN PLUS to model their process, Option four will be the next best option.

IV. DATA COLLECTION FOR GENERIC TRUEX MODEL

Experimental and calculational studies were conducted to obtain improved data for incorporation into the GTM.

A. Correction of Activity Values at Ionic Strengths Higher than Experimental Data (G. F. Vandegrift, R. J. Jaskot, J. M. Copple)

The equations that are used to calculate activity (γ) and osmotic coefficient (ϕ) in SASPE have a Debye-Hückel term followed by terms in the form of a power series:

$$\log \gamma_{ij} = \frac{-AZ_iZ_j\sqrt{I}}{1 + B\sqrt{I}} + \beta I + CI^2 + DI^3 + EI^4 \quad (1)$$

$$\phi = 1 - 2.3025 \left[\frac{AZ_iZ_j}{B^3I} \right] \left[1 + B\sqrt{I} - 4.605 \log(1 + B\sqrt{I}) - \frac{1}{(1 + B\sqrt{I})} \right] \\ - \frac{\beta I}{2} - \frac{2}{3} CI^2 - \frac{3}{4} DI^3 - \frac{4}{5} EI^4 \quad (2)$$

where Z_i and Z_j are the charges of the cation and anion of salt ij ; I is the molal ionic strength; and A , β , B , C , D , and E are constants specific to salt ij . When these equations are used to calculate log activities or osmotic coefficients at ionic strengths higher than those used to generate the equations, the resultant values can be far from correct. One of the worst examples is aluminum nitrate, where both β and E are negative; at ionic strengths above 10, nitrate activities drop off considerably, while at just below an ionic strength of 10 they rise dramatically as ionic strength increases. To minimize this problem, it was decided to draw a tangent to the log activity and osmotic coefficient vs. ionic strength curves just below the maximum ionic strength and to use this line to extrapolate to a region of ionic strengths above the maximum that Eqs. 1 and 2 were appropriate.

Table 4 shows the compositions of solutions that were used to compare calculations of activities by the old and the revised SASPE macro. Some of the tests (1, 3, 4, 5, and 8) were designed to have compositions such that the old and revised should calculate the same values for activities of

Table 4. Compositions of Test Solutions Used to Compare Old and Revised SASPE

Test Number	Concentration, M						
	H ⁺	Al ³⁺	Na ⁺	SO ₄ ²⁻	F ⁻	Fe ³⁺	Nd ³⁺
1	1	0.1					
2	6	2	4				
3	10						
4	15				14		
5	24				23		
6	24			10			
7	0.01	2.1	5				
8	0.1					0.1	
9	0.1	1.5	5			1	0.5

water and hydrogen and nitrate ions. For the remaining tests (2, 6, 7, and 9), the results were quite different because the ionic strengths of the solutions were much higher for one or more components than were used to fit the data. Water activities should always be ≤ 1 ; this was not the case in the old SASPE, but is with the revised SASPE. Table 5 shows the results of incorporating these tangents into SASPE.

Table 5. Composition Calculations (based on molar scale) by Old and Revised SASPE on Nine Test Solutions

Test Number	Water Activity		H ⁺ Activity		NO ₃ ⁻ Activity	
	Old	Revised	Old	Revised	Old	Revised
1	0.961	0.961	0.753	0.753	1.028	1.028
2	>9,999,999	0.021	18.264	18.264	0.000	5003.686
3	0.454	0.454	35.211	35.211	35.211	35.211
4	0.004	0.004	0.012	0.012	0.457	0.457
5	0.000	0.000	0.010	0.010	0.418	0.418
6	0.000	0.000	55.027	1,402,573	2.714	8.758
7	30.699	0.151	0.019	0.019	0.000	695.648
8	0.991	0.991	0.066	0.066	0.317	0.317
9	5,812.711	0.052	0.200	0.200	0.000	1957.44

After testing, the revised SASPE was incorporated into GTM version 2.4.1 and distributed throughout the DOE.

B. Activity Coefficient and Osmotic Coefficient for Al(NO₃)₃
(M. C. Regalbuto)

Molar activity coefficients of single electrolyte solutions at the total ionic strength of the mixed electrolyte solution can be estimated by SASPE for a given number of electrolytes. Data had been collected for Al(NO₃)₃ to improve the accuracy of the activity calculation for this electrolyte. The data have been fit in order to obtain the constants needed to calculate the activity coefficient and the osmotic coefficient. Using the data given in Table 6, as well as molal activity versus total ionic strength and a simple power series similar to the one adopted by the National Institute of Standards and Technology, an equation was obtained to calculate the activity. This equation is given below for $I \leq 10.2$:

$$\log \gamma = \frac{-1.5324\sqrt{I}}{1+B\sqrt{I}} + \beta I + CI^2 + DI^3 + \dots \quad (3)$$

where γ is the molal activity coefficient; I is the molal ionic strength; and B , β , C , and D are constants fitted using the data.

The osmotic coefficient, for single-component electrolyte solutions, can be obtained using the following equation for $I \leq 10.2$:

$$\phi = 1 - 2.3025 \left[\frac{1.5324}{B^3 I} \right] \left[1 + B\sqrt{I} - 4.605 \log (1 + B\sqrt{I}) - \frac{1}{(1 + B\sqrt{I})} \right] \\ - \frac{\beta I}{2} - \frac{2}{3} CI^2 - \frac{3}{4} DI^3 - \dots \quad (4)$$

where ϕ is the osmotic coefficient; I is the molal ionic strength; and B , β , C , and D are constants whose values are the same as those in Eq. 2.

The constants β , C , and D were derived by fitting the calculated values to the data; the function minimized (S) was obtained using solver in Excel 3.0 and

$$S = \sum_{i=1}^{np} (\gamma_{\text{exp}} - \gamma_{\text{est}})^2 \quad (5)$$

The values for γ_{exp} and γ_{est} are obtained experimentally and estimated for a given ionic strength, respectively, and np is the total number of experimental points obtained. We chose the value of the constant B to be that reported for $\text{Cr}(\text{NO}_3)_3$ because of the similar behavior of $\text{Al}(\text{NO}_3)_3$ and $\text{Cr}(\text{NO}_3)_3$. The value used for B was 1.622. Values for the other constants given in Eqs. 3 and 4 were then fitted to the data; these are $\beta = 0.2545$, $C = -4.5 \times 10^{-2}$, and $D = 3.04 \times 10^{-3}$. The minimized value of S is 0.01007.

In the previous model used by the GTM to estimate the $\text{Al}(\text{NO}_3)_3$ activity coefficients, the range of ionic strengths over which the activity coefficients were obtained was 0.3-8.35 molal. In the new model the range has been extended. Beyond the range of 0-10.2 molal, the values for the constants B , β , C , and D are not valid. For values of the ionic strength beyond 10.2, a simple line tangent to the curves (given by Eqs. 3 and 4) can be used to estimate the activity coefficients and the osmotic coefficients. The equations used to estimate the activity coefficients and the osmotic coefficient for ionic strength greater than 10.2 are as follows:

$$\log \gamma = 0.281 I - 2.52 \quad (6)$$

$$\phi = 0.539 I - 3.23 \quad (7)$$

Table 6. Ionic Strength vs. Activity Coefficient

Ionic Strength	Activity Coefficient
10.2	2.16
8.67	1.05
7.12	0.827
5.62	0.675
4.84	0.550
3.39	0.459
2.72	0.479
2.04	0.502
1.37	0.558
0.533	0.678
0	1

C. Chemical Properties of Bismuth (B. Srinivasan)

Irradiated uranium fuels have been treated by the bismuth phosphate process to recover the plutonium formed in these fuels. This reprocessing has resulted in radioactive wastes containing uranium, TRU elements, and substantial quantities of bismuth. These wastes are stored in single-shell tanks at the Hanford site. It is proposed to apply the TRUEX process to the bismuth phosphate wastes in order to separate the TRU elements from the long-lived fission products as well as other inactive components. The extraction properties of bismuth from aqueous solutions into the TRUEX solvents must be experimentally determined to apply the GTM for the bismuth phosphate wastes; the presence of bismuth may modify the solvent extraction properties of the TRU elements.

The chemistry of bismuth in aqueous solutions is reviewed here to provide an understanding of the nature of bismuth complexes that may be encountered in the treatment of the wastes by the TRUEX process. Since radioactive isotopes of bismuth will be used as tracers in the experimental studies, a short description of the radiochemistry of bismuth is also presented. The radiochemistry of bismuth has been reviewed by Bhatki.¹

Bismuth (Z=83) is a Group VB element in the periodic table. The electronic configuration of the neutral atom is as follows: filled shells up to $n = 4$, $5s^2$, $5p^6$, $5d^{10}$, $6s^2$, $6p^3$.

Among the valence shell electrons, the $6s$ pair appears to be inert.² Thus, most of the compounds of bismuth are those associated with the III oxidation state, corresponding to the half-filled $6p$ level. Only a very few compounds of the V state are known, but none in aqueous solutions.¹ Therefore, redox reactions involving the Bi(III)-Bi(V) couple are either nonexistent or unknown. The Bi(V)-Bi(III) couple is strongly oxidizing and is capable of oxidizing water to oxygen³:

Hydrolysis reactions (including the formation of polymeric species), formation of complexes (mainly with inorganic ligands such as nitrate, phosphate, oxalate, fluoride, and sulfate), and the solubility of precipitates in aqueous solutions are of interest to our studies on the extraction behavior of bismuth into the TRUEX solvents. Also investigated were the properties of the radioactive isotopes of bismuth.

1. Hydrolysis Reactions

Bismuth exists in aqueous solutions as Bi(III). It is easily hydrolyzed, even in solutions which are considered to be acidic (pH of 1 to 2) forming basic salts. In less acidic or neutral solutions, oxy salts are precipitated. Simple aquo ions of the type $\text{Bi}(\text{H}_2\text{O})_n^{3+}$ are unknown; a series of polymeric cations can be detected in the solution before precipitation. In neutral perchlorate solutions, the polymeric species exists as $(\text{Bi}_6\text{O}_6)^+$ or in its hydrated form $[\text{Bi}_6(\text{OH})_{12}]^{6+}$. At higher pH, $[\text{Bi}_6\text{O}_6(\text{OH})_3]^{3+}$ is formed.⁴

Redox potentials pertaining to typical hydrolysis reactions of bismuth are given below³:

2. Complex Formation and Ion Exchange

Bismuth(III) can form several complexes either by donating its lone pair of electrons to suitable acceptor molecules or by accepting electrons from donor molecules. The complexes which are formed by the association of electronegative elements such as the halogens are of the latter type. Cationic, neutral, and anionic complexes of bismuth are known with halides and other inorganic ligands. Stability constants (K values) have been determined for various complexes under a variety of conditions. The log K values taken from Smith⁵ are shown in Table 7. The chloride and nitrate complexes of bismuth derived from ion exchange behavior of the complexes are discussed below.

Table 7. Critical Stability Constants (K) of Complexes of Bismuth with Inorganic Ligands. The letter M represents Bi(III) and L represents Ligand. Data obtained from Ref. 5.

Equilibrium	Log K ^a		
Hydroxide Ion			
(assuming HL/H·L = 14.6)			
ML/M·L	12.36 (25°,0.1)	12.60 (25°, 3.0)	12.9
ML ₃ /M·L ₃	31.9 (25°, 0.1)		33.1
ML ₄ /ML ₃ ·L		0.95	1.1
M ₆ L ₁₂ /M ₆ ·L ₁₂		164.95	
		170.49 (25°, 3.0)	
M ₉ L ₂₀ /(M ₆ L ₁₂) _{1.5} ·L ₂	23.9 (25°, 0.1)		
M ₉ L ₂₁ /M ₉ L ₂₀ ·L	10.6 (25°, 0.1)		
M ₉ L ₂₂ /M ₉ L ₂₁ ·L	11.1 (25°, 0.1)		
ML ₂ /(M ₂ O ₃) (s)		-5.34	-5.4
Fluoride Ion			
ML/M·L	1.42 (30°, 2.0)		
Chloride Ion			
ML/M·L	(2.36) (20°, 2.0)	2.2 (25°, 3.0)	
ML ₂ /M·L ₂	3.5 (20°, 2.0)	3.5 (25°, 3.0)	
ML ₃ /M·L ₃	5.4 (20°, 2.0)	5.8 (25°, 3.0)	
ML ₄ /M·L ₄	6.1 (20°, 2.0)	6.8 (25°, 3.0)	
ML ₅ /M·L ₅	6.7 (20°, 2.0)	7.3 (25°, 3.0)	
ML ₆ /M·L ₆	6.6 (20°, 2.0)	7.4 (25°, 3.0)	
Bromide Ion			
ML/M·L	2.37	2.22	3.06
	2.32 (25°, 2.0)	2.63 (25°, 3.0)	3.12 (25°, 4.0)
ML ₂ /M·L ₂	4.2	(4.4)	5.6
	4.4 (25°, 2.0)	5.0 (25°, 3.0)	5.7 (25°, 4.0)
ML ₃ /M·L ₃	5.9	6.2	7.4
	6.3 (25°, 2.0)	6.7 (25°, 3.0)	8.2 (25°, 4.0)
ML ₄ /M·L ₄	7.3	(7.2)	8.6
	7.8 (25°, 2.0)	8.1 (25°, 3.0)	10.0 (25°, 4.0)

(contd)

Table 7. (contd)

Equilibrium	Log K ^a		
ML ₅ /M·L ₅	8.2 9.2 (25°, 2.0)	8.7 (9.0) (25°, 3.0)	(9.2) 11.9 (25°, 4.0)
ML ₆ /M·L ₆	8.3 9.5 (25°, 2.0)	8.8 9.8 (25°, 3.0)	(8.7) 11.8 (25°, 4.0)
Iodide Ion			
ML/M·L	3.63		
ML ₄ /M·L ₄	15.0 (20°, 2.0)		
ML ₅ /M·L ₅	16.8 (20°, 2.0)		
ML ₆ /M·L ₆	18.8 (20°, 2.0)		
M·L ³ /ML ₃ (s)	-18.09 (20°, 2.0)		
Nitrate Ion			
ML/M·L	0.72 (0.72) (25°, 2.0)	0.81 0.72 (25°, 3.0)	1.7 0.92 (25°, 4.0)
ML ₂ /M·L ₂	(0.94) 0.98 (25°, 2.0)	0.90 0.96 (25°, 3.0)	2.5 1.23 (25°, 4.0)
ML ₃ /M·L ₃	(0.2) (25°, 2.0)	0.7 (0.1) (25°, 3.0)	1.1 (25°, 4.0)
ML ₄ /M·L ₄	(0.6) (25°, 2.0)	(-0.2) (25°, 3.0)	0.4 (25°, 4.0)
Hydrogen Sulfate Ion			
ML/M·L		1.98 (25°, 3.0)	
ML ₂ /M·L ₂		3.41 (25°, 3.0)	
ML ₃ /M·L ₃		4.08 (25°, 3.0)	
ML ₄ /M·L ₄		4.34 (25°, 3.0)	
ML ₅ /M·L ₅		4.60 (25°, 3.0)	
Sulfide Ion			
M ₂ ·L ₃ /M ₂ L ₃ (s)		-100	

^aTemperature in °C and ionic strength are shown in parentheses. If not shown, then the log K values in columns 2, 3, and 4 correspond to the following:

Col. 2: 25°C, 0.5M

Col. 3: 25°C, 1.0M

Col. 4: 25°C, 0M

Bismuth forms strong anionic complexes with hydrochloric acid, even at low acid concentrations (0.5M), and therefore, it is not absorbed by cation exchange resin.⁶ On the other hand, bismuth solutions in nitric and sulfuric acids are absorbed effectively by cation exchange resins at low concentrations of the acid and to a significant extent even at higher concentrations.⁷ Bismuth is strongly adsorbed from perchloric acid solutions at all concentrations.⁶

Anion exchange resins adsorb bismuth readily even at low acid concentrations of HCl.⁸ The distribution ratio decreases slowly with increasing HCl concentration. In contrast to hydrochloric acid solutions, bismuth in nitric acid solutions is strongly adsorbed by anion exchange resins only when the concentration of the acid exceeds 2M. Bismuth is also strongly adsorbed from NH₄NO₃ solutions.⁸

A summary of the distribution ratios as a function of the acid concentration is shown in Tables 8 and 9.

Table 8. Distribution Ratios for Bismuth in Acid Solutions for BioRad AG50W-X8 Cation Exchange Resin^a

Acid	Conc., N						Reference
	0.1	0.2	0.5	1.0	2.0	4.0	
HNO ₃	>10 ⁴	7430	371	61.0	8.0	3.0	7
H ₂ SO ₄	10 ⁴	10 ⁴	6800	235	32.3	6.4	7
HCl						<1 (9N)	6
HClO ₄						860 (9N)	6

^aDistribution ratios as defined in the references are as follows:

Strelow⁷: Amount of ion in resin per gram of dry resin/amount of ion in water phase per mL of water phase.

Nelson⁶: Amount of ion per liter of bed (resin phase)/amount of ion per liter of solution. These volume distribution ratios can be converted to weight distribution ratios (i.e., per kilogram of dry resin) by knowing the density of the resin bed as a function of acid concentration.

^bData for HNO₃ given by Strelow⁷ were corrected in 1976 and given in Bhatki¹ and reproduced above.

Table 9. Distribution Ratios^a for Bismuth in Acid Solutions for Dowex-1 Anion Exchange Resin

Acid	Conc., M				Reference
	0.25	0.5	4	12	
HCl	2x10 ⁵			57	8
HNO ₃		1.6	26		8
HNO ₃ + 10M NH ₄ NO ₃	180				8

^aDistribution coefficients as defined by Nelson⁸: Amount per kilogram dry resin/amount per liter solution.

3. Solvent Extraction

A summary of the solvent extraction properties of bismuth given here is derived from the detailed review of the radiochemistry of bismuth by Bhatki¹ and the solvent extraction of metals by De.⁹ The original sources of information as given here are taken from the above two references.

The extraction of bismuth may be based on ion association or upon the formation of a chelate complex. Examples of ion association systems are extractions of bismuth from aqueous solutions containing chloride, nitrate, thiocyanate, etc.; examples of chelate systems are dithiozone, cupferron, thenoyltrifluoroacetone (TTA), 8-hydroxy quinoline. The solvent extraction properties in chloride and nitrate media are reviewed here. Information available on TBP extraction of bismuth is also included, since the TRUEX solvent contains TBP as one of the components.

Bismuth is 34% extracted into diethyl ether from 6.9M HI and <10% from 1.5M HI/1.5N H₂SO₄.^{10,11} Carrier-free ²¹⁰Bi has been extracted into n-butyl alcohol from HCl solutions.¹² Bismuth can be separated from tantalum and niobium in aqueous HF solutions by extracting the latter two elements with methyl isobutyl ketone.¹³ Bismuth is 7% extracted by diethyl ether from 8M HNO₃,¹⁴ and partly extracted by various ethers from HNO₃.¹⁵ In addition, Th, Bi, and Po can be quantitatively separated from Pb and Ra with mesityl oxide.¹⁶ Dibutyl carbitol can remove traces of polonium from large amounts of active bismuth from HNO₃ solutions—a separation process that may be useful in the preparation of ²¹⁰Bi free from ²¹⁰Po.¹⁷ Bismuth in HClO₄ (0.1-0.6M) solutions can be extracted into TBP as the thiourea-TBP complex.¹⁸

4. Solubility of Bi(III) Compounds

Solubility and hydrolysis reactions of trihalide compounds of bismuth have been studied in great detail. A qualitative comparison of the solubility of trihalides in water is given below.²

BiF ₃	Insoluble in water, but soluble in concentrated HF with the formation of complexes such as H ₃ (BiF ₆).
BiCl ₃	Dissolves in water and yields BiOCl as the product of hydrolysis; BiCl ₃ dissolves in alcohol, acetone, methyl cyanide, and nitrobenzene. A solution of it in hydrochloric acid is reduced by hypophosphorous acid to give a dull grey powder of metallic bismuth.
BiBr ₃	Dissolves in water and yields BiOBr as the product of hydrolysis.
BiI ₃	It is less soluble than the chloride and bromide. The crystals are dark brown to black.

Bismuth nitrate behaves similarly to bismuth chloride, with large excess of water bismuth subnitrate (BiONO₃) forming. The compounds Bi₂(SO₄)₃·nH₂O and KBi(SO₄)₂ are also easily hydrolyzed to basic salts.

Bismuth phosphate, which is of immediate interest to our studies, is a white, heavy, crystalline solid. It is quite insoluble in water and in dilute nitric acid. The solubility of the compound increases rapidly with increasing acidity.¹⁹

Solubility products of selected compounds of bismuth are shown in Table 10.²⁰ Also refer to Table 10 for the solubility of bismuthyl chloride, bismuthyl bromide, bismuth triiodide, bismuthyl nitrate, and bismuth sulfide.

5. Radiochemistry of Bismuth

Bismuth-209 is the only stable bismuth isotope known. But several radioactive isotopes of bismuth have half-lives in the range of a few days to several years, and they are suitable for tracer studies (see Table 11).

Table 10. Solubility Products of Bismuth Compounds²⁰

Substance	pK _s	K _s
BiAsO ₄	9.36	4.4 x 10 ⁻¹⁰
BiOBr + 2H ⁺ = Bi ³⁺ + Br ⁻ + H ₂ O	6.52	3.0 x 10 ⁻⁷
BiOCl = BiO ⁺ + Cl ⁻	8.2	7 x 10 ⁻⁹
BiOCl + 2H ⁺ = Bi ³⁺ + Cl ⁻ + H ₂ O	6.68	2.1 x 10 ⁻⁷
BiOCl + H ₂ O = Bi ³⁺ + Cl ⁻ + 2OH ⁻	30.75	1.8 x 10 ⁻³¹
BiI ₃	18.09	8.1 x 10 ⁻¹⁹
BiOOH	9.4	4 x 10 ⁻¹⁰
1/2Bi ₂ O ₃ + 3/2H ₂ O + OH ⁻ = Bi(OH) ₄ ⁻	5.30	5.0 x 10 ⁻⁶
BiPO ₄	22.89	1.3 x 10 ⁻²³
Bi ₂ S ₃	97	1 x 10 ⁻⁹⁷

Table 11. Radioactive Isotopes of Bismuth Suitable for Tracer Studies

Isotope	Half-life	Type of Decay
²⁰⁵ Bi	15.3 d	EC, ^a β ⁺ , and several gammas ^b
²⁰⁶ Bi	6.24 d	EC, β ⁺ , and several gammas
²⁰⁷ Bi	30 y	EC, and several gammas
²¹⁰ Bi	5.01 d	β ⁻ , and weak X-rays

^a EC = electron capture.^b Gammas of several energies are released by this one isotope's decay.

Bismuth-210 is a suitable tracer for the TRUEX solvent extraction studies. Carrier-free ²¹⁰Bi for these studies can be easily obtained from a ²¹⁰Pb source, which is in equilibrium with its daughters. The radioactive decay of ²¹⁰Pb is shown below:

Bismuth-210 can be separated from both Po and Pb isotopes by an ion exchange column containing "Sr specific" resin. This resin shows strong adsorptive properties toward Po and Pb in 1M HNO₃ solution, allowing bismuth to pass through unaffected.²¹

Bismuth-210 in the aqueous and organic phases can be determined using a liquid scintillation counter.²² The growth of ²¹⁰Po in the freshly separated fraction of ²¹⁰Bi may be ignored if the sample is counted within about one week of separation, corresponding to one half-life of ²¹⁰Bi. The activity ratio of ²¹⁰Bi/²¹⁰Po is about 28 at the end of 5 days. If necessary, a small correction for the ²¹⁰Po activity can be made to deduce the true ²¹⁰Bi activity levels.

D. Concentrations of Fluoboric Acid
(B. Srinivasan and S. Weber)

Attempts continue to determine the concentrations of fluoboric acid (HBF_4) and its hydrolysis products (those containing boron) by a titrimetry procedure. In a dilute solution of fluoboric acid, the first stage of hydrolysis is the dominant one (see Eq. 11), and the second and third stages (Eqs. 12 and 13) may be neglected.

The last stage of hydrolysis is the conversion to boric acid (H_3BO_3). Dilute solutions of fluoboric acid along with its hydrolyzed species can be quantitatively converted to boric acid by carrying out hydrolysis in the presence of CaCl_2 and NaOH at elevated temperatures (80-100°C). The concentration of the boric acid thus formed can be quantitated by direct titration with standard alkali, or the boric acid may be neutralized with excess alkali, which can then be back titrated against standard HCl . During this period, we tried to establish the experimental conditions for the quantitative determination of fluoboric acid by the back titration method. The experimental procedure is described below.

A sample of concentrated fluoboric acid (nearly 8M) containing about 2 to 3 milliequivalents of H^+ was diluted to about 40 mL with deionized water. Next, 6 mL of 15% CaCl_2 was added to the acid, and the mixture heated to boiling for about 5 min when the first signs of a white precipitate of CaF_2 appeared. Then, at periodic intervals (every 10 min), 2M NaOH was added in incremental amounts (1 mL at a time) until a clear excess of NaOH was present. The mixture was kept hot at about 80°C throughout the addition of NaOH , and the total volume was maintained at about 40 mL. The CaF_2 precipitate was removed from the clear solution by centrifugation, the precipitate washed once with distilled water, and the washings added to the clear solution. The solution was titrated against standard hydrochloric acid (0.5M HCl). In some cases, 1 mL of a saturated solution of mannitol was added before the titrations.

The titration curve showed two clearly distinguishable end points, one occurring in the vicinity of $\text{pH} = 10$, and the other at about $\text{pH} = 4$ to 5. An example of the titration curve is shown in Fig. 1. Apparently, the first end point corresponds to the concentration of excess NaOH present in the solution, and the difference between the first and second end points corresponds to the concentration of $\text{NaB}(\text{OH})_4$ formed from the alkaline hydrolysis of fluoboric acid.

The concentrations of a stock solution of 48-50% fluoboric acid and two other dilute solutions prepared from this stock solution, as determined by the back titration method, are given in Table 12. The experimentally determined concentrations are in reasonable agreement with the expected concentrations calculated from the density and percent fluoboric acid in the stock solution. Addition of mannitol seems to yield higher results.

The experimental procedure followed for the back titration method is labor intensive and requires the constant attention of the analyst. Several attempts were made to simplify the hydrolysis procedure, and none was successful in achieving the high degree of hydrolysis shown in Table 12. In the simplified procedures, NaOH and CaCl_2 were added to the fluoboric acid at the beginning,

Fig. 1.

Back Titration of Hydrolysis Product of
30 mL of 0.076M Fluoboric Acid
against Standard HCl (0.457M) in
Presence of Mannitol

Table 12. Determination of Fluoboric Acid
Concentration by Back Titration Method

HBF Conc., M		Remarks
Calculated	Determined	
7.6	7.34	Mannitol added
	7.74	
0.76	0.814	
	0.813	
0.076	0.077	
	0.079	Mannitol added

instead of the gradual addition of NaOH in the procedure above. A list of the simplified procedures tried is given below:

1. Hydrolysis at room temperature using NaOH, but with no CaCl_2 .
2. Hydrolysis at room temperature using NaOH, in presence of CaCl_2 .
3. Hydrolysis at room temperature using NaOH, in presence of CaCl_2 for a long period. The maximum time of hydrolysis in these experiments was 7.5 h.
4. Hydrolysis at 70°C , in presence of NaOH and CaCl_2 . These experiments were also done over a long period, with the maximum time of hydrolysis corresponding to about 72 h (over the weekend).

In conclusion, it appears that the back titration method yields quantitatively valid results only if the fluoboric acid is neutralized slowly by stepwise addition of NaOH to a mixture of fluoboric acid and CaCl_2 kept at or near boiling temperature. Less labor-intensive methods may be developed through further studies.

E. Cadmium Distribution Ratio (L. Nuñez)

Distribution ratios for cadmium (D_{Cd}) were measured using radionuclide tracers. Figure 2 shows the effects of nitric acid and sodium nitrate concentrations on D_{Cd} , where the organic-to-aqueous (O/A) ratio equals one. Because cadmium extracts into the TRUEX solvent as $\text{Cd}(\text{NO}_3)_2$, D_{Cd} is highest at the highest concentration of nitrate ion.

Fig. 2. Distribution Ratio of Cadmium as Function of Nitric Acid and Nitrate Salt Concentrations. (Conditions: $T = 25^\circ\text{C}$; $\text{O/A} = 1$; TRUEX-NPH solvent solutions containing NaNO_3 were not pre-equilibrated; HNO_3 concentrations in the aqueous phase were calculated by the GTM.)

Cadmium is a major component of high-level wastes stored at the Idaho Chemical Processing Plant (ICPP) from the reprocessing of naval fuel. Distribution ratio data for cadmium are necessary to develop an accurate model for predicting cadmium extraction behavior in TRUEX processing of this waste. To develop a model for D_{Cd} , the important aqueous species effects must be expressed in terms of activities. The GTM was used to calculate the activities of water $\{\text{H}_2\text{O}\}$, hydrogen $\{\text{H}^+\}$, and ion nitrates $\{\text{NO}_3^-\}$, as well as the organic-phase concentrations of CMPO and TBP not bound to HNO_3 ($[\text{CMPO}]$ and $[\text{TBP}]$).

The cadmium extraction as a function of nitric acid and the nitrate salt was modeled by using the following chemical equilibrium:

for the organic phase, and

for the aqueous phase.

A relationship for the cadmium distribution ratio is derived as follows:

$$D_{\text{Cd}} = \frac{[\overline{\text{Cd}(\text{NO}_3)_2 \cdot \text{CMPO}}]}{([\text{Cd}^{2+}] + [\text{Cd}(\text{NO}_3)^+])} \quad (16)$$

Using the thermodynamic equilibrium and the stability constant, this equation becomes

$$D_{\text{Cd}} = K_1 \frac{[\overline{\text{CMPO}}] \{\text{NO}_3^-\}^2}{(1 + \beta \{\text{NO}_3^-\})} \quad (17)$$

For further simplicity of analysis, the inverse is taken of Eq. 17, and variables are separated to obtain

$$\frac{[\overline{\text{CMPO}}] \{\text{NO}_3^-\}}{D_{\text{Cd}}} = \left(\frac{1}{K_1} \{\text{NO}_3^-\}^2 + \beta / K_1 \{\text{NO}_3^-\} \right) \quad (18)$$

A plot of $[\overline{\text{CMPO}}] \{\text{NO}_3^-\} / D_{\text{Cd}}$ versus $1/\{\text{NO}_3^-\}$ gives $1/K_1$ as slope and β/K_1 as the intercept in y (see Fig. 3).

Fig. 3.

Graphical Analysis of D_{Cd} to Obtain Stability Constant and Thermodynamic Equilibrium Constant in Organic Phase

Equation 17 for the distribution ratio for cadmium takes the following form:

$$D_{\text{Cd}} = 1.07 \frac{[\overline{\text{CMPO}}] \{\text{NO}_3^-\}^2}{(1 + 0.48 \{\text{NO}_3^-\})} \quad (19)$$

F. Phosphoric Acid Distribution Ratio
(L. Nuñez, L. Everson, and S. Weber)

Phosphate can be found in high concentration in the single-shell tank waste at Hanford because the bismuth phosphate process is used to recover plutonium from uranium irradiated in the 1950s. Phosphate has been also generated by the hydrolysis of the minor quantities of TBP that have accumulated in all PUREX reprocessing wastes. An accurate model predicting the extraction behavior of H_3PO_4 is an important factor in the design of the TRUEX process flowsheet for these wastes. Distribution ratios for H_3PO_4 ($D_{\text{H}_3\text{PO}_4}$) were determined by a radiotracer method using ^{32}P -containing H_3PO_4 and by potentiometric titrations to measure phosphoric acid concentrations.

The phosphoric acid D values show a linear increase as a function of phosphoric acid concentration in a log-log plot (Fig. 4). The measurements show that at high phosphoric acid concentrations, the maximum D value is 0.1, and at low concentrations, D values are in the 0.01 range. Third-phase formation occurred for those solutions with phosphoric acid concentration larger than 6M, and these data are not included in the plot.

Fig. 4.

Distribution Ratios of Phosphoric Acid
as Function of Pre-equilibrated Phosphoric
Acid Concentration for TRUEX-NPH
Solvent at 25°C (O/A = 1)

The phosphoric acid D values at all NaNO_3 concentrations show a general increase as a function of nitric acid in a log-log plot (Fig. 5) at low HNO_3 concentrations and then tend to decrease with increased nitric acid concentration.

Phosphoric acid concentrations of both the aqueous and organic phases were measured by potentiometric titration. The organic phase was titrated directly in all cases. In a few cases, the H_3PO_4 was back-extracted into an aqueous phase and titrated; the results were the same. Contacts were made at O/A ratios of 1/1 and 10/1. The data (Fig. 6) follow a polynomial fit (by least squares analysis) of second order; this is indicative of a dimer species involved in the extraction with the TRUEX solvent.

Fig. 5. Distribution Ratios of Phosphoric Acid as Function of Nitric Acid and Nitrate Salt Concentrations for TRUEX-NPH Solvent at 25°C (OA = 1; NaNO_3 was not pre-equilibrated)

Fig. 6.

Potentiometric Titration Results of $[\text{H}_3\text{PO}_4]_{\text{org}}$ vs. $[\text{H}_3\text{PO}_4]_{\text{aq}}$ for 1:1 and 10:1 O/A Volume Ratios

V. CENTRIFUGAL CONTACTOR DEVELOPMENT

(R. A. Leonard, D. B. Chamberlain, D. G. Wygmans, J. A. Dow,* and S. E. Farley**)

The Argonne centrifugal contactor is modified as necessary to work with specific solvent extraction processes. For each new process, solution densities and organic-to-aqueous (O/A) flow ratios are reviewed, and if necessary, the rotor weirs are modified. In support of our contactor development efforts, vibrational measurements are made using proximity probes and real-time analyzers. The results are related to rotor design by the use of a vibrational model for rotating systems.

A super high-throughput centrifugal contactor (SHTCC) is now being designed to increase contactor throughput by a factor of 4 to 8 yet keep the unit safe with respect to nuclear criticality by its geometry. Thus, one contactor line will be able to handle the process throughput that would otherwise have required 4 to 8 lines. In addition to the work on the SHTCC, we looked at possible reasons for an anomalous flow occurrence in the minicontactor.

A. Super High-Throughput Centrifugal Contactor

A SHTCC was designed to increase contactor throughput by a factor of 4 yet keep the unit safe with respect to nuclear criticality by its geometry, that is, keep the rotor diameter at 10 cm. The general outlines for such a unit were worked out in FY 1991. This included the idea that rotor speed has to be limited to about 3600 rpm so that power consumption does not become excessive. The detailed conceptual design has now been completed. It is ready to be converted into an appropriate engineering drawing from which a prototype SHTCC can be built.

During this reporting period, we completed work on the detailed conceptual design of the rotor, the motor/rotor coupling, the contactor housing, and the support frame. We also sketched the overall design and looked at criticality considerations in choosing stage spacing. Further work has been put on hold because of a cut in funding.

1. Rotor Design

Starting with the 10-cm contactor built and tested for Hanford in 1987 (ANL-88-49, pp. 127-130), we have developed a new design that will increase its throughput (both organic and aqueous phases) from 5 to 48 L/min. The original design had a nominal throughput of 10 L/min based on the use of tetrachloroethylene (TCE) as the diluent. Now, as we expect to use normal dodecane (nDD) as the diluent, the nominal throughput would only be 5 L/min. This throughput was doubled to 10 L/min by increasing the rotor speed from 30 to 60 Hz (1800 to 3600 rpm). By moving the aqueous underflow radially outward so that the full volume of the separating zone can be used for coalescing the two phases, the nominal throughput was increased from 10 to 12 L/min. By making the separating zone four times longer with corresponding increases in the weir length and the cross-sectional area available for flow in the underflow to the more-dense-phase (aqueous-phase) weir, the nominal throughput was increased to 48 L/min. Thus, the 10-cm SHTCC will have a nominal throughput that is almost ten times that of the 10-cm contactor built and tested for Hanford in 1987.

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** Co-op student from the University of Evansville.

Detailed design calculations show that the SHTCC rotor mass below the circular weir for the more dense phase will be 26.5 kg (58.3 lb). The mass of the water in the rotor will be 6.0 kg (13.1 lb). The outer wall of the rotor will be 105 mm at the separating zone (the lower body of the rotor) and 133 mm at the weir zone (the upper body of the rotor). The overall length of the rotor, except for its shaft, will be 1078 mm. The extra weir length was obtained by using four rectangular tube weirs for both the more-dense-phase and less-dense-phase weirs, as shown in ANL-93/21, pp. 50-56. For convenience in post-fabrication machining of the more-dense-phase weirs, the circular weir for this phase was retained. The extra cross-sectional area for the underflow can be accommodated by the larger diameter of the upper rotor body. Because the upper portion of the rotor has this larger diameter, its bottom surface will be used as a slinger ring for the lower collector ring. The lip of the upper ring will act as the steady bearing for the rotor. The dispersion disk will be omitted since the rotor is four times its normal length.

In the new SHTCC design, it is expected that the steady bearing will not normally be touched, even though it is in place and ready to limit rotor vibrations. On startup, this will be accomplished by the rapid startup of the motor. On shutdown, this will be accomplished by the use of a 2-kW (2-hp) Baldor Series Eleven Inverter. With this electronic variable frequency drive, we should be able to stop the rotor after only a few revolutions. To date, the ability to do this has only been demonstrated during startup using 4-cm rotors. If fast startup and shutdown works for the 10-cm contactor, it will prevent banging of the contactor rotor on the steady bearing as the rotor passes through its first natural frequency.

A face-mounted Baldor motor (model VM8016T designed for dirty duty) with power of 1.5 kW (2-hp) and operating frequency of 60 Hz (3600 rpm) will drive the rotor. Using the design of the rotor, the motor/rotor coupling, and an estimate of the vibrational characteristics for the motor, we calculated the first three natural frequencies for the rotating motor/rotor mass using the Beam worksheet developed earlier (ANL-91/26, p. 167). These calculated values were 9.2, 93.9, and 376 Hz. As a check, these three natural frequencies were also calculated using the BEAM IV program (Virginia Polytechnical Institute and State University) and found to be the same. A key feature of these results is that the first natural frequency is well below the operating speed of 60 Hz, while the second natural frequency is more than 40% above the operating speed. Thus, based on earlier tests on a solid 4-cm SHTCC rotor, vibrations should not be a problem for the SHTCC at this operating speed, which is well above its first natural frequency (first critical speed).

2. Motor/Rotor Coupling

The motor/rotor coupling will use the coupling-nut design proposed earlier (ANL-91/26, p. 167). The coupling will be pinned to the shaft on the motor and will screw onto a threaded shaft extending upward from the top surface of the rotor body. This arrangement makes it easy to disconnect the rotor from the motor and the motor/rotor coupling. The design gives a simple stiff coupling, which has worked well for the remote-handled 4-cm contactor. With a distance of 127 mm (5 in.) between the face of the motor and the top face of the rotor, we calculated the first three natural frequencies reported above. If necessary, this distance could be increased or decreased slightly to fine-tune the first two natural frequencies.

3. Contactor Housing

The contactor housing was designed so that the superficial velocity of the liquid flowing in the collector rings and in the interstage lines is typical of that for earlier contactors with

diameters from 2 to 25 cm. Since the upper portion of the rotor is larger in diameter than the lower portion, the downward-facing horizontal surface where the upper rotor necks in to join the lower rotor will be used as a slinger ring for the lower (less dense phase) collector ring. A gap of 2.54 cm (1 in.) for the annular mixing zone will give 98.6% extraction efficiency for the contactor stage, will require a 0.95 kW (1.27 hp) motor, and will result in 5.2 L of liquid in the mixing zone at a total throughput of 48 L/min. Thus, the total liquid in the rotor plus the mixing zone will be 11.1 L. Based on the power for normal flows and the knowledge that the need to make experimental tests at even higher flows will require even more power, a 1.5 kW motor was selected for the prototype SHTCC. The mass of this contactor stage is estimated to be 207 lb (94.1 kg) empty, 234 lb (106.1 kg) full of water. For design of the support frame, a stage mass of 250 lb (113.5 kg) was used.

Because of the need for a vibrational analysis of the various support members (including the contactor housing, which supports the motor mount, the motor, and the rotor) the 11-section Beam worksheet reported earlier (ANL-91/26, p. 167) was modified to make it easier to use. This new Excel worksheet, which is entitled "Beam Structure," allows one to specify one of five boundary conditions: free-free (the only option on the original Beam worksheet), fixed-free, pinned-pinned, fixed-fixed, and fixed-pinned. The Beam Structure worksheet was checked at each boundary condition by running an identical problem on the BEAM IV program and found to give essentially the same results.

A simple worksheet with only one section and no rotational capabilities, called the "f(1) Beam" worksheet, was also compared with the new Beam Structure worksheet for the three boundary conditions available on the f(1) Beam worksheet: fixed-free, pinned-pinned, and fixed-fixed. Errors between the two worksheets were often significant but not unreasonable, typically 30% or less.

To estimate the stiffness of the contactor housing as it rises out of the horizontal support frame, the housing was taken to be a tube with an outside diameter of 168.3 mm (6-5/8 in.), a wall thickness of 6.4 mm (1/4 in.), a length of 406 mm (16 in.), and 68.1 kg (150 lb_m) at the free end. Using the fixed-free boundary condition, the Beam Structure worksheet gave a first natural frequency of 181.0 Hz; the f(1) Beam worksheet, 181.3 Hz; and the BEAM IV program, 180.2 Hz. Since the first natural frequency of the contactor housing is three times the operating speed, its stiffness will not be a problem.

4. Support Frame

Using the Beam Structure worksheet described above, the horizontal support frame and the vertical legs were designed for the SHTCC. Based on the size of the expected test booth, a two-stage prototype SHTCC test stand was chosen as the design basis. Note that we will initially have only one stage. Thus, one of the openings for a contactor stage on the support frame will be unused. For the design calculations, we assumed that both stages were in place. The spacing between contactor stages is 457 mm (18 in.). The overall length of the horizontal support frame is 914 mm (36 in.). The length for each of the two legs is 762 mm (30 in.). Each stage is assumed to weigh 113.5 kg (250 lb). A 254-mm x 254-mm (10-in. x 10-in.) box beam is used for both the support frame and the legs, with a wall thickness of 3.2 mm (1/8 in.) and 9.5 mm (3/8 in.), respectively.

For the support frame with two stages, one at 40% and one at 60% of the distance from one end, the first natural frequency is 218 Hz when the pinned-pinned boundary conditions are

used. Using the $f(1)$ Beam worksheet with the 227 kg (500 lb) of the two stages distributed uniformly along the beam, we found that the first natural frequency is, as expected, somewhat higher, 286 Hz. Since the first natural frequency of the support frame is more than three times the operating speed, its stiffness will not be a problem. Since the box beam mass is 23.6 kg (52 lb), the total mass supported by the legs is 251 kg (552 lb).

For one leg with a mass of 227 kg (500 lb) at its free end (a conservative value, as the mass should be distributed between the two legs), the first natural frequency is 113.1 Hz when the fixed-free boundary conditions are used. For a more realistic mass of 125.3 kg (276 lb), the first natural frequency becomes 148.7 Hz. The $f(1)$ Beam worksheet for these two cases gives very similar results for these two cases, 113.2 and 149.0 Hz, respectively.

A sketch of a two-stage 10-cm SHTCC, included here as Fig. 7, shows how the two stages are mounted on the support frame. While both contactor stages are shown, initial plans are to build only one prototype stage. The overall height of the unit will be 1.83 m (72 in.). The inside height of the contactor test booth is somewhat larger, 2.39 m (94 in.). This height is measured between the 203 mm (8-in.) I-beams in the test booth. The SHTCC stages will probably be located between two I-beams spaced 914 mm (36 in.) apart and on either side of the entrance. At the I-beams, the available height in the test booth is only 2.18 m (86 in.). Removal of the motor/rotor assembly will be reviewed as a part of the final design to verify that it can be done safely. One method is to have openings in the roof of the test booth through which the assembly can be hoisted. A second method is to lift up the motor/rotor assembly a few inches, disconnect the rotor from the rest of the assembly, remove the motor with the motor mount block and coupling, and then take out the rotor in the space left by the motor/rotor assembly.

Fig. 7.

Three Views of Design for
Two-Stage 10-cm SHTCC

5. Nuclear Criticality

One of the basic objectives in building the SHTCC is to show that one can increase contactor throughput by a factor of 4 to 8 yet keep the unit safe with respect to nuclear criticality by its geometry. To see that we will have nuclear criticality safety by geometry, the design of the 10-cm SHTCC was reviewed with E. K. Fujita and R. M. Lell, both of the Reactor Analysis Division of Argonne National Laboratory. Based on this review, the planned contactor diameter (based on a 10-cm rotor) will give nuclear criticality safety by geometry if the spacing between contactor stages is sufficient. Fujita and Lell estimated that the required spacing would be only a few inches, specifically, they thought that six to eight inches (15 to 20 cm) would probably be enough. The spacing between contactor stages, which is currently about three inches (8 cm), could be increased easily to meet this additional criterion for criticality safety by geometry. Because each stage can be essentially isolated from the other stages with a reasonable amount of space between each stage, the basic concept of nuclear criticality safety by geometry for the SHTCC seems to be appropriate.

During this review of the SHTCC, it was pointed out that nuclear criticality safety can be achieved by controlling (1) the geometry, (2) the concentration of fissile material, or (3) the total mass of fissile material. Since this is the case, each project should be reviewed to see if the SHTCC is really necessary. Quite often, control of the concentration or total mass of the fissile material may be all that is required. Further information is available in Refs. 23 and 24, which are considered to be very conservative. The reviewers recommended that a detailed analysis of nuclear criticality safety of the SHTCC be done only for very specific cases where contactor dimensions and process compositions are known.

Without any detailed process compositions known, various factors were reviewed to determine if the stage-to-stage spacing shown in Fig. 7 is a reasonable first choice. Single-parameter limits for nuclear criticality safety state that either the maximum diameter is 154 mm for an infinitely long cylinder of a solution containing $^{239}\text{Pu}(\text{NO}_3)_4$ or the maximum concentration for ^{239}Pu should be less than 7.3 g/L.²⁴ For three-dimensional arrays of cylinders that have a diameter of 127 mm (5 in.), 1.6-mm aluminum walls, and a very high concentration of fissile material (479.8 g/L of ^{235}U), and that are infinitely long, the surface-to-surface spacing between cylinders must be 127 mm (5 in.).²³ The SHTCC stage diameter is 210 mm (8-1/4 in.) for the upper zone containing the collector rings and 168.3 mm (6-5/8 in.) for the lower zone containing the separating zone of the rotor. The center-to-center spacing of the stages is 457 mm (18 in.). While the diameters of the SHTCC stages are somewhat larger than the reference cylinder, they are not infinitely long. In addition, the stages form a two-dimensional array since they are in a straight line. In addition, the concentrations of fissile material in waste processing will not be nearly as high as cited by Paxton.²³ Thus, the 457-mm (18-in.) center-to-center spacing proposed for the SHTCC stages appears to be realistic.

B. Minicontactor

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Significant amounts (>1%) of aqueous phase were seen from time to time in some organic-phase interstage lines of the minicontactor (2-cm contactor) during Verification Run 10, see ANL-91/42, pp. 124, 139-140. Because the reason for this problem was not fully identified at the time, additional experimental work was carried out on the minicontactors. This additional work indicates that, as was suspected earlier, an insert (flow restrictor) in each aqueous feed inlet at each stage was the root cause of this problem. The use of this insert in the minicontactor was stopped after our initial bad experience during Verification Run 10.

There are no inserts in the organic interstage lines as the organic phase wets the fluorinated ethylene propylene (FEP) plastic tubing used for the interstage lines, and so flows smoothly between the stages.

1. Factorial Test

Based on Verification Run 10 and subsequent exploratory tests (ANL-91/42, pp. 121-128), three factors appeared to cause a significant amount of aqueous phase (>1%) in the organic-phase stage exit (A in O) of the minicontactor. These factors were (1) the flow restrictor, (2) the slinger ring gap, and (3) the rotor runout. The aqueous and organic flow rates represent two additional factors. Using these five factors, a 2^5 factorial test was carried out as described by Box et al.²⁵ The basic idea was to find out which combination of factors gives rise to >1% A in O.

A schematic of the experimental setup for the 2^5 factorial test is shown in Fig. 8. A flow restrictor, shaped as shown in Fig. 9, was located in the aqueous inlet to stage 15A as the aqueous phase flowed in its interstage line from stage 16A to stage 15A. There were no flow restrictors in the organic interstage lines. The aqueous (DF) feed, which was 0.01M HNO_3 , was fed to stage 16A. The organic (DX) feed, which was 30% TBP in normal dodecane, was fed to stage 15A. The occurrence of high A in O (>1%) was monitored by collecting the organic (DP) effluent from stage 16A. At high flow rates, a 5-min sample was collected; at low flow rates, a 20-min sample. Thus, a typical test took 20 min.

Fig. 8. Minicontactor Setup for the 2^5 Factorial Tests

Fig. 9. Sketch of Insert for Aqueous Inlet to 2-cm Contactor Stage

Each of the five factors had two values for this test. The flow restrictor was either in or out; the aqueous (DF) flow rate was either high (20 mL/min) or low (5 mL/min); the organic (DX) flow rate was either high (20 mL/min) or low (5 mL/min); the slinger ring gap was either high (1.44 ± 0.15 mm) or low (0.44 ± 0.02 mm); and the rotor runout was either high (0.18 ± 0.03 mm, which is 7 ± 1 mil) or low (0.041 ± 0.003 mm, which is 1.6 ± 0.1 mils).

Appropriate dimensions were measured on all 40 minicontactor stages to determine the following: the desired range of slinger ring gaps (the vertical gap from the bottom surface of the slinger ring on the rotor to the top surface of the lip on the upper collector ring), rotor bottom gap (the vertical gap between the bottom surface of the rotor and the top surface of the stationary vanes at the bottom of the rotor), and the rotor runout (the total variation in the sideways movement of the rotor wall at the bottom of the rotor as the rotor is turned by hand). For the original 16-stage minicontactor with stages labeled 1 through 16, the average height of the bottom vanes was 1.59 ± 0.07 mm, the average gap for the slinger rings was 0.94 ± 0.29 mm, the average gap for the rotor bottoms was 1.54 ± 0.39 mm, and the average difference by which each slinger ring gap was greater than its rotor bottom gap was 0.60 ± 0.16 mm. For the new 24-stage minicontactor with stages labeled 1A through 24A, these average dimensions were 1.54 ± 0.10 mm, 0.69 ± 0.35 mm, 1.30 ± 0.41 mm, and 0.62 ± 0.22 mm, respectively.

For the factorial tests, rotor 13A was used in stage 16A for the case where the slinger ring gap and the rotor runout were both high; rotor 7A for the case where they were both low; rotor 4A for the case where the slinger ring gap was high and the rotor runout was low; and rotor 11A for the case where the slinger ring gap was low and the rotor runout was high. For all tests, rotor 12A was used in stage 15A because this gave an average rotor runout with an average slinger ring gap.

Results from the 2^5 factorial test, which are listed in Table 13, show that in no case was the A in O greater than 1%. In this table, the test number indicates the unrandomized test order. The order in which the tests are listed in the table was the actual test order. After the first 16 tests, we decided to undertake two sets of measurements for the second 16 tests. The last 16 tests typically took 40 min.

After the factorial test, two tests, Nos. 21 and 7, were repeated because the amount of A in O was closest to 1%. After four 20-min repeats of each test, the largest amount of A in O that was seen was only 0.1%. We concluded that no combination of these five factors was totally responsible for the high values of A in O seen earlier. As a result, we turned to looking at the effect that gas bubbles can have on liquid movement through an interstage line when a flow restrictor is present.

2. Partial Gas Bubble Blockage

Because none of the five factors in the 2^5 factorial test caused a significant amount of aqueous phase ($>1\%$) in the exiting organic phase, we explored the possibility that a gas bubble could partially or completely block the flow in the aqueous interstage line when the insert was in place. An apparent air-blocked interstage line was previously reported (ANL-91/42, pp. 139-140). At the time, the insert was in the end of the interstage line, which was disconnected from the next stage. The line hung down so that the insert was two or three times lower than normal. While the line was blocked as determined by the incoming liquid backing up in the line, a significant amount of aqueous ($>1\%$) phase was observed in the organic phase exiting the same stage that was feeding the blocked aqueous interstage line. It was not proven that the large air bubble in the middle of the liquid in the aqueous

Table 13. Results of the 2^5 Factorial Test

Test No.	Flow Restrictor	Aqueous Flow, mL/min	Organic Flow, mL/min	Slinger Ring Gap	Rotor Runout	A in O (from stage 16A), %	O in A (from stage 15A), %
11	in	5	5	High	Low	<0.1	<0.1
6	in	20	20	Low	High	<0.1	0.6
4	in	20	5	Low	Low	<0.1	<0.1
7	in	20	20	High	Low	0.5	0.6
21	out	20	20	High	High	0.9	0.2
30	out	5	20	Low	High	<0.1	<0.1
31	out	5	20	High	Low	<0.1	<0.1
18	out	20	5	Low	High	<0.1	<0.1
16	in	5	20	Low	Low	<0.1	<0.1
10	in	5	5	Low	High	<0.1	<0.1
25	out	5	5	High	High	<0.1	<0.1
1	in	20	5	High	High	<0.1	<0.1
28	out	5	5	Low	Low	<0.1	<0.1
13	in	5	20	High	High	<0.1	0.8
19	out	20	5	High	Low	<0.1	0.8
24	out	20	20	Low	Low	<0.1	0.7
9	in	5	5	High	High	<0.1	0.7
						<0.1	<0.1
12	in	5	5	Low	Low	<0.1	<0.1
						0.1	<0.1
26	out	5	5	Low	High	<0.1	<0.1
						<0.1	0.3
15	in	5	20	High	Low	<0.1	0.2
						<0.1	0.1
3	in	20	5	High	Low	0.1	0.6
						<0.1	0.6
29	out	5	20	High	High	<0.1	0.1
						<0.1	0.3
5	in	20	20	High	High	<0.1	0.8
						<0.1	0.3
8	in	20	20	Low	Low	<0.1	<0.1
						<0.1	<0.1
23	out	20	20	High	Low	<0.1	<0.1
						<0.1	<0.1
2	in	20	5	Low	High	<0.1	<0.1
						<0.1	<0.1
17	out	20	5	High	High	<0.1	<0.1
						<0.1	<0.1
32	out	5	20	Low	Low	<0.1	0.8
						<0.1	0.2
27	out	5	5	High	Low	<0.1	0.8
						<0.1	0.1
22	out	20	20	Low	High	<0.1	<0.1
						<0.1	<0.1
14	in	5	20	Low	High	<0.1	<0.1
						<0.1	<0.1
20	out	20	5	Low	Low	<0.1	<0.1
						<0.1	<0.1

interstage line was blocking the aqueous-phase flow. In fact, it is more likely that the gas bubble was simply trapped in the line. A small gas bubble in the stainless steel insert may have been the actual cause of the blockage. However, as we could not see inside the insert, this could not be confirmed.

Because of these questions about how gas bubble blockage might work, we carried out a series of controlled tests. The objective was to determine if a gas bubble could block the flow in the aqueous interstage line when the insert was in place and the line was connected to the next stage. The experimental setup and the results of the various tests are reported next.

a. Experimental Setup

In the experimental setup, a PVC tube with a 90° bend was put over the aqueous inlet port with the insert in place. The inside diameter of the PVC tube was 9.6 mm (3/8 in.), the same as for the FEP tube used for the interstage line. The tube rose upward at the same angle as the interstage line for the aqueous phase. A FMI metering pump (Fluid Metering, Inc., Oyster Bay, NY) supplied the desired flow rate for the distilled water to the top end of this feed tube. With this basic system in place, we determined the effect of the aqueous flow rate on the liquid level in the interstage line. The liquid levels are all reported as vertical height of the liquid above the centerline to the stage inlet.

Once the liquid level was determined as a function of flow rate, various bubble sizes were introduced to determine what effect, if any, they had on the liquid level at a given flow rate. We tried several techniques for injecting air bubbles of known volume. The technique that we chose consisted of a metering pump that could handle either gas or liquid. As the pump was running, its intake tube was lifted out of the liquid feed for the time required to take in the desired volume of air. A C-FLEX tubing with an outside diameter of 2.4 mm (3/32 in.) and an inside diameter of 1.6 mm (1/16 in.) fed the liquid and air into the PVC feed tube. Since the outside diameter of the C-FLEX tubing was less than 3.2 mm (1/8 in.) of the inside of the insert, the bubbles could be introduced either inside or outside of the insert. A small-diameter glass tube inserted into the middle of the C-FLEX tubing allowed the volume of the gas bubble to be verified. With both the volume inside the C-FLEX tubing and the pump flow rate known, the time at which the bubble could be released inside the insert was calculated. As soon as a bubble was released inside the insert, the C-FLEX tubing was pulled back to a position just outside the mouth of the insert. In this position, the C-FLEX tubing has essentially no effect on the liquid level in the PVC tubing. Even just inside the insert, the C-FLEX tubing has only a small effect on the liquid level (see Fig. 10). Note that the centerline of the exit ports on the aqueous side of the minicontactor is 27 mm (1.06 in.) vertically above the centerline of the inlet ports. Thus, at least up to 20 mL/min, the aqueous phase does not normally back up into the exit port, even with the insert in place.

b. Bubbles Outside the Insert

Tests were done to determine the effect of bubbles released just upstream from the face of the insert. Four bubble volumes (0.5, 1, 2, and 4 mL), and three flow rates (16, 26, and 36 mL/min), were used. These flow rates include the liquid flow rate of 6 mL/min in the C-FLEX tube used to carry the gas bubble of a given volume into the interstage line just before the mouth of the insert. Note that a gas bubble with a diameter of 10 mm has a volume of 0.52 mL. The total volume inside the insert is only slightly larger, 0.64 mL. Smaller bubbles were not used as they disappeared when they passed through the FMI pump head.

Fig. 10. Effect of Flow Rate on the Height of Water in the Line to the Aqueous Inlet Port. In case 1, the bubble tube comes down and stops just outside the aqueous insert. In case 2, the bubble tube comes down and stops just inside the aqueous insert.

Each of the twelve tests was repeated six times, and the behavior of the injected bubbles and the liquid level was noted each time. The injected bubble volume produced one to four actual bubbles in the feed line. Most of the bubbles floated up out of the line. A few of the bubbles entered the insert. The rest of the bubbles stayed just outside the insert. In no case did these bubbles cause the liquid level in the feed line to rise.

c. Bubbles Inside the Insert

Tests were also done to determine the effect of bubbles released just inside the insert. The bubble-injection tube was allowed to remain in the insert throughout the test since, as shown by Fig. 10, it has almost no effect on the column height.

Initial test were done using 0.5-, 1-, and 2-mL bubbles at flow rates of 16, 26, and 36 mL/min. After several tests at each of the various flow rates, we discovered that the water backed up from 1 to 17 mm above its normal height at 16 mL/min. This was the first time during these bubble insertion tests that bubbles were seen to cause the liquid to back up in the interstage lines.

Since the liquid backed up only at the lowest flow rate, 16 mL/min, it appeared that significant changes in the height of the water column occur only at lower flow rates. To explore this effect further, tests were conducted with bubble sizes of 0.5, 1, and 2 mL and flow rates of 4, 8, 12, 16, and 20 mL/min. During these tests, the height of the water column was recorded every five seconds after the bubble entered the insert. Typical results are shown in Figs. 11 to 13.

Fig. 11. Effect of 0.5-mL Bubble on the Transient Height of Water in the Line to the Aqueous Inlet Port for Various Water Flow Rates. Flow rates, in mL/min, are given by the number part of the run code in the legend. Three runs, labeled A, B, and C, were done at each flow rate. For example, run 20B is the second run done at the 20-mL/min flow rate. Two runs are plotted at each flow rate to show how the results can vary.

Figure 11 shows the variation of water height with time for 0.5-mL bubbles. The bubble-injection rate is 4 mL/min so that the bubbles are injected over a period of 7.5 s. Except for the lowest flow rate, where the flow in the bubble-injection tube was stopped after the bubble was injected, the liquid flow in the bubble-injection tube was considered to be a part of the flow rate in the interstage line. A review of this figure shows several trends. First, the time necessary for the water column to rise, reach its maximum height, and then return to its original height appears to increase as the flow rate decreases. Consequently, the flow rate of 4 mL/min takes the longest to complete this cycle (about 40 s). Second, although each of the flow rates has different initial and final column heights, all flow rates appear to have a similar maximum height for the water column. This height was between 16 and 20 mm above the centerline of the aqueous inlet. This phenomenon suggests that, at this maximum height, enough water pressure is available to keep or restart the bubble moving through the insert.

Figure 12 shows the variation of water column height with time for 1-mL bubbles. Although the volume of the insert cavity is only 50% of the volume of the 1.0-mL bubble, this 1.0 mL of air was pumped into the insert over a period of 15 s without any of the air escaping out the entrance to the insert. Thus, some air must have been escaping from the exit of the insert even as more air was being added to the insert. Throughout the time the air was present inside the insert, these tests showed a behavior similar to that observed during the 0.5-mL bubble tests. The most noticeable differences between these tests and earlier tests were the slightly greater increases in the vertical height of the water column and the longer times for the water column to rise and fall.

Fig. 12. Effect of 1-mL Bubble on the Transient Height of Water in the Line to the Aqueous Inlet Port for Various Water Flow Rates. Flow rates, in mL/min, are given by the number part of the run code in the legend. Three runs, labeled A, B, and C, were done at each flow rate. For example, run 20B is the second run done at the 20-mL/min flow rate. Two runs are plotted at each flow rate to show how the results can vary.

The transient column heights produced were between 15 and 21 mm above the centerline of the aqueous inlet and took a maximum time of 50 s to return to their initial heights.

Figure 13 shows the variation of water column height with time for 2-mL bubbles. For this case, the 2-mL volume of air was pumped into the aqueous insert over a 30-s period of time. The maximum height of the transient water column during this series of tests was greater than that for either the 0.5- or 1-mL bubble tests. Maximum heights were between 17 and 30 mm above the centerline of the aqueous inlet. Since the centerline for the aqueous outlet is only 27 mm above the centerline of the aqueous inlet, some of these bubbles could cause the aqueous phase to back up into the aqueous collector ring, where some liquid could bypass the slinger ring on the contactor rotor and emerge with the exiting organic phase. Note that, at flow rates greater than 12 mL/min, the maximum liquid height is more a plateau than the peak that appears at lower flow rates.

To determine the extent of gas bubble blockage inside the insert, the three figures showing liquid height as a function of time were analyzed. The apparent liquid backup rate was determined from the rate at which the liquid level rises in the inlet tube. As the liquid level was noted only every 5 s, the error in these backup rates is on the order of 15 to 30%. The results, given in Table 14, show that in most cases where blockage occurred, it was only partial. Partial blockage is inferred when the calculated backup rate is only a small fraction of the total feed rate. When the backup rate is close to the total feed rate, the gas bubble has probably caused complete, if temporary,

Fig. 13. Effect of 2-mL Bubble on the Transient Height of Water in the Line to the Aqueous Inlet Port for Various Water Flow Rates. Flow rates, in mL/min, are given by the number part of the run code in the legend. Three runs, labeled A, B, and C, were done at each flow rate. For example, run 20B is the second run done at the 20-mL/min flow rate. Two runs are plotted at each flow rate to show how the results can vary.

backup rate is close to the total feed rate, the gas bubble has probably caused complete, if temporary, blockage of the liquid flow. As noted above, the flow restarts when the rise in the liquid level is high enough.

As shown in Table 14, essentially complete blockage resulted for 0.5-, 1.0-, and 2.0-mL injections of air at a total liquid flow rate of 4 mL/min. This was also true for 1- and 2-mL injections of air at a total liquid flow rate of 12 mL/min about 50% of the time. During verification run 10 (ANL-91/42, pp. 121-128), the greatest amount of A in O was observed in the scrub section between stages 4 and 5. In this section, the aqueous flow rate was only 3.5 mL/min. In tests after the verification run, the greatest amount of A in O was observed in the second strip section between stages 10 and 11. In this section, the aqueous flow rate was also low, only 7 mL/min. Thus, the use of inserts in the interstage line of the aqueous phase can cause significant amounts of aqueous phase (>1%) in the organic-phase interstage lines of the minicontactor (2-cm contactor) if the aqueous flow rate is low and a gas bubble gets in the insert.

d. Source of Gas Bubbles

The question remains as to how gas bubbles get into the insert during the actual verification runs. This question was not answered. However, we did observe during the current tests that very small gas bubbles formed with time in the water flowing through the aqueous interstage lines. Occasionally, bubbles would merge to form larger bubbles; usually these bubbles floated to the surface of the water in the aqueous feed line. It is probable that similar bubbles collected inside the insert and eventually formed a large bubble capable of temporarily blocking the flow through the

Table 14. Effect of Bubble Volume and Flow Rate on the Apparent Rate of Liquid Backup in the Aqueous Inlet Line

Bubble Volume, mL	Run Code	Flow Rate, mL/min		Total Flow Rate, mL/min	Apparent Rate of Liquid Backup, ^a mL/min
		Pump 1 (primary)	Pump 2 (bubble injection)		
0.5	20A	16	4	20	2.7
	20B	16	4	20	0.9
	12A	8	4	12	3.4
	12B	8	4	12	3.8
	4B	4	0 ^b	4	3.1
	4C	4	0 ^b	4	3.8
	20A	16	4	20	0.9
1.0	20B	16	4	20	1.1
	12C	8	4	12	10.3
	12B	8	4	12	3.4
	4A	4	0 ^b	4	2.9
	4B	4	0 ^b	4	4.7
	20A	16	4	20	4.3
	20B	16	4	20	2.6
2.0	12A	8	4	12	5.1
	12C	8	4	12	8.6
	4A	4	0 ^b	4	2.6
	4C	4	0 ^b	4	3.7
	20A	16	4	20	4.3

^aBackup rates were calculated for the time just prior to the highest liquid level in the line leading to the insert (flow restrictor) in the aqueous phase feed line.

^bPump 2 was operated at a flow rate of 4 mL/min only until the bubble was injected into the insert. Then pump 2 was turned off.

insert (flow restrictor) into the mixing zone of the minicontactor. Since we could not see inside the insert, the possible presence of these small bubbles would go unnoticed during normal contactor operation. Such a mechanism would explain why we did not observe the high levels of aqueous phase in the organic interstage lines during the first hour of verification run 10, and why, when aqueous phase did appear there, it was erratic.

This work confirms that small bubbles in the aqueous insert could back up the aqueous phase into the stage from which aqueous phase is coming and cause the appearance of significant amounts of aqueous phase (<1%) in the organic phase exiting from that stage. The presence of a fine droplets of organic phase in the aqueous phase, which would be present during normal contactor operation, could possibly enhance this effect. Because of the mechanism involved (that is, the aqueous phase backing up into the aqueous collector ring and then flowing under the slinger ring on the contactor rotor to the organic collector ring), the effect was more pronounced when the gap between the slinger ring on the rotor and the lip on the aqueous-phase collector ring was larger than normal.

VI. PROCESSING OF NEW BRUNSWICK LABORATORY WASTE SOLUTION

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Residue solutions generated from plutonium analysis 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, as well as U, Pu, Np, and Am. Originally destined for storage at the Idaho National Engineering Laboratory and eventual disposal at the Waste Isolation Pilot Plant in New Mexico, these wastes now appear to have no place that will accept them. In this project, the TRUEX process will be used to convert the bulk of this waste into a nonTRU (i.e., low-level) waste by removing the TRU elements to levels of less than 0.1 nCi/g. After processing, the nonTRU waste stream will be transported to the Plant Facilities and Services-Waste Management Operations (PFS-WMO) at ANL for final disposal. The recovered plutonium will be converted into solid PuO_2 for return to NBL for storage and subsequent transport to the DOE defense complex.

Approximately 200 L of the mixed waste generated by NBL and ANL will be converted into a nonTRU waste using the TRUEX process. This demonstration will show the applicability of this process to the much larger volume of similar wastes being generated at Rocky Flats Plant, Los Alamos National Laboratory, and the Hanford site, and will act as a basis for evaluating this process as a future waste treatment process at ANL/NBL.

The bulk of the waste that will be processed is being stored by WMO. To process these wastes, they will be transported to the Chemical Technology (CMT) Division, Building 205. Because of the fissile-material limits in Building 205, transfers and subsequent processing will be completed in five to six batches, with each batch containing a maximum of 50 g of fissile material. Since the composition of each batch differs, modifications will be made to each flowsheet (e.g., stages in each section, feed-stream flow rates) to optimize the process for each batch. Flowsheets will be developed on the basis of calculations generated by the Generic TRUEX Model and a small number of test-tube experiments.

A simplified flowsheet for processing the plutonium-containing waste solutions is shown in Fig. 14. The TRUEX solvent extraction process will be completed in a 20-stage centrifugal contactor installed in a glovebox. The organic solvent (TRUEX-nDD) that will be used in this process consists of 1.4M TBP and 0.75M CMPO, in n-dodecane.

The bulk of the solution generated by this program will be the nonTRU waste stream that will be transferred to WMO for disposal. Prior to transferring to WMO, this waste will be neutralized so that WMO can feed it directly into its evaporator. The americium product stream shown in Fig. 14 will be saved for use in ongoing laboratory experiments in CMT.

The plutonium product stream will be evaporated to dryness, then converted to an oxide by calcining in an oven at $>600^\circ\text{C}$. A glovebox is available in another laboratory in Building 205 for the concentration, precipitation, and conversion steps. The product from the calcining operation, PuO_2 , will then be reduced to the metal in another CMT facility, then returned to NBL for storage and shipment to Idaho.

Fig. 14. General Flowsheet for Processing Plutonium Waste Solutions

A solvent wash stream is also generated by the TRUEX process. Based upon processing the first 12 g of plutonium in this program, this stream will be a TRU waste, meaning that WMO cannot handle, nor accept, this solution for disposal. Therefore, this stream will be recycled back into the TRUEX process.

A. Acidified Carbonate Waste Processing

1. Background

Approximately 50 L of waste solution was generated from (1) processing of the first 12 g of plutonium (batch 1), (2) centrifugal contactor decontamination efforts, and (3) reprocessing of the batch 1 raffinate. To process this solution using the TRUEX process, nitric acid was added to completely neutralize the carbonate present and to make the final solution approximately 1M in nitric acid. Oxalic acid was also added to the waste solution to help prevent the formation of plutonium polymers; the final oxalic acid concentration was 0.1M.

The volume of waste that had to be processed exceeded the capacity of the feed container (DF feed tank). Therefore, the solution was processed in two batches. Approximately 80 L of waste was processed. Processing began on October 3, 1991, and was completed on October 9, 1991. Details of these runs are given in the following sections.

2. Ammonium Oxalate Stripping of Plutonium

To avoid the precipitation problems encountered in the plutonium strip section during batch 1 processing, a new plutonium stripping agent was desirable. Earlier experiments performed with ^{238}Pu at tracer concentrations showed that ammonium oxalate was a very effective stripping agent for plutonium. Plutonium forms a tri-oxalato complex at high oxalate ion concentrations, and this would tend to remove plutonium from the TRUEX solvent. Oxalic acid would not be as effective as ammonium oxalate since it is poorly ionized. The tri-oxalato americium complex is not as strong, and americium oxalate may precipitate under conditions that would keep plutonium in solution. At "macro" concentrations, e.g., 2 mg/mL for plutonium and 0.2 mg/mL for americium, the concentrations expected in NBL reprocessing runs, it is possible that plutonium and americium oxalates will precipitate and plug the contactors and their connecting lines. Stripping experiments were performed with plutonium and americium to evaluate this possibility.

One milliliter of a stock solution containing about 4 mg/mL Pu in 1.1M HNO_3 was extracted into 2 mL TRUEX-NPH (load step). The organic phase that formed was 0.2M HNO_3 . This phase was scrubbed with 2 mL of 0.05M HNO_3 to reduce the acidity to about 0.07M HNO_3 , a concentration expected in an actual reprocessing run. The organic phase was then contacted with two successive 1 mL portions of 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to strip the plutonium. The phases separated, and no precipitate was observed.

The results are shown in Table 15. All measurements to determine the distribution ratios were made by liquid scintillation counting. The plutonium concentration in the loaded TRUEX solvent was about 2.5 mg/mL, very close to the desired value. The distribution ratio for the loading (extraction) step was only 15, although the expected value is about 750 at the calculated aqueous acidity. This difference may be due to the presence of either small amounts of the organic phase in the aqueous phase or the presence of other alpha emitters (e.g., ^{237}Np) in the aqueous feed. The layers were separated by gravity settling for 2 h in the glovebox. No centrifuge was available. A cleaner separation could have been obtained if a larger aliquot of the aqueous phase were removed and centrifuged before samples were taken. The distribution ratio of 84 obtained for the scrub step implies an acidity of about 0.1M HNO_3 in the aqueous phase.

Table 15. Results of Ammonium Oxalate Strip of Plutonium in TRUEX-NPH

Step	Distribution Ratio	Material Balance, %
Extraction	15	—
Scrub	84	98.2
Strip 1	2.0×10^{-6}	98.1
Strip 2	0.019	115

The scrubbing was nearly complete, as shown by the very low distribution ratio in strip 1. Only about $2 \times 10^{-4}\%$ of the plutonium remained in the organic phase after one strip. Little additional plutonium was removed by the second strip, as had been observed at tracer concentrations (ANL-93/21, p. 65). This large increase in distribution ratios between the two strips may be due to the presence of either (1) acidic chelating impurities in the NPH that form much stronger complexes with the actinides than CMPO or (2) small amounts of other alpha emitters (e.g., ^{237}Np) that form weaker oxalate complexes than plutonium.

3. Ammonium Oxalate Stripping of Americium

An oxalate strip test similar to that performed with plutonium as described above was performed with ^{243}Am , except that the americium concentration in this loaded organic solution was 0.28 mg/mL, or $1.15 \times 10^{-3}\text{M}$, as determined by liquid scintillation counting. (The specific activity of ^{243}Am is 4.45×10^{11} dpm/g.) One milliliter of this solution was contacted with 1 mL 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ for the first strip test. No precipitate was apparent initially. However, after the solutions were allowed to stand overnight, the aqueous phase contained about half the alpha activity found immediately after the phases were separated, and a small amount of precipitate was obvious in the bottom of the vial containing the oxalate solution. Either the precipitate, presumably $\text{Am}_2(\text{C}_2\text{O}_4)_3$, formed slowly, or the solution was not examined closely enough on the first day. A second strip of the organic phase was performed with 1 mL of fresh 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The aqueous phase for this contact contained $5.1 \times 10^{-6}\text{M}$ americium.

To test the effect of oxalate concentration on the stripping ability and complex formation, the above experiment was repeated with 0.14M and 0.45M $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Since americium oxalate precipitated in each stripping test at $1.15 \times 10^{-3}\text{M}$ americium, the same test was also performed at an initial concentration of $1.15 \times 10^{-4}\text{M}$ americium in the TRUEX phase.

The results obtained with an americium concentration of $1.15 \times 10^{-3}\text{M}$ are given in Table 16. In the first test with 0.28M ammonium oxalate, the material balance is low (78%), probably because the aqueous phase concentration was calculated from the measured alpha activity, and some of the americium had precipitated when the solution was sampled for counting. The distribution ratio was also calculated from the measured alpha activity, and if it is corrected for the apparent americium loss, about 20%, the distribution ratio for strip 1 becomes about 6×10^{-4} . Material balances were not calculated for the 0.14M and 0.45M oxalate stripping tests because of the loss of americium by precipitation. The trend in the distribution ratios indicated that the americium stripping is more effective as the oxalate concentration increases. The precipitates from the strip tests were washed with water and dissolved in 4M HNO_3 . The washings and solution were analyzed by scintillation counting and found to contain americium. The precipitate volume from 0.45M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ was smaller than from the 0.15M solution. This indicates, as do the distribution ratios, that more complexation occurs at higher oxalate concentrations.

Table 16. Results of Ammonium Oxalate Strip of Americium in TRUEX-NPH

$[(\text{NH}_4)_2\text{C}_2\text{O}_4], \text{M}$	Step	Distribution Ratio	Material Balance, %
0.28	Extraction	68	96
0.28	Strip-1	7.6×10^{-4}	78
0.28	Strip-2	3.7×10^{-3}	100
0.14	Strip-1	6.3×10^{-4}	—
0.14	Strip 2	0.024	97
0.45	Strip-1	2.2×10^{-4}	—
0.45	Strip-2	0.037	95

Ammonium oxalate is not very soluble in water. A 0.45M solution is supersaturated, and the salt precipitates with time. The 0.45M solution was prepared by heating the salt-water mixture until a clear solution was obtained and then cooling to room temperature. The solution remained clear for about 2 h, long enough to perform the experiment, but later the salt crystallized.

An approximate solubility for ammonium oxalate was obtained by evaporating 5 mL of a saturated solution (prepared at 23°C) to dryness in a weighed beaker and weighing the dried salt. The solubility was 0.31M. The 0.28M solution was measured in the same way and was found to be 0.25M.

Although of little practical interest, it would be informative to measure the stripping of americium at very high oxalate concentrations. The ammonium and sodium salts are not very soluble. However, the potassium salt can give a 1.9M solution, and the cesium salt, 8.8M, according to *Lange's Handbook*.²⁶ These latter salts could be used to determine if a stronger oxalate complex of americium can form.

A significant finding was that at an americium concentration of 1.15×10^{-4} M, stripping with 0.28M ammonium oxalate was as effective as at 1.15×10^{-3} M, and precipitation of americium oxalate did not occur.

4. Flowsheet

Based upon results from the batch tests and calculations with the GTM, a flowsheet was developed for processing the acidified carbonate waste. This flowsheet, shown in Fig. 15, incorporates several significant improvements over the previous flowsheets, including a new

Fig. 15. Flowsheet Schematic for Acidified Carbonate Waste Processing

plutonium strip solution, 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, which eliminates the plutonium oxalate precipitation that occurred in the first test. The flow rate of the plutonium strip feed (FF) was kept low to reduce the volume of the plutonium-product stream to be evaporated to dryness. In addition, a scrub feed (DS) was incorporated into the flowsheet to add the required amount of $\text{Al}(\text{NO}_3)_3$ to (1) increase the distribution ratio of plutonium in the extraction section and (2) strip oxalic acid from the solvent before it entered the americium strip section and acted to put plutonium in the americium product stream. At the high oxalic acid concentration in the feed (0.1M), the Pu(IV) was severely complexed, which prevented its extraction. Tests using the GTM plus batch extraction tests on the feed verified that adding $\text{Al}(\text{NO}_3)_3$ and HNO_3 lowered the $\text{C}_2\text{O}_4^{2-}$ concentration in solution to the point that the waste could be processed.

A few changes, indicated in Fig. 15, were made once the run was underway. Two of these changes modified the solvent wash section to improve solvent cleanup. To improve this very important portion of the flowsheet, the flow rates for the two solvent washes (GF and HF) were increased from 50 mL/min to 200 mL/min in order to decrease the O/A flow ratio in these two stages. This improves operation by making these two stages work with the aqueous solution as the continuous phase, thereby reducing the amount of carryover of the carbonate in the organic phase. Another change was to switch the aqueous solution in the bottom of the organic feed tank from sodium carbonate to nitric acid. An acid rinse of 0.25M HNO_3 was added to the solvent feed tank in order to re-acidify the TRUEX solvent before it was recycled into the extraction section. Incorporating an acid rinse stage seems to reduce the amount of foam generated by the solvent as it passes through the system, possibly by reducing the amount of colloids present in the solvent. Finally, the HP collection container seen in Fig. 15 was added during the run for reasons explained later.

5. Discussion of Run

Before processing began, all feed pumps, as well as the americium product (EW) pump, were calibrated. The results of these calibrations are given in Table 17, along with flow-rate measurements taken during the run. The other raffinate pumps (DW and HP) and the pump used to transfer the DW raffinate over to the hood were set at a flow rate high enough to stay ahead of the raffinate flows.

The reason for the increase in the flow rate of the carbonate wash pumps (GF and HF) after 58 min will be dealt with later in this report. The flow rate from the DX pump was checked frequently because of a problem with restarting the DX flow after shutdown. This pump had to lift the solvent out of the tall glass container, a distance about one foot above the level of the solvent. Leaks in the tubing connections at the DX filter would (1) allow the solvent to leak back down to the tank level during periods when the pump was not running and (2) decrease the vacuum head of the pump for lifting the solvent back up upon restart. Thus, re-establishing the flow to the pump after an overnight period of shutdown often required priming the pump. The easiest method of pump priming was to increase the flow rate considerably, allowing the pump to overcome the leakage of air into the lines. Therefore, the flow rate from this pump had to be reset many times.

Processing of the acidified carbonate waste began on October 3, 1991, and proceeded intermittently through October 9, 1991, taking a total of 850 min. An outline of the major perturbations to the system during processing is given in Table 18, with explanation to follow.

On October 3, shortly after all feed flows except DF had been established, not enough solvent was in the DX tank to continue processing. All of the solvent had been used to fill the

Table 17. Flow Rates of Feed Pumps during Acidified Carbonate Waste Processing

Pump	Running Time, ^a min	Flow Rate, mL/min
DF	0	114
DS	0	53
DX	0	54
EF	0	56.3
EW	0	3.0
FF	0	12.4
GF	0	61
HF	0	53
GF	58	210
HF	58	200
DX	63	90
DX	95	80
DX	102	64
DX	407	54
DX	770	60

^aTime during the run that flow rate was checked.

contactor stages. Therefore, the system was shut down, more solvent was bagged into the glovebox and added to the solvent tank, and the procedure for restarting the system was then initiated. Shortly thereafter, all interstage lines on the organic side of the contactors showed considerable foaming in the organic solvent. Since the DX solvent had last been contacted with sodium carbonate (in stages 19 and 20 as well as in the DX tank), this foaming suggests the presence of carbon dioxide, formed by carbonate ions dispersed in the solvent reacting with the acid in the aqueous phase. If the generation of CO₂ was the reason why the solvent foamed, one would expect this to occur only in the first (or first couple) of stages. Since the DF feed, with a much higher acid concentration than the other aqueous feeds, had not been started yet, it was started promptly in an attempt to solve this problem. However, starting the DF feed did not eliminate the foam.

Since the addition of the DF feed did not solve the foam problem, generation of CO₂ was probably not the cause. Another possibility is that some surface-active impurity in the solvent is removed when an acid rinse follows the carbonate washes. Without the acid rinse, this impurity causes the solvent to foam. However, a fault with this reasoning is, why does an acid rinse remove this impurity, while the acid solutions in the process do not?

After 48 min of running time, about 200 mL of organic phase was noticed in the HF feed container. Apparently, solvent carryover had occurred in the HW effluent from stage 20, but this had not been observed. The organic phase was pumped out of this container by raising the HF pump's pickup tube high enough so that the solvent was being pumped into the aqueous entrance to stage 20. Thus, for about 4 min, the solvent flow into stage 20 was about 100 mL/min, and there was no aqueous flow into that stage during this time. This solvent carryover problem did not recur during the rest of the processing run.

It was later noticed that the solvent exiting stage 20 (HP) was backing up at the HP filter. This filter was connected to the organic effluent line of stage 20 on one side and to the HP pump on the other. The pump pumped the solvent back up to the DX feed tank. Increasing the flow

Table 18. Time Line of Major Events in TRUEX Processing of Acidified Carbonate Waste

Date	Time of Day	Running Time, min	Event/Observation
10/3/91	2:00 PM	0	Startup begun. DF pump not started.
	2:28 PM	28	Shutdown. More solvent added.
	4:00 PM	28	Restart.
	4:04 PM	32	Foam noted in organic influent line to every stage. DF pump started.
	4:20 PM	48	Large amount of organic phase in HF container noted. Organic pumped from HF container to DX container by pumping it back through stage 20.
	4:30 PM	58	Shutdown. New HP container/pump system implemented. Carbonate wash in DX container replaced with acid rinse. GF & HF flow rates increased to 210 and 200 mL/min, respectively.
10/4/91	1:20 PM	58	Restart.
	1:25 PM	63	HP flow measured as 90 mL/min. DX pump reset for lower flow rate of about 50 mL/min.
	1:47 PM	85	DF pump started.
	2:04 PM	102	HP flow rate measured as 64 mL/min.
	2:35 PM	133	HF replaced with fresh Na ₂ CO ₃ . GF replaced with Na ₂ CO ₃ taken from DX tank on 10/3/91 at 4:30 pm.
	4:35 PM	253	Shutdown.
10/7/91	1:22 PM	253	Restart.
	1:33 PM	264	DF pump started.
	3:10 PM	361	pH of acid rinse measured as approximately 4; 100 mL of 6M HNO ₃ added to acid rinse.
	3:56 PM	407	HP flow rate measured as 54 mL/min.
	4:40 PM	451	Shutdown. HF replaced with fresh Na ₂ CO ₃ .
10/8/91	9:12 AM	451	Startup. DF pump started.
	11:50 AM	602	Shutdown. Waste solutions and acid added to DF tank. Mixer left on overnight.
10/9/91			
	10:52 AM	602	Restart.
	10:57 AM	607	DF pump started.
	12:20 PM	690	HF flow lost due to carryover into DX tank. DX flow lost (replaced by flow of acid rinse). Shutdown. Approximately 800 mL fresh Na ₂ CO ₃ added to HF. HNO ₃ added to acid rinse.
	12:45 PM	690	Restart.
	12:58 PM	703	DF pump started.
	2:05 PM	770	HP flow rate measured as 60 mL/min.
	3:08 PM	833	DF flow lost, DF tank empty.
	3:25 PM	850	Shutdown. DF mixer observed to be broken. Lack of filter on DF line noted.

rate of the HP pump provided a temporary fix to this problem, and a change in the HP pump configuration was planned for a more permanent solution. This backup of organic may have caused the organic carryover into the HF tank noted previously, since inhibiting the organic effluent from the stage would eventually flood the stage with the less-dense phase and cause it to flow out the more-dense phase exit.

Before processing was restarted on October 4, a number of changes were made to the system to solve problems that had been encountered. The HP pump configuration was changed, whereby the solvent exiting stage 20 was discharged into a 0.5-L bottle. The HP pump then pumped the solvent out of the container, through the filter, and up to the DX tank. This new configuration not only solved the problem of solvent backing up at the filter but also provided for easier sampling of the HP stream.

To acidify the solvent before it entered the extraction section, the third carbonate wash (0.25M Na_2CO_3 in the DX feed tank) was replaced with an acid rinse (approximately 0.25M HNO_3 in the DX feed tank). This was shown in previous tests to eliminate the foaming of the TRUEX solvent. To help improve the operation of the two solvent-cleanup stages, the flow rates for the GF and HF carbonate pumps were increased to approximately 200 mL/min to provide an O/A flow ratio in these stages of about 0.25. At those conditions, we believe that the carryover of aqueous in the organic solvent is reduced.

The DX line between the DX pump and stage 1 also needed rework. This line came down from the pump to a point slightly lower than the organic entrance to the stage, then rose up to the stage, causing a backup of solvent entering the stage. To fix this, the DX pump was raised up by placing a container lid underneath it, thus raising the DX line to stage 1.

Processing continued smoothly on October 4 and ran for about three hours. As can be seen in Table 18, the only perturbations to the system, other than startup and shutdown, were the variability of the solvent flow and the changing of the carbonate wash feeds. Since the solvent was pumped into stage 1, but its flow rate was measured exiting stage 20, considerable time was needed to make sure that the flow rate was within an acceptable range. The carbonate wash feeds were on full recycle, and these solutions were monitored to ensure that activity in them did not get too high.

On October 7, 1992, processing continued for slightly more than three hours. During that time the only major system change was the addition of acid to the DX tank. This was done because of the decreasing acidity of the acid rinse. After shutdown, the HF feed was replaced with fresh sodium carbonate.

At some undocumented time, either on October 7 or 8, about 3.25 L of waste that had been previously collected in the glovebox was added to the feed tank. About 2.5 L of this was a mixture of the americium product and the solution used to flush the americium strip section from the January 1991 processing of batch 1. About 0.75 L was aqueous drainage from stages 1-14 from the January 1991 processing.

After about 2-1/2 hours of processing on October 8, the level in the DF tank was below a point that could be seen on the container (i.e., < 6 L), and the processing was stopped. About 20 L of waste which needed processing was present in numerous bottles in the glovebox. Most of this (about 17 L) was 0.25M Na_2CO_3 left from stage flushing and carbonate wash changes. These solutions were to be added to the DF carboy for processing. Before these bottles were emptied into

the DF carboy, enough solution (3 L of 10M HNO_3) to acidify the carbonate was poured into the carboy; the waste bottles were then emptied into the DF carboy. A couple of small bottles that had a high amount of solids present or that had been determined to contain solutions not compatible with the process were set aside. The DF tank level after these additions was around the 27-L mark. The mixer for the DF tank was then left on overnight.

On October 9, 1992, a new DF sample was drawn before processing began. After about 1 1/2 hours of processing, it was noticed that the DX flow into stage 1 had stopped. This problem was apparently precipitated by aqueous-phase carryover in the organic effluent from stage 20. This carbonate had been pumped up into the DX feed tank. Because the HF solution was on full recycle, the level in that HF tank had dropped below the pickup tube to the HF pump, and HF flow to stage 20 had also stopped.

The additional aqueous phase pumped into the DX tank (estimated at 400 mL) raised the aqueous-phase level in that tank up past the pickup tube for the DX pump. The reason why the DX flow stopped instead of changing to aqueous-phase flow is not entirely clear, but may have to do with the leaks in the DX pump line described previously, coupled with the different wetting properties of the two phases on the Teflon tubing.

The high volume of aqueous-phase carryover in the organic effluent from stage 20 was possibly caused by the sampling methods for the HW stream. The aqueous-exit line for stage 20 came out of the contactor, made a 90° turn to the right, went straight for about 4 in. (10 cm), and made a 90° turn down into the HF container. Sampling of HW consisted of pivoting this tube so that the 4 in. (10 cm) section pointed upward, placing the sample bottle over the end of the tube, pivoting the tube downward to collect the sample, raising the tube again to remove the sample bottle, and pivoting the tube back down into the HF container. If this tube were left in the upright position, no exit would be available for the aqueous phase, and the stage would flood with the more-dense phase, leading to aqueous-phase carryover into the organic effluent. To account for the approximately 400 mL of aqueous phase that was pumped into the DX tank, however, the tube would have had to be left in the upright position for more than 2 min (the HF flow rate was 200 mL/min). Whether or not this was the cause of the other-phase carryover problem has not been determined, but we found that the HW sample drawn prior to the carryover problem was taken by a participant not familiar with the normal sampling technique. No recurrence of this problem was observed throughout the rest of the processing run.

As soon as these problems were noted, a quick shutdown was accomplished by turning off all feed pumps except, possibly, the GF pump. Approximately 200 mL of the aqueous phase in the DX tank was pumped out, bringing the aqueous-phase level there to an acceptable height below the pickup tube. The pH of this phase was determined to be about 3, meaning that the aqueous phase left in the tank could still function as an acid rinse. The 200 mL of aqueous solution removed from the DX tank was added to the DF feed tank.

Fresh 0.25M Na_2CO_3 for use as HF feed was then pumped into the glovebox using a spare line. First about 600 mL was pumped through the line to flush it. This was acidified with 5M HNO_3 and added to the DF feed tank. Approximately 800 mL was then pumped into the HF feed tank. With these adjustments made, all pumps except the DF pump were started again. Scintillation analysis of a DW sample taken 10 min later showed that the system was working properly, so the DF feed was started.

About 3-1/2 hours later, the DF tank was empty, and the system shutdown procedure was completed. At this time, it was noted that the DF filter had not been installed. Also noted was the fact that the propeller on the DF mixer had broken. This propeller had been intact on October 8 when the new DF was being added to the tank.

6. Sample Analysis

The samples taken during processing were measured for alpha activity by scintillation counting. Since the gamma counter was inoperable, gamma counting could not be done immediately. The DW samples were taken in the hood and counted for one minute immediately to ensure that the DW raffinate was within acceptable activity limits. All other samples had to be bagged out of the glovebox, which was usually done at the end of the day. At the end of the day, each scintillation cocktail prepared that day was counted for 20 min. All samples were taken in 7-mL plastic scintillation vials.

During processing, samples of the DW raffinate were taken about every 30 min. The DW raffinate flowed out of stage 1 into a pump, which deposited this solution in a 4-L container. A transfer pump then pumped this raffinate through a 1- μ m filter over to the hood, where the raffinate 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 8-9 L, the transfer pump was shut off to allow replacement of the carboy. Since the collection point of DW samples was downstream of the 4-L container, they are not instantaneous samples, but an average sample over a short period of time.

The results of the scintillation counting of DW samples (Fig. 16) show that the total alpha activity of the raffinate was generally between 2 and 6 cpm/ μ L, with considerable fluctuations. This range is considerably above the goal of 0.22 cpm/ μ L (corresponding to 0.1 nCi/mL), but it is acceptable to WMO for disposal.

Most of the minor fluctuations in the activity in the DW raffinate can be explained by the shutdown and startup procedures. This will be discussed later. The DW sample taken at 690 min of running time (i.e., the highest peak in Fig. 16, at 13 cpm/ μ L) actually contained total alpha activity of 27 cpm/ μ L and has been scaled down so as not to dwarf the rest of the bars. This peak occurred at the time when there was no DX feed flow. Since there was no organic flow into stage 1 at this time, the plutonium and americium entering with the DF feed would not have been extracted from the aqueous phase but would exit in the DW raffinate. The high activity level in the DW sample taken at 628 min is not so easy to explain, but as will be seen later, it corresponds in time to a drastic jump in activity in the organic effluent (HP). It is also possible that the counting results for the sample taken after 655 min of running time (the sample between the two high peaks) represent a bad data point (due to time constraints, only one scintillation cocktail per sample was counted, instead of the normal practice of counting two). Given the assumption that this sample may have contained more activity than counting showed, the DW activity level may have been rising over all three samples (taken between 628 and 690 min); the DX flow problem, noted earlier, occurred just prior to 690 min.

The americium product (EW) was pumped into a collection bottle from a side tube welded to the aqueous interstage line between stages 10 and 11. Samples were taken at the line entering the bottle. Because of the low flow rate of this stream (3 mL/min), each sample took about 1 min to collect. Counting results for the EW samples (Fig. 17) show that the activity in these samples rose considerably over the first portion of processing (up until about 400 min). Some rise in

Fig. 16. Scintillation Counting Results vs. Time for DW Samples during Acidified Carbonate Waste Processing. Note that the x-axis is not to scale because of the bar-chart format.

americium content is expected, since the americium was being pinched between the extraction and americium strip sections of the flowsheet. It is possible that the rise in activity between 200 and 300 min occurs because of this pinching effect, and that the drastic rise in activity between 300 and 400 min was due to the introduction of concentrated americium product from batch 1 into the DF carboy.

The pinching effect should lead eventually to a plateau (steady state) for the americium concentration in EW. The activity level between 400 and 550 min could be that expected plateau. The sample taken at about 600 min, which exhibits a sharp drop in activity, was taken after the system had been running awhile with the second batch of DF feed, and the continued drop between 550 and 750 min is probably due to equilibrium being attained with the lower activity in this feed. The rise in activity for the final sample may be due to normal fluctuations in the data.

The plutonium product (FW) was collected by placing 1-L bottles under the aqueous exit from stage 14. Samples were taken by placing the sample bottle under the exit tube. The general downward trend in scintillation counting results for FW samples (Fig. 18) is probably due to the plutonium which had precipitated in the contactors during previous processing runs slowly being flushed out of the contactors. A similar trend had been seen during pre-processing stage flushing. Additional evidence to support this conclusion is that the plutonium concentration in this stream is greater than can be accounted for given the feed concentration. The first two slight jumps in the activity, located at about 300 and 425 min, are not easily explained but may also be the result of previously trapped plutonium being flushed out in a more erratic pattern. The jump at about 600 min, followed by a more gradual decline in activity, is more likely related to the new DF feed solution incorporated after 600 min of running time. It is possible that, although the total alpha activity in this new DF feed solution was lower than previously seen, this drop was due to a drastic

Fig. 17. Scintillation Counting Results vs. Time for EW Samples during Acidified Carbonate Waste Processing

Fig. 18. Scintillation Counting Results vs. Time for FW Samples during Acidified Carbonate Waste Processing

decrease in the americium concentration (as evidenced in the EW samples) and a slight increase in plutonium concentration.

The total solution recycle for the carbonate washes was accomplished by having the feed bottles sit close to the aqueous exit for the appropriate stage, with a short tube going from the exit into the feed container. Samples for these washes were taken by placing the sample bottle under this exit tube. Thus, the samples were of the aqueous effluents for these stages (GW and HW), not the feeds (GF and HF).

The alpha activity in the GW samples, shown in Fig. 19, generally rose over the course of time, except for a drastic drop between the first and second samples, and a slight drop in a couple of other places. The general upward trend in activity is expected because the GF feed was under full solution recycle. The drop in activity after the first sample is a result of GF being replaced with fresh solution shortly after sample 1 was taken. The slight drop around 425 min may be simply due to sampling and/or counting errors, but the drop at about 750 min seems to be real.

Fig. 19. Scintillation Counting Results vs. Time for GW Samples during Acidified Carbonate Waste Processing

Since the HF feed was also under full recycle, the HW samples should also show an upward trend. The scintillation counting results for these samples (Fig. 20) exhibit such an upward trend, with three exceptions. These three drops in activity are the result of the HF feed being either replaced or diluted with fresh sodium carbonate. The rate of increasing activity around 200 and 550 min is most likely due to the use of solution recycle. The more drastic rises seen at 300 and 600 min correspond to spikes in HP activity, and most likely have another cause. This will be discussed later in this report.

As stated previously, the organic effluent from the stage 20 (HP) pump was changed after the first day of processing. Because of difficulty in collecting an HP sample, no HP samples were taken that first day (i.e., before the HP pump changes). All HP samples were taken by interposing the sample bottle between the tube exiting stage 20 and the collection bottle from which the HP pump sent the solvent back to the DX tank. Although full solvent recycle was being used, HP activity does not represent DX activity. The solvent pumped up to the DX tank first bubbled through an aqueous solution (as noted earlier), then entered the solvent reservoir, containing about 2 L of TRUEX solvent. With a solvent flow rate of about 50 mL/min, this reservoir represents a holdup of about 40 min.

Scintillation counting results of HP samples (Fig. 21) show that most samples had an activity level between 6 and 10 cpm/μL. Major deviations from that range occurred at around 300 and 600 min. The reason for the jumps in activity in these samples is unclear, although they accompany a rapid rise in activity in the HF feed, as will be seen later.

Fig. 20.

Scintillation Counting Results vs. Time
for HW Samples during Acidified
Carbonate Waste Processing

Fig. 21.

Scintillation Counting Results vs. Time
for HP Samples during Acidified
Carbonate Waste Processing

The DF feed was pumped from the 50-L carboy over to the aqueous-side interstage line between stages 6 and 7. The DF samples were taken by opening the valve on the outlet side of the DF pump for a short time. The alpha activity level in the DF feed, given in Table 19, remained fairly constant, as expected, up to 576 min. However, when the waste bottles were added to the DF tank (at 602 min), the alpha activity in this feed had decreased to only about one-half the activity of the initial DF feed.

The aqueous phase in the DX tank (IF) was sampled periodically using a long 1/4-inch tube on a syringe. Scintillation counting results for IF samples are given in Table 19. Sample 1 was taken when this aqueous phase was a third carbonate wash, and samples 2 and 3 were samples of the acid rinse solution. A slight rise in IF activity over time is expected due to the acid rinse picking up a small amount of activity from the HP solvent being "bubbled through" it. The actual increase in IF activity seen between samples 2 and 3 may be partially due to the fact that the spike in HP activity around 600 min occurred between these two IF samples. An increase in HP activity, as seen at 631 min, would lead to a similar rise in IF activity at the same time, assuming a constant D value.

Table 19. Sample Time and Liquid Scintillation Counting Results of DF and IF Samples

Sample Number	Sample Time, min	Scintillation Counts, cpm/ μ L	Notes
DF Samples			
1	331	1020.0	
2	576	969.3	
3	602	550.0	
IF Samples			
1	253	4.2	sodium carbonate
2	336	2.4	nitric acid
3	680	3.9	nitric acid

Figure 22 shows a graph of the magnitude of activity in DW and HP samples over time, along with important events noted which perturbed the system.

Fig. 22. Magnitude Comparison of Scintillation Counting Results for DW and HP Samples during Acidified Carbonate Waste Processing. (The y-axis uses no units to better illustrate relative changes in activity between streams.)

Figure 22 shows that much of the erratic nature of the DW activity corresponds to shutdown and restart of the system. Upon shutdown the DF feed pump is the first pump to be turned off, and it is the last pump to be turned on upon startup. Therefore, there was usually a minimum of 10 min surrounding each shutdown/startup sequence during which the stages were being flushed. This may account for the lower-than-normal activity in many of the samples taken immediately following a shutdown. In many cases a higher-than-normal rise in DW activity is evidenced in the first or second sample following a shutdown. This may be a result of the system's inability to reach steady state quickly after the start of the DF feed.

The curve for the HP samples shows that the sudden jump in HP activity at 628 min corresponds to a similar jump in the DW activity. Because samples were intermittent, the exact timing of a peak cannot be determined, so the fact that these two peaks are close should not be confused with actual simultaneity. It may be that the high activity in HP around 628 min led to a large increase in activity in the DX reservoir. Then, as this higher-activity DX was pumped into the extraction section, it led to the rise in DW activity at 628 min. As stated earlier, the spike in DW activity at 690 min is best explained by the loss of DX flow and should not, then, be coupled with any rises in DX activity.

The curves of activity level versus time for the DF, EW, FW, and HP samples are superimposed in Fig. 23. The two data points giving the drop in DF activity around 600 min are actually points of discontinuity, since the DF feed was changed during this time span. This drop corresponds to a sudden drop in EW activity and a rise in FW activity, as noted earlier.

The sudden rise in FW activity at about 300 min corresponds to a sudden rise in HP activity. If this FW rise was due to a large amount of plutonium being flushed out of the plutonium strip section, as hypothesized earlier, it is possible that this amount was more than could be carried by the plutonium strip, and thus some was carried out with the solvent and contaminated the carbonate washes on the way. A similar coincidence of rise in activity in HP and FW occurs around 600 min, after the new DF feed was started.

The changes of activity over time in the HP, GW, HW, and IF samples are compared in Fig. 24. Because of the use of full solution recycle in the carbonate washes and a plutonium D value considerably less than 1 for the contacts of sodium carbonate with the TRUEX solvent, one would expect the activity level for the GW and HW streams to normally rise over time, unless fresh solution were added to the carbonate feeds. Therefore, unexpected drops in the activity of GW and HW samples deserve attention.

Such a drop occurs in GW activity after 700 min. This corresponds to a drop in HW and HP activities. Activity in the HW stream dropped at this time because of the addition of fresh sodium carbonate to the HF container. The coincidental drops in HP and GW activities are most likely due to cleaner-than-normal solvent entering stage 19. With the activity in the GF feed very high at this time, the D value for the contact in stage 19 may have been very close to 1. Thus, the TRUEX solvent may have been cleaning up the carbonate wash during this period.

The sudden rise in HP activity at around 300 and 600 min corresponds to a rise in HW activity. The similar slopes in these HP and HW curves at those points result from a constant D value for these two phases. The source of the activity during these two periods must, of course, be the solvent flowing into stage 20. Since the solvent entering stage 20 had just been contacted with sodium carbonate in stage 19, one might expect to find a similar sudden rise in GW stream activity accompanying the sudden rise in HP activity, but this is not evidenced.

Fig. 23. Comparison of Scintillation Counting Results for DF, EW, FW, and HP Samples during Acidified Carbonate Waste Processing

During other periods of time, when HP activity is more constant, the activity accumulation in the HW stream appears to be much slower. During these times of slow activity rise in the HW stream, similar slopes are seen in the HW and GW curves, and the reason for this slight rise in activity in the GW and HW streams is that these two streams were on full solution recycle.

The waste processing resulted in 15 carboys of DW raffinate. They were initially filled to about 80% of capacity. This left enough room to add NaOH, which was needed to neutralize the waste solution. Once this level was reached, the DW transfer pump was shut off while an empty carboy was moved into place, after which the transfer pump was turned back on again. The full carboy was stirred for about 5 min, then sampled. After scintillation counting showed that the activity level of the carboy's contents was in an acceptable range, 200 μ L of phenolphthalein was added while stirring continued. Then 10M NaOH was added to neutralize the carboy contents. All carboys were 10-L capacity, except carboys 14 and 15, which were 20-L capacity. Carboy 15 had only about 5 L of solution when processing was finished.

The scintillation counting results for samples taken from these carboys are given in Table 20. The carboys were numbered sequentially as they were taken from the hood but are listed in Table 20 according to when they were filled. Carboy number 4 was filled during the processing attempt in January and had been left in the hood awaiting word from WMO regarding its

Fig. 24. Comparison of Scintillation Counting Results for GW, HW, IF, and HP Samples during Acidified Carbonate Waste Processing

Table 20. Sample Time and Liquid Scintillation Counting Results of DW Raffinate Carboy Samples

Carboy Number	Approximate Sample Time, min	Scintillation Counts, cpm/ μ L	TRU Concentration, nCi/mL
4	N/A	4.05	1.84
1	150	1.99	0.90
3	240	1.20	0.55
2	240	4.15	1.89
5	253	2.54	1.15
6	280	3.01	1.37
7	350	5.51	2.50
8	450	5.42	2.46
9	460	4.84	2.20
10	500	5.13	2.33
11	520	5.93	2.70
12	580	5.40	2.45
13	630	6.93	3.15
14	740	6.40	2.91
15	850	5.95	2.70

acceptability for disposal. Carboy number 3 was originally overfilled, and later part of its contents was pumped into carboy 2 before either of those carboys were sampled. As can be seen in Table 20, most of the carboys contain an alpha activity level between 2 and 6 cpm/ μ L. The sample times listed in Table 20 are approximations of when the samples were taken, not when the carboy was filled.

B. Processing of Batch 2

A second batch of waste solutions containing uranium and plutonium was transferred from WMO contained in five 5-gal (18 L) waste pails. The solution in these waste pails contains 13.31 g of plutonium and 16.27 g of uranium. The composition of these waste pails, as reported by NBL, is given in Table 21. This batch has been designated CMT-NBL-2. Results in treatment of this waste are given below.

Table 21. Composition of Waste Pails Constituting Batch 2

Waste Pail Number	Disposal Requisition Number ^a	Number of Bottles	Solution Volume, L	Total Pu Content, g	U-235 Content, g	Total U Content, g
288636	RL-1354	13	6.8	2.589	1.25E-4	0.059
289722	RL-1357	21	5.5	8.555	0.012	1.658
289777	RL-1359	10	8.0	2.126	0.017	3.047
288570	RL-1309	12	18.8	0.040	9.990	10.00
289771	RL-1335	4	5.3	0.004	0.011	1.508
Totals		60	44.4	13.31	10.03	16.27

^aLiquid Radioactive Waste Disposal Requisition Number.

1. Flowsheet Sensitivity Analysis

Using the waste composition data supplied by NBL and GTM (version 2.4.2a), we created a flowsheet to process batch NBL-CMT-2. Although the waste disposal requisition from NBL did not specify a ^{241}Am concentration, that TRU element will be present because of the ^{241}Pu decay. Therefore, an approximation of $2.5 \times 10^{-8}\text{M}$ americium was used in the modeling. Our previous studies had shown that the flowsheet design was insensitive to variations in the americium concentration.

Based on previous work, the flowsheet shown in Fig. 25 was used as a base case. Because of the use of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ as the plutonium stripping agent, the plutonium strip section cannot be modeled by the GTM; thus, only the extraction, scrub, and americium strip sections were modeled. The flowsheet shown in Fig. 25 leaves seven contactor stages available for plutonium strip and carbonate wash sections. As was done in the processing of the acidified carbonate waste, five of these would be used as plutonium strip stages, with the remaining two becoming single-stage carbonate wash sections.

Various perturbations to this base-case flowsheet were run on the GTM, and the results are given in Table 22. As seen in this table, decreasing the americium product (EW) flow rate lowers the americium recovery, while increasing that flow rate raises the americium recovery, but neither has much of an effect on Pu or U recovery. Although increasing americium recovery is a major priority, inherent in increasing the EW flow rate is the disadvantage of increasing the volume of

Fig. 25. Base Case for GTM Modeling of Batch 2 Flowsheet

solution needing further processing; thus, increasing the strip flow rate is not a very desirable way to increase americium recovery.

Simulation 5 (Table 22) involved moving the scrub feed to stage 7, thus making the scrub section one stage and the americium strip section six stages. We also eliminated the acid from the scrub. By dedicating more stages to americium stripping and to scrubbing the acid from the solvent, americium recovery was considerably better. Therefore, these changes were incorporated into the following simulations.

For simulations 1-5, the TRU activity level of the DW raffinate is uncomfortably close to the ceiling of 0.1 nCi/mL. Increasing the Al(NO₃)₃ in the scrub, as done in simulations 6 and 7, lowers this activity level to a more acceptable level. Moving the location of the EW stream within the americium strip section hurts americium recovery, as seen in simulations 8-10.

Of simulations 1-10, simulation 7 offered the best promise of high recovery of plutonium and americium along with low raffinate activity. Further modeling was necessary to determine the sensitivity of this simulation to minor fluctuations, and to examine further design changes such as the addition of another americium strip stage. Simulation number 11 added another stage to the americium strip section, making that a seven-stage section and leaving six stages available for plutonium strip and solvent cleanup sections. This greatly enhanced the americium recovery and became the new base case for design perturbations. This base case is shown in Fig. 26.

Simulation 12 differed from 11 only in that neptunium was added to the DF feed. Based on preliminary gamma counts of the DF feed, we estimated that the neptunium concentration in the DF feed was about $1.2 \times 10^{-5} \text{ M}$; 90% of the neptunium was modeled as Np⁴⁺, with the remaining 10% modeled as NpO₂⁺. The NpO₂⁺ is the only slightly/nonextractable species. The only

Table 22. Results from GTM Sensitivity Analysis for Batch 2 Flowsheet

Simulation Number	Simulation Description	Am ^a Recovery, %	Pu ^b Recovery, %	U ^b Recovery, %	DW Raffinate TRU Activity, nCi/mL
1	Base Case	87.42	99.87	99.67	1.33E-03
2	EW Flow Decreased to 1.5 mL/min	80.10	99.91	99.82	1.53E-03
3	EW Flow Increased to 6 mL/min	89.95	99.82	99.46	1.01E-03
4	EW Flow Increased to 9 mL/min	89.60	99.77	99.39	7.72E-04
5	DS Moved to Stage 7 HNO ₃ in Scrub Eliminated	95.99	99.69	99.20	1.50E-03
6	DS Moved to Stage 7 HNO ₃ in Scrub Eliminated Al in Scrub Increased to 2M	91.82	99.82	99.53	2.60E-06
7	DS Moved to Stage 7 HNO ₃ in Scrub Eliminated Al in Scrub Increased to 1.75M	93.19	99.82	99.46	7.15E-06
8	DS Moved to Stage 7 HNO ₃ in Scrub Eliminated Al in Scrub Increased to 2M EW Moved to Stage 10	87.53	99.96	99.89	2.61E-06
9	DS Moved to Stage 7 HNO ₃ in Scrub Eliminated Al in Scrub Increased to 2M EW Moved to Stage 12	79.12	99.65	99.06	5.46E-06
10	DS Moved to Stage 7 HNO ₃ in Scrub Eliminated Al in Scrub Increased to 1.75M EW Moved to Stage 12	80.00	99.65	99.02	1.70E-05
11: New Base Case	Am Strip Section Increased to 7 Stages	99.82	99.10	99.46	7.15E-06
12	Np modeled in DF Feed	99.82	99.10	99.46	7.15E-06
13	[HNO ₃] in DF Decreased to 1M	99.78	99.26	99.38	2.26E-04
14	[HNO ₃] in DF Decreased to 1.5M	99.78	99.18	99.42	3.56E-05
15	[HNO ₃] in DF Increased to 2.5M	99.82	99.03	99.49	3.19E-06
16	[HNO ₃] in DF Increased to 3M Al in Scrub Increased to 2M	99.82	98.97	99.53	1.59E-06
17	DS Flow Decreased to 45 mL/min EF Flow Increased to 55 mL/min	99.69	99.58	99.20	5.55E-06
18	DX Flow Decreased to 40 mL/min	99.54	99.94	98.78	3.01E-05
19	DX Flow Increased to 60 mL/min	99.93	87.48	99.88	2.18E-06

^aAm-product stream.^bPu/U-product stream.

Fig. 26. New Base Case for GTM Modeling of Batch 2 Flowsheet

expected change between simulations 11 and 12 was a possible jump in the DW raffinate activity, which was not seen, presumably because of the small amount and low specific activity of the neptunium. The neptunium concentration of $1.2 \times 10^{-5} \text{M}$ was included in the DF feed for simulations 13-19.

Because the amount of HNO_3 in the DF feed is an important but unknown quantity, simulations 13-16 varied this parameter to determine the sensitivity of the flowsheet to this acid concentration. As can be seen in Table 22, decreasing the nitric acid levels in the feed had little effect on the americium recovery but increased the DW raffinate activity. The slight improvement in americium recovery results from the lower concentration of nitric acid extracted into the organic phase of the americium strip section--this improves the strip efficiency. The lowered acid concentration in the DF feed, however, lowers plutonium D values and increases the alpha activity. Higher acid concentrations (simulations 15 and 16) have the opposite effect. Even so, the flowsheet was found to be relatively stable over this range of nitric acid concentrations.

Simulation 17 attempted to enhance americium recovery by increasing the americium strip flow rate, while maintaining the aluminum concentration and the organic-to-aqueous (O/A) flow ratio in the extraction section. This change aided plutonium recovery slightly but at the expense of americium recovery, so this was not incorporated.

Finally, the DX (solvent) flow rate, which had previously been subject to variation over the time of a processing run, was varied in simulations 18 and 19. A drop of 10% in this flow improved plutonium and slightly decreased americium recoveries, and slightly increased the DW raffinate activity. A 10% rise in this flow rate, on the other hand, hurt plutonium recovery significantly. Therefore, care should be taken during the run to ensure that the DX flow rate does not exceed 50 mL/min. One change already undertaken to aid in this endeavor is a change of the DX pump to one more suitable for this low flow rate.

Based on the results given in Table 22, simulation 11 appears to be the optimum design.

2. Preliminary Batch Tests

Five batch extraction tests were completed to ensure that the feed for batch 2 could be processed. These tests showed that both nitric acid and aluminum nitrate must be added to the feed in order to increase plutonium D values to an acceptable level. (By "acceptable level," we mean that a nonTRU raffinate can be generated with six extraction stages.) The $\text{Al}(\text{NO}_3)_3$ complexes the H_3PO_4 present in the feed solution and adds nitrate salt to the system, both of which improve plutonium and americium D values.

Results from these preliminary extraction tests are listed in Table 23. For these tests the flowsheet that we expect to use to process batch 2 was simulated by adding the appropriate volume of scrub solution [DS, 1M $\text{Al}(\text{NO}_3)_3$] and americium strip solution [EF, 0.04M HNO_3]. The data show that an aluminum nitrate concentration of 0.57M is needed to increase the alpha-activity D value to 100. For test 5, the americium D value was measured (by gamma counting) to be 40; this value is adequate for our flowsheet.

Table 23. Summary of First Set of Extraction Experiments

	Experiment Number				
	1	2	3	4	5
Volume of DF Feed, mL	1	1	1	0.5	0.8
Volume of 6M HNO_3 Addition, mL	0	0	0.5	0.25	0.4
Volume of DS Feed [1M $\text{Al}(\text{NO}_3)_3$], mL	0.5	1	1	1	1.6
Volume of EF Feed [0.04M HNO_3], mL	0.5	0	0	0	0
Volume of TRUEX-nDD, μL	0.5	0.5	0.625	0.44	0.7
O/A Ratio for Contact	0.25	0.25	0.25	0.25	0.25
$\text{Al}(\text{NO}_3)_3$ Concentration, M	0.25	0.50	0.40	0.57	0.57
Estimated HNO_3 Concentration, M	1.00	1.00	2.00	1.43	1.43
Volume Percent of DF in DW Raffinate	50	50	40	29	29
D Value for α Activity	5	16	52	98	118
D Value for Americium (59.5 keV)	—	—	—	—	40

The experiments reported in Table 23 were not optimized; we only wanted to determine if appropriate D values could be generated. Therefore, three additional sets of experiments were completed to optimize the nitric acid and aluminum nitrate additions. This is important because the more nitric acid and aluminum nitrate that are added to the feed, the more NaOH that is needed to neutralize these solutions after processing. The results of these additional experiments are reported in Tables 24 to 26.

For the four extractions reported in Table 24, the nitric acid concentration was varied while the aluminum nitrate concentration was held constant at 0.5M. Liquid scintillation results (total alpha activity--plutonium plus americium) showed that adding 10M HNO_3 to the feed produced a D value of 48, which is not high enough for our process. The amount of nitric acid that can be

added is limited by the volume of waste solution to be processed and the limiting size of the DF feed tank (about 50 L). Six liters is about the maximum amount of nitric acid that can be added to the present feed tank. Because of the relatively low concentration of americium in the feed, americium D values of 40 are adequate for our flowsheet. Waste loading (%DF in the raffinate) is also acceptable at 43%.

Table 24. Summary of Second Set of Extraction Experiments

	Experiment Number			
	6	7	8	9
Volume of DF Feed, mL	0.43	0.43	0.43	0.43
Volume of HNO ₃ Addition, mL	0.07	0.07	0.07	0.07
Concentration of HNO ₃ Addition, <u>M</u>	4	6	8	10
Volume of DS Feed [<u>2M</u> Al(NO ₃) ₃], mL	0.25	0.25	0.25	0.25
Volume of EF Feed [<u>0.04M</u> HNO ₃], mL	0.25	0.25	0.25	0.25
Volume of TRUEX-nDD, μ L	0.25	0.25	0.25	0.25
O/A Ratio for Extraction Contact	0.25	0.25	0.25	0.25
Al(NO ₃) ₃ Concentration, <u>M</u>	0.50	0.50	0.50	0.50
Estimated HNO ₃ Concentration, <u>M</u>	1.14	1.27	1.41	1.54
Volume Percent of DF in DW Raffinate	43	43	43	43
D Value for α Activity	42.5	39.1/40.4	44.2	48
D Value for Americium (59.5 keV)	—	33.5/52.1	31.3	30.4

A third set of experiments was completed (Table 25) where the aluminum nitrate concentration was increased from 0.50 to 0.57M, and the nitric acid was again varied. At the higher nitric acid concentrations, the alpha activity D value improved significantly. This finding indicates that high nitric acid and aluminum nitrate concentrations are both important.

Table 25. Summary of Third Set of Extraction Experiments

	Experiment Number				
	10	11	12	13	14
Volume of DF Feed, mL	0.432	0.432	0.432	0.432	0.432
Volume of HNO ₃ Addition, mL	0.068	0.068	0.068	0.068	0.068
Concentration of HNO ₃ Addition, <u>M</u>	10	4	6	8	10
Volume of DS Feed [<u>2M</u> Al(NO ₃) ₃], mL	0.30	0.30	0.30	0.30	0.30
Volume of EF Feed [<u>0.04M</u> HNO ₃], mL	0.25	0.265	0.265	0.265	0.265
Volume of TRUEX-nDD, μ L	0.265	0.265	0.265	0.265	0.265
O/A Ratio for Extraction Contact	0.25	0.25	0.25	0.25	0.25
Al(NO ₃) ₃ Concentration, <u>M</u>	0.57	0.56	0.56	0.56	0.56
Estimated HNO ₃ Concentration, <u>M</u>	1.47	1.07	1.19	1.32	1.45
Volume Percent of DF in DW Raffinate	41	41	41	41	41
D Value for α Activity	80	56.1	57.1	75.2	72.7
D Value for Americium (59.5 keV)	41.4	48.6	41.2	43.2	43.4

Results from the last set of extraction experiments are reported in Table 26. In this series of three tests, the nitric acid concentration was held fairly constant at about 1.26M while the aluminum nitrate concentration was increased from 0.56M (in Expt. 9) to 0.66M (in Expt. 12). The measured alpha-activity D value ranged from 73 in Expt. 14 to 100 in Expt. 17. These values are in the range that should be adequate for processing batch 2. Therefore, the compositions/flow ratios used in Expt. 17 were selected as a basis for the flowsheet for processing batch 2. Six liters of 8M HNO₃ will be added to the feed tank to increase the nitric acid concentration. The aluminum nitrate concentration in the scrub will be 2M, and the necessary amount of aluminum nitrate will be added by setting the flow rate of this stream to 70 mL/min. The americium strip flow rate will remain at the planned 50 mL/min, as will the solvent feed rate (DX). The resulting flowsheet, including the plutonium strip and carbonate wash sections not modeled, is shown in Fig. 27.

Table 26. Summary of Fourth Set of Extraction Experiments

	Experiment Number			
	14 ^a	15	16	17
Volume of DF Feed, mL	0.432	0.432	0.432	0.432
Volume of HNO ₃ Addition, mL	0.068	0.068	0.068	0.068
Concentration of HNO ₃ Addition, M	10	8	8	8
Volume of DS Feed [2M Al(NO ₃) ₃], mL	0.30	0.325	0.35	0.375
Volume of EF Feed [0.04M HNO ₃], mL	0.265	0.265	0.265	0.265
Volume of TRUEX-nDD, μ L	0.265	0.265	0.265	0.265
O/A Ratio for Extraction Contact	0.25	0.24	0.24	0.23
Al(NO ₃) ₃ Concentration, M	0.56	0.60	0.63	0.66
Estimated HNO ₃ Concentration, M	1.45	1.29	1.26	1.24
Volume Percent of DF in DW Raffinate	41	40	39	38
D Value for α Activity	72.7	79.2	84.7	99.6
D Value for Americium (59.5 keV)	43.4	43	48.9	52.1

^aFor comparison purposes, this test was copied from Table 25.

3. Flowsheet Batch Tests

To help determine if the flowsheet as shown in Fig. 27 would give acceptable results, a series of batch contacts was completed to simulate that flowsheet. A summary of the results of scintillation and gamma analysis of the samples from these batch contacts, along with the contact O/A volume ratios, is given in Table 27. Note that the countercurrent flow in Fig. 27 is not attainable using this type of batch contact. Therefore, we cannot undertake an exact correlation between the batch-contact results and precise flowsheet predictions.

As can be seen from Table 27, the value for D_{Pu} is high for the first three extraction contacts, then drops off rapidly. By the fifth extraction contact, almost no activity is being extracted, even though the aqueous activity (0.7 dpm/ μ L) is still above the process goal of 0.22 dpm/ μ L (0.1 nCi/mL). This residual activity is not due to americium; the americium appears to extract as expected. The exact nature of the aqueous activity after six contacts, whether due to Pu, Np, or U, is not readily discernible.

Since organic samples were not taken after the first three americium strip contacts because of the need to conserve the volume of organic phase, D values for these contacts are not available. The aqueous gamma activity for the contacts, however, shows that the americium profile in the aqueous phase peaks after the third contact, and drops off drastically thereafter. This is about as expected, given the batch nature of the contacts. The americium profile in the flowsheet is expected to peak in the fourth americium strip stage.

Further analysis shows that almost 99.9% of the americium was stripped from the organic phase after six americium strip contacts. Whether this amount of americium recovery can be achieved in the processing flowsheet has yet to be demonstrated. About 22% of the plutonium was also stripped into the aqueous phase during these contacts, with most of this plutonium being stripped during the fifth and sixth contacts. Again, given that these were batch contacts, this would not be expected in the countercurrent contacts experienced in the actual flowsheet.

In the plutonium strip contacts, the D_{Pu} value is very good, and most of the activity has been stripped from the organic phase after four contacts. However, the material balance for these contacts is not very good, as seen from the organic and aqueous activities after the third and fourth contacts. This is probably due to difficulties experienced in separating the two phases after each contact. At this point, the volume of organic phase was very small, and efforts to recover most of it from the contact probably resulted in carrying over a small volume of the aqueous phase into the next contact.

Table 27. Results of Distribution Ratio Measurements for NBL Waste Pre-Run Assessment

Contact Type	O/A Volume Ratio	D _{Pu} Value	D _{Am} Value	Aqueous Alpha Activity, dpm/μL	Organic Alpha Activity, dpm/μL	Aqueous Gamma Activity @ 59.5 keV, cps/μL	Organic Gamma Activity @ 59.5 keV, cps/μL
Extraction							
1	0.23	157	58.0	769	9.87E+04	4.98E-01	2.89E+01
2	0.23	93.9	59.6	36.1	2.96E+03	2.76E-02	1.65E+00
3	0.23	180	23.5	2.58	1.32E+02	4.71E-03	1.11E-01
4	0.23	5.80	a	0.830	6.90E+00	a	4.61E-03
5	0.23	0.459	a	0.686	4.41E-01	a	a
6	0.23	0.009	a	0.668	6.10E-03	a	a
Scrub							
1	0.417	35500	1370	12.42	1.03E+05	0.02	30.0
Am Strip							
1	1.0			1.12E+03		2.80E+00	
2	1.0			4.70E+03		1.06E+01	
3	1.0			6.16E+03		1.23E+01	
4	1.0	25.0	0.572	3.64E+03	8.33E+04	6.97E-01	4.19E-01
5	0.94			5.13E+03		5.10E-01	
6	1.13	13.6	0.439	5.07E+03	6.84E+04	7.35E-02	6.06E-02
Pu Strip							
1	1.0	1.75E-04	a	4.72E+04	8.28E+00	4.69E-02	a
2	4.0	2.83E-03	a	1.02E+04	2.96E+01	1.00E-02	a
3	4.0	1.24E-03	a	4.23E+03	5.23E+00	1.02E-02	a
4	4.0	2.65E-03	a	1.99E+03	5.25E+00	7.40E-03	a

^aBelow detectable limits.

Since no major problems in the flowsheet were indicated by these batch contacts, we decided to implement the flowsheet shown in Fig. 27 and proceed with processing of batch 2.

4. Solvent Cleanup

Two separate batches of TRUEX-nDD solvent had been used to process waste in the glovebox. About 2.4 L of solvent was used to process batch 1 and the DW raffinate from batch 1. Our inability to strip plutonium and americium from this solvent (hereafter referred to as the "old solvent") led to the failure of our first attempt to process the acidified carbonate waste. Because of the problem with stripping the old solvent, about 1.5 L of new solvent was then passed into the glovebox and used to process the acidified carbonate waste. Based on past experience, we decided that both the old and new solvents contained a significant concentration of degradation products. Prior to their use in future processing runs, these degradation products must be removed from the TRUEX solvent. Furthermore, a solvent-cleanup method that would remove these degradation products during waste-processing runs is desirable. Three possible methods for stripping these

degradation products are discussed below. For all methods, the effectiveness in stripping the degradation products was evaluated by scintillation counting of the solvent. Because the presence of degradation products makes the solvent hard to strip of activity, the activity level before and after processing gives a good first indication whether the stripping has been effective. Further tests will be necessary, however, to ensure that the degradation products have indeed been eliminated by whatever method appears to be effective.

a. Batch Contacts with HEDPA

Experience has shown that 1-hydroxyethane-1, 1-diphosphonic acid (HEDPA) is an effective metal-ion stripping agent. Therefore, aqueous solutions containing various concentrations of HEDPA, some also containing NaOH, were contacted with the two solvents. All contacts were made at an O/A volume ratio of 1, and two contacts in series were made for each stripping solution.

The contacts, along with the scintillation counting results and total alpha-activity D value resulting from the contacts, are summarized in Table 28. Several conclusions were drawn from the results in Table 28. First, the 0.5M HEDPA solutions are more effective in stripping the activity than 0.25M concentrations. Also, the addition of NaOH to the stripping solution generally tended to make the first contact less effective, but the second contact more effective in stripping the activity from the solvent. Overall, however, the stripping solutions were most effective when NaOH was not present.

Because none of these contacts brought the activity level in the old solvent down to an acceptable level, HEDPA was eliminated as a possible treatment method.

b. Batch Contacts with Alumina and Resins

Two papers on the use of solid sorbents were reviewed.^{27,28} In these two studies, a variety of solid sorbents were tested to determine their effectiveness in removing acid degradation products from TRUEX solvents. Both papers concluded that the use of sodium carbonate as the primary cleanup method was not adequate for returning the solvent to pristine condition; additional solvent cleanup steps are necessary following the sodium carbonate wash. Tse et al.²⁷ recommended the use of Amberlyst A-26 anion exchange resin or neutral alumina to remove acid degradation products from the solvent. Chiarizia²⁸ recommended the use of a strong base anion exchange resin (like Amberlyst A-26), acid-washed activated charcoal, or acid-washed alumina. To select one of these solid sorbents to (1) clean up the degraded solvent now in the system and (2) install in the glovebox for use during the NBL program, we initiated a study using three of these solid sorbents: acid-washed alumina, neutral alumina, and Amberlyst A-26 anion exchange resin.

In this study, samples from two batches of degraded TRUEX-nDD solvent were used. These two solvent batches both contain acid degradation products, though the old solvent contains a much higher concentration of these degradation products. Both solvents were contacted with 300 mg/mL of activated acid-washed alumina (Aldrich, Brockmann I, 150 mesh) and with 300 mg/mL of activated neutral alumina (Aldrich, Brockmann I, 150 mesh). Contact times were 30 min. Contacts were completed in culture tubes. Mixing was completed for one minute every 4-5 min during the 30-min contact. Mixing was accomplished by both vortex mixing and shaking the culture tubes by hand. Culture tubes were then centrifuged, and samples of the organic were removed for liquid scintillation analysis. Results are reported in Table 29.

Table 28. Alpha Activity Levels and Distribution Ratios from Contacts of TRUEX Solvents with Various HEDPA Solutions

Organic Phase	Aqueous Phase	Contact Number	Organic Activity, cpm/ μ L	Aqueous Activity, cpm/ μ L	Total Alpha D Value
New Solvent	0.25M HEDPA	1	1.35	569	0.002
		2	0.230	0.920	0.3
New Solvent	0.5M HEDPA	1	1.00	513	0.002
		2	0.180	0.670	0.3
New Solvent	0.25M HEDPA, 0.25M NaOH	1	3.87	509	0.008
		2	0.190	3.32	0.06
New Solvent	0.5M HEDPA, 0.5M NaOH	1	1.72	503	0.003
		2	0.160	1.27	0.1
Old Solvent	0.25M HEDPA	1	269	2960	0.09
		2	61.9	188	0.3
Old Solvent	0.5M HEDPA	1	183	3010	0.06
		2	49.9	105	0.5
Old Solvent	0.25M HEDPA, 0.25M NaOH	1	289	2980	0.1
		2	26.3	229	0.1
Old Solvent	0.5M HEDPA, 0.5M NaOH	1	288	2950	0.1
		2	29.4	213	0.1

As shown in Table 29, the acid-washed alumina removed 81.6% of the activity from the old solvent (970,000 down to 179,000 cpm/200 μ L), and 88.4% of the activity from the new solvent (109,000 to 12,600 cpm/200 μ L). With the new solvent, the neutral alumina was more effective, removing 95% of the activity. Its effectiveness for the older, more degraded solvent was similar to the acid-washed alumina.

Two tests were completed with the Amberlyst A-26 anion exchange resin. This resin had previously been converted to the hydroxide form. For one test, 150 mg/mL of resin was contacted with the TRUEX-nDD solvent for one minute; a second test was completed with 30-min contact times. Samples of both degraded solvents were tested; results are reported in Table 29. For the resin contacts, the 30-min contact was more effective than the 1-min contact (with both organics). The effectiveness of the resin was similar to the neutral alumina contacts; the resin was not as effective for the older, more degraded solvent.

Table 29. Results from TRUEX Solvent Cleanup Using Solid Sorbents

Cleanup Method	Amount of Sorbent, mg/mL	Contact Time, min	Scintillation Counting Results, cpm/200 μ L	
			New Solvent ^a	Old Solvent ^b
Initial Organic			109,000	970,000
Acid-Washed Alumina	300	30	12,600	179,000
Neutral Alumina	300	30	5,500	183,000
Anion Resin ^c	150	1	10,500	359,000
Anion Resin ^c	150	30	5,700	201,000

^aNew solvent replaced old solvent and was used to process acidified carbonate waste.

^bOld solvent is TRUEX-nDD that was removed from system after attempted restart.

^cAnion resin was washed Amberlyst A-26 converted to hydroxide form.

Because alumina will be easier to dispose of than the organic resin, we further tested the use of acid-washed and neutral alumina to clean up the solvent. Using the solvent treated once with acid-washed alumina, a contact was completed with 0.25M Na₂CO₃. After equilibration, samples of both phases were collected and counted by liquid scintillation. Results, reported in Table 30, showed that the activity of the organic had decreased by a factor of 100 for the old solvent (to 9,900 cpm/200 μ L) and by a factor of 370 for the newer, less degraded solvent. The high activity level indicates that acid degradation products remain in the TRUEX solvent.

Using the solvent originally treated with the neutral alumina, a second contact was completed with neutral alumina at the same conditions as the first contact (i.e., 300 mg/mL of solvent and 30-min contact time). Results from this contact, as reported in Table 30, showed that for the newer, less degraded solvent, the alumina was as effective as the sodium carbonate wash (dropping the total activity to 237 cpm/200 μ L). However, for the older, more degraded solvent, the second alumina wash was not very effective, only dropping the activity by 61% (down to 71,000 cpm/200 μ L).

Based upon these results, it appears that using acid-washed or neutral alumina will be effective in removing degradation products. However, additional contacts appear to be required. Why these solvents contain such large amounts of degradation products is still unknown.

c. Alumina Column Processing

Since the contacts with both types of activated alumina gave good results in the batch tests described above, both solvent batches were passed through alumina-packed columns. Activated neutral alumina, with a Brockmann I activity level and <150 mesh particle size, was packed in 1-in. (2.5-cm) dia by 12-in. (30-cm) long glass columns. The bed support for the columns consisted of 10 μ m Teflon mesh stretched over a coarse Teflon support grid. A diagram of the column setup is shown in Fig. 28. The columns were packed using freshly made TRUEX solvent to create the slurry. While the columns were being packed, a pump set for a flow rate of about 20 to 30 mL/min was used to draw the solvent through the column. During processing, however, the solvent flowed through the columns by gravity.

Table 30. Additional Results from the Cleanup of the TRUEX Solvent Using Solid Sorbents and Sodium Carbonate

	Old Solvent ^a (cpm/200 μ L)		New Solvent ^b (cpm/200 μ L)	
	Organic	Aqueous	Organic	Aqueous
Initial Solvent	970,000		109,000	
Initial Wash with Acid Alumina after Carbonate Wash ^c	179,000 9,900	— 77,000	12,600 297	— 6,700
Initial Wash with Neutral Alumina after Second Contact with Neutral Alumina ^d	183,000 71,000		5,500 237	

^aOld solvent is TRUEX-nDD that was removed from the system after attempted restart.

^bNew solvent replaced old solvent and was used to process acidified carbonate waste.

^cCarbonate concentration was 0.25M Na₂CO₃. Contacted for 1 min at an O/A ratio of 1/1.

^dAlumina concentration was 300 mg/mL of solvent; contact time was 30 min.

Two sets of column apparatus were available and were packed three times each for a total of six columns packed for processing both the old and new solvents. In general, the solvents were run through two columns in series. As soon as the first-pass column was deemed to be loaded, either because of the high activity level of the effluent or because of color changes in the column, flow through that column was halted. The loaded column was emptied of the loaded alumina, wiped clean with paper towels, and repacked with fresh alumina. This freshly packed column then was used as the second-pass column.

The new solvent was processed first, using two columns in series. Table 31 gives the alpha activity in samples of the effluent taken during processing, as well as the activity of the total volume of this solvent after processing. Three columns were packed with alumina and used to process this solvent. As shown in Table 31, two passes of this solvent through the alumina dropped the alpha activity greater than three orders of magnitude below the original level. Since the activity level of this solvent is now close to background levels, we decided that no further processing with

Table 31. Alpha Activity Level Effluents from Alumina Column Processing of TRUEX Solvents

	Scintillation Counts, cpm/ μ L	
	Grab Samples ^a	Batch Sample ^b
New Solvent (~1.3 L)		
Feed	N/A	545
1st Pass	0.25-0.40	N/A
2nd Pass	0-0.075	0.17
Old Solvent (~2.6 L)		
Feed	N/A	4,850
1st Pass	4-225	N/A
2nd Pass	0.45-7.5	4.2
3rd Pass	N/A	0.895

^aSamples collected at various times during run.

^bSample of processed solvent.

alumina was necessary, provided that further tests (D values for ^{241}Am) show that the solvent is sufficiently free of degradation products.

The two columns which had been used to clean the new solvent were then used to process the old solvent, with the alumina changed as necessary. After the old solvent had been passed through two columns in series, the activity level (4.2 cpm/ μL) was still high enough to merit passing the solvent through fresh alumina once more. Two freshly packed columns were used in parallel for this third pass. Table 31 gives the alpha activity of samples of the effluent taken during processing, as well as the activity of the total volume of this solvent after processing. As shown in Table 31, the third pass through alumina brought the alpha activity level of the old solvent down to about 1 cpm/ μL , for a decontamination factor of about 5000. Six packings of alumina (including those which were used to process both the new and the old solvents) were used for all processing of the old solvent.

All of the column packings used in processing the old and new solvents exhibited color bands which formed at the top of the column and moved downward through the column as processing continued. The type of color bands varied from column to column, depending on the solvent being processed and the number of passes that the solvent had made through columns. In all cases, the movement of the color bands was slower than could be accounted for simply by the movement of the solvent through the column.

It was assumed that the first band (i.e., the first color change up from the bottom of the column) indicated the presence of degradation products held by the alumina. Therefore, the flow through the columns was usually stopped, and the alumina was replaced before this first band passed through the column. One such band, a light brown band with light yellow above and below it, was allowed to pass through a column being used as the second-pass column for the old solvent. Surprisingly, the alpha activity level of the solvent coming from this column decreased as the band passed through, and it decreased further after the band had fully passed out of the column. However, as noted above, care must be taken in equating this change in activity level with a change in the amount of degradation products present in the effluent.

Figure 28 shows the color bands that developed in the packing of a column used for the first pass of the old solvent. The numbers in parentheses below the color in the figure give the gamma activity level of that color band.

The major problem experienced in using the alumina columns for this processing was the extremely low flow rates through them. This gravity-driven flow rate was usually about 4 mL/min. In an attempt to increase this flow rate, holes were drilled in the bottom collar, and the tubing connector of the apparatus was increased to about twice the original diameter. Since this made very little difference in the flow rate, alumina fines were suspected of plugging the holes in the Teflon mesh which formed the bed support. Therefore, one column was packed with about 1/2 in. (1.3 cm) of glass wool between the alumina and the bed support. This glass wool, then, kept the alumina from contacting the Teflon mesh. With these changes, the flow rate increased by at most a factor of two, still leaving the flow rate at less than 10 mL/min.

It seemed possible that the greatest limiting factor in the solvent flow through the columns was the size of the Teflon mesh that forms the bed support. If an alumina column is to be incorporated into the flowsheet for waste processing, a flow rate of greater than 50 mL/min is desired. Therefore, Teflon mesh with a larger pore size, along with a larger alumina particle size, needed testing.

Fig. 28.

Alumina Column Setup with Colors and Gamma Field Values for First-Pass Column of Old Solvent

A larger-pore Teflon mesh (105 μm) for the bed support and alumina of a larger particle size (-60 mesh) were purchased to increase the flow rate through the column. Several trial packings were made to determine if a flow rate of around 50 mL/min could be attained using the new mesh and alumina. The alumina was first screened through an 80-mesh sieve, so that the particle size of the alumina used in these tests was between 80 and 60 mesh.

The 1-in. (2.5 cm) dia by 12-in. (30-cm) long column with the drilled-out fittings was packed with alumina to a height of about 2 in. (5 cm) over the bed support. The flow rate due to gravity (no pump was used) through the column was measured at about 1 mL/min. Since this is much slower than desired, the column was disassembled, and the Teflon mesh was replaced to ensure that no plugging of the mesh pores by the alumina would affect later tests.

The column was again packed with about 2 in. (5 cm) of alumina, but this time about 3/4 in. (2 cm) of compressed glass wool was inserted between the alumina bed and the Teflon mesh. The flow rate due to gravity through this setup was not improved over the previous column, again being about 1 mL/min. The column was again disassembled, and an inspection of the Teflon mesh confirmed that the glass wool had kept the alumina from contact with the mesh.

To determine if the major pressure drop in the column was related to the bed support and/or the holes in the fittings, solvent was run through a column similar to the one in the previous test, excluding the alumina. The flow rate due to gravity through this setup was measured at about 150 mL/min, indicating that the low flow rates experienced previously were probably related to the pressure drop across the alumina bed itself. Activated alumina of larger particle size could not be located.

Since pumping the solvent from the bottom of the column into the organic feed tank seemed necessary, and since this would probably increase the flow rate through the column, a final trial column was packed with alumina. Again, glass wool was placed between the alumina bed and the Teflon-mesh bed support. The pump used during this packing was set at about 20 mL/min. During packing, the glass wool was compressed considerably more than when flow was due to gravity. By the same token, packing of the alumina is expected to be tighter when a pump is used. The maximum pumped flow rate through the fully packed column [about 11-in. (28-cm) bed height] was about 13 mL/min. Although the pump was still set at about 20 mL/min, part of the flow through the tube was air that leaked into the tubing past the fittings. Since the solvent flow rate needed for batch 2 processing (around 50 mL/min) is not attainable through the column, the solvent passing through the column will have to be a side stream, flowing at about 25% of the main solvent flow rate.

During the alumina processing of the solvent, as expected, the decontamination of the solvent was strongly related to the residence time of the solvent on the column. Solvent that sat in a column overnight contained considerably less activity than the effluent collected prior to shutdown for the night. Thus, increasing the flow rate through the alumina will be accompanied by a decrease in the ability of the alumina to extract the degradation products. A single pass of the solvent through an alumina column at 14 mL/min during waste processing may not be sufficient to keep the solvent sufficiently clear of degradation products. However, degradation product concentrations generated during one pass through the contactors will be very low.

d. Testing of Processed Solvent

To verify that the acid degradation products had been removed from the solvents and that the solvent could be used to process the next batch of waste, D values were measured for ^{241}Am in solution at two nitric acid concentrations (0.01 and 2.0M). To prepare the two solvents for the americium D-value measurement, two samples from both solvents were first contacted at an O/A ratio of 1/1 with 0.25 M Na_2CO_3 . Following the carbonate contact, samples of both phases were collected and counted on the scintillation counter. Results from this analysis are given in Table 32. Based upon these results, one contact with 0.25M sodium carbonate was adequate for removing a majority of the residual activity from the TRUEX solvent. The material balance for the activity in these samples is not very good, however. Following the carbonate contact, five contacts with 0.05M or 2M HNO_3 were completed. The purpose of these contacts was to first remove any residual carbonate from the organic phase (two contacts), then to pre-equilibrate the solvent (three contacts).

In addition to the two NBL solvents, americium D values for three other TRUEX samples were measured:

TRUEX-1 Second crystallization of CMPO from four batches of CMPO originally purified in January and February 1991 (Batches 1-4).

Table 32. Liquid Scintillation Counting Results from Sodium Carbonate Contacts with TRUEX NBL Solvents

	Sample #1 (cpm/200 μ L)		Sample #2 (cpm/200 μ L)	
	Organic	Aqueous	Organic	Aqueous
Old Solvent ^a	5.6	50	6	64.75
New Solvent ^b	1.1	1.15	0.55	3.35

^aInitial activity of this solvent was 180 cpm/200 μ L.

^bInitial activity of this solvent was 34 cpm/200 μ L.

TRUEX-2 Impure CMPO, lot #IVDEV0071, dated December 1988, labeled CMPO #5 (MAT-1-857-69).

TRUEX-3 Second crystallization of CMPO from batches 5 and 6 (MAT-1-857-91).

These three solvents were pre-equilibrated by contacting them with the appropriate nitric acid solution (0.05 or 2M). Sodium carbonate washes of these solvents were not done.

The ^{241}Am -containing stock solution used for this test was originally believed to be 2M HNO_3 . Therefore, to achieve a nitric acid concentration of 0.01M HNO_3 , 15 μL of ^{241}Am stock solution was pipetted into 3 mL of water. This solution was then used to contact the organic solutions. For the 2M contacts, 100 μL of ^{241}Am stock solution was added to 2.9 mL of 2M HNO_3 . After the tests were completed, we discovered that the ^{241}Am stock solution was 1M HNO_3 instead of 2M. This should not affect the 2M data but may significantly alter the results at 0.01M, because the real acid concentration was closer to 0.005M. Reference D values for americium are 0.01 for 0.01M HNO_3 and 25 for 2M HNO_3 . Americium D values for 0.005M HNO_3 are not available.

Scintillation counting results are reported in Table 33, while gamma counting results are reported in Table 34. For the scintillation results, the counts between 100 and 500 keV were selected as the alpha peak. For gamma counting, the americium peak at 59.5 keV is reported.

Based upon this analysis, the gamma and scintillation results are comparable (as they should be). The D values for the low-concentration acid are greater than the expected value of 0.01, but this may be due to the lower acidity in the samples. The values at 2M are comparable, indicating that the CMPC concentration is appropriate for this solvent. In addition, the americium D values at 0.005M HNO_3 indicate that the new solvent contains a greater concentration of acidic impurities than the old solvent. This is surprising, since the old solvent was, before cleanup, much more degraded than the new solvent. Additional measurements will be completed to verify these results.

5. Solids Dissolution

Four forms of solids, all containing high activity levels, were present in the glovebox:

- Approximately 0.25 cm^3 of black solids filtered from the TRUEX solvent after batch 1 processing.

Table 33. Scintillation Results for D_{Am} Tests Using Various Solvents

	0.005M HNO ₃ ^{a,b}			2.0M HNO ₃ ^a		
	Organic, cpm/800 µL	Aqueous, cpm/200 µL	D Value	Organic, cpm/200 µL	Aqueous, cpm/800 µL	D Value
Old Solvent ^c	455	2330	0.049	17700	2370	30
	449	2280	0.049	17800	2350	30
New Solvent ^d	892	2090	0.11	17700	3000	24
	937	2080	0.11	17900	3020	24
TRUEX-1 ^e	501	2180	0.058	18100	2720	27
	541	2170	0.062	17600	2640	27
TRUEX-2 ^f	735	2090	0.088	18000	2640	27
	750	2100	0.089	18300	2750	27
TRUEX-3 ^g	454	2250	0.050	17800	2810	25
	471	2280	0.052	18300	2790	26

^aDuplicate equilibrations not completed; duplicate samples collected for counting purposes.

^bOriginally planned to be 0.01M, but was actually closer to 0.005M HNO₃.

^cBatch of TRUEX-nDD solvent used to process first batch of waste solution. This solvent was highly degraded.

^dBatch of TRUEX-nDD solvent used to process acidified carbonate waste.

^eSecond crystallization of CMPO from four batches of CMPO originally purified in January and February 1991 (Batches 1-4).

^fImpure CMPO, lot # IVDEV0071, dated December 1988.

^gSecond crystallization of CMPO from batches 5 and 6 (MAT-1-857-91).

- An unknown amount of solids that had accumulated on plugged filters.
- Approximately 200 cm³ of light gray solids, hereafter called Ames solids, which were sent to us in a 2-L bottle filled with aqueous waste from Ames, Iowa, as part of the batch 2 feed shipment (RL #288570).
- Approximately 250 cm³ of white solids, hereafter called DF solids, which were collected from the bottles used to hold the DF solutions, as well as from a leak in the DF carboy secondary container.

Attempts to dissolve these solids concentrated on the last two items, but it is desirable that any method found for dissolving these solids be applicable to the others. Since an accurate method for counting a known volume of solids on the scintillation and gamma counters has not been developed, this work was more qualitative than quantitative.

The source of the DF solids is the following. After all solutions transferred from Waste Management Operations (WMO) had been put into the DF carboy, the carboy leaked feed solution into its secondary container and, from there, to the glovebox floor. The solution remaining in the carboy was pumped into other containers, and the liquid on the glovebox floor was recovered as much as possible. The acid in the feed had reacted with the lead shielding inside the secondary

Table 34. Gamma Results for D_{Am} Tests Using Various Solvents

	0.005M HNO ₃ ^{a,b}			2.0M HNO ₃ ^a		
	Organic, cps/200 µL	Aqueous, cps/200 µL	D Value	Organic, cps/200 µL	Aqueous, cps/200 µL	D Value
Old Solvent ^c	0.204	5.41	0.038	39.2	1.4	28.0
	0.206	5.44	0.038	39.4	1.4	28.1
New Solvent ^d	0.485	4.97	0.098	44.4	1.77	25.1
	0.512	5.01	0.102	44.1	1.72	25.6
TRUEX-1 ^e	0.265	5.11	0.052	46.2		
	0.243	5.12	0.047	46.1	1.58	29.2
	0.248	5.06	0.049	45.5	1.58	28.8
TRUEX-2 ^f	0.418	4.77	0.088	45.1	1.58	28.5
TRUEX-3 ^g	0.259	5.24	0.049	43	1.64	26.2

^aDuplicate samples not collected; where two or three values reported, samples counted that many times.

^bOriginally planned to be 0.01M, but was actually closer to 0.005M HNO₃.

^cBatch of TRUEX-nDD solvent used to process first batch of waste solution. This solvent was highly degraded.

^dBatch of TRUEX-nDD solvent used to process acidified carbonate waste.

^eSecond crystallization of CMPO from four batches of CMPO originally purified in January and February 1991 (Batches 1-4).

^fImpure CMPO, lot # IVDEV0071, dated December 1988.

^gSecond crystallization of CMPO from batches 5 and 6 (MAT-1-857-91).

container, creating about 250 cm³ of solid. (Considerable work was needed to recover from the leak and to ensure that the feed solutions could be processed. Both the carboy and the secondary container were replaced. The lead shielding that had been on the inside of the old secondary container was placed on the outside of the new secondary container, so that in the future, if the carboy leaks, solution would not contact the lead.)

The DF solids were probably a lead compound, most likely lead chloride or lead phosphate. Gamma spectrum analysis of some of this solid showed the presence of Pu, Am, U, and Pa—a daughter of Np.

a. Attempts with 2M HNO₃

Contacting the solids with 2M HNO₃ showed that, although the solids could not be dissolved, some of the activity could be leached out, albeit slowly.

b. Attempts with Silver Persulfate

Silver persulfate has been used in other laboratories as a strong oxidizing agent effective in dissolving PuO₂. The oxidizing property comes from the presence of the Ag²⁺ ions, which give the solution a characteristic brown tint. The Ag²⁺ ions are present because of the following redox reaction:

The plutonium in the solids is then oxidized in the following redox reaction:

Provided that there is an abundance of persulfate ions present, the silver from the left side of reaction 21 is then oxidized according to reaction 20, so that a small amount of silver is used over and over again until the persulfate ions are used up. A common silver persulfate solution used for this purpose is 1M HNO_3 , 0.1M $\text{K}_2\text{S}_2\text{O}_8$, and 0.02M AgNO_3 . The presence of the Ag^{2+} ions, and thus the oxidizing capability of the solution, is indicated by the presence of the brown color. The solution becoming clear indicates that reaction 20 is no longer proceeding in a forward direction, and no further oxidation of the plutonium solids will occur.

Since silver chloride would precipitate if it formed in the oxidizing solution, the suspected presence of lead chloride in the DF solids was a concern. To test if chloride or another species that might precipitate silver was present, the DF solids were rinsed with 0.02M HNO_3 , and the supernate from the rinse was decanted. Upon addition of an equal volume of the silver persulfate solution to this supernate, the solution turned cloudy white. Centrifuging this mixture showed the presence of a white precipitate and a clear supernate, indicating that all the silver had most likely precipitated. A similar test done on a 0.02M HNO_3 solution used to rinse the Ames solids yielded the same results.

To determine if the silver would oxidize some of the plutonium before the precipitation occurred, a small amount of the rinsed DF solids and the rinsed Ames solids was added to separate volumes of the silver solution. Again, both mixtures immediately turned cloudy white, and centrifuging showed that both mixtures contained a white precipitate and a clear supernate. Scintillation counting of the supernates showed activity levels in the same range as those attainable in the supernate of a 2M HNO_3 solution used to rinse the solids.

Because of the presence of chloride or another species that precipitates silver, the silver persulfate solution was not useful for dissolving the DF solids or the Ames solids. However, it may be useful in dissolving the other solids in the glovebox, since these other solids should not contain any chloride or phosphate.

c. Attempts with HNO_3 and HF

A 1M HNO_3 -0.01M HF solution was contacted with the DF solids, and scintillation counting of the supernate showed that about five times more activity could be leached out by using this solution than could be attained using 2M HNO_3 in a similar contact. Similar results were attained with the Ames solids.

Since this HF solution has given the best results of the solutions tried, a large volume was prepared, imported into the glovebox, and mixed with the DF solids and Ames solids in separate containers. After 24 h, the supernate from the DF solids bottle was sampled, and the bottle was shaken vigorously for about 2 min. Another sample of the supernate about seven hours later showed the activity in the supernate unchanged over this seven-hour period. The next day a mixer was put in the DF solids bottle, and the bottle's contents were mixed well for about six hours. A sample of the supernate after mixing showed the activity in the supernate still the same as in the

previous two samples. The alpha activity level in all three cases was about 2200 dpm/ μ L, and it would appear that this represents some form of complexation or solubility limit for this solution.

Given the uncertain time frame for recovery of activity from these solids, we decided that processing of batch 2 would proceed with the feed solution as-is, and that efforts at dissolving or leaching the solids would proceed after that processing is complete.

VII. DECONTAMINATION OF GROUNDWATERS CONTAINING VOLATILE ORGANIC COMPOUNDS

(J. C. Hutter, M. A. Tranovich, 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 U.S. Department of Energy and Air Force. The process uses two unit operations, membrane-assisted solvent extraction (MASX) and membrane-assisted distillation stripping (MADS). Using a natural oil solvent such as sunflower oil, the MASX process extracts dilute VOCs from water. 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 Corp., prototype radial cross-flow modules will be developed and tested for the MASX/MADS application. A field demonstration at ANL is being planned to test the MASX/MADS process.

The MASX/MADS system (Fig. 29) 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 VOC pollutants 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 under 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 back to the MASX unit by vaporization of the VOCs.

Fig. 29. Flow Diagram of MASX/MADS Process

As shown in Fig. 29, contaminated groundwater is fed to the extraction modules where it is contacted with a nonvolatile solvent. Because of 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 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.

A. Analytical Procedures to Detect VOCs in Natural Oils or Water

The U.S. Environmental Protection Agency (EPA) has developed analytical procedures to detect VOCs in water. The EPA method 502.2 matches the requirements for the VOCs of interest and was used as a basis for the methods used for our aqueous samples. This method requires a gas chromatograph equipped with a PID (photoionization detector) and ELCD (electrolytic conductivity detector). Aqueous samples were analyzed using the same purge-and-trap cycle specified in method 502.2. A Supelco, Inc., 30 m x 530 μ m VOCOL column was used to separate the various VOCs. For the oil samples, a nearly identical purge-and-trap cycle was used, except the purge cell was heated to 90°C. Typical separation achieved using this analytical technique for both water and oil samples is shown in Fig. 30.

Fig. 30. Volatile Organics Detected with Electrolytic Conductivity Detector from a Sunflower Oil Sample (10°C for 25 min, then 10°C/min to 150°C)

Data were handled by a Spectraphysics SP-4290 integrator and a Winner386 chromatographic software package. This software package and integrator system are typical for this type of application. The data are processed using an external standard calibration procedure. Reports of area counts and concentrations can be generated. In addition, laser printed output of the chromatographic results can be displayed.

Care must be taken during sample handling and preparation so that no VOCs are lost or inadvertently added to the system. Thus, all samples were taken in sealed vials without any headspace. Totally enclosed glass syringes were used to transfer samples to the purge cell. It was important to use all glass and steel equipment, since plastic materials were found to leave residuals in the sample matrix which interfered with our analytical procedure.

B. Determination of Henry's Law Constants

The design of the MADS design requires precise values of the Henry's law constants for VOCs in various candidate natural oils. These data were collected using the sparged gas reactor shown in Fig. 31. Experimental work with this reactor is in progress.

Fig. 31.

Sparged Reactor for Henry's Law Experiments

Mass transfer of a sparingly soluble component from a liquid phase to a gas phase is a liquid-phase-controlled process. For a fine-bubble diffused system, considerable evidence exists that equilibrium between the gas and liquid phase is rapidly approached by the sparingly soluble component. For trace amounts of various VOCs in water, equilibrium is reached within 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.²⁹ The technique requires accurate concentration vs. time data for desorption of a VOC from a sparged reactor. This technique was applied to measure the Henry's law constants for various VOCs above various natural oil solvents.

In our experiments, oil charged with trace amounts of VOCs was placed in the reactor shown in Fig. 31. Nitrogen gas was then sparged into the reactor. The VOCs were stripped from the liquid phase, and concentration-vs.-time data were collected from grab samples of the liquid phase. An external jacket heat exchanger controlled the temperature of the reactor vessel. The contents of the reactor were assumed to be well mixed due to the mixing pattern induced by the sparged gas.

A material balance on the liquid phase in the reactor is given by

$$V \frac{dC}{dt} = -G y \quad (22)$$

$$V \frac{dC}{dt} = -G \frac{HRTC}{P} \quad (23)$$

where V = reactor liquid volume, L

C = VOC concentration, mol/L

t = time, s

y = gas phase mole fraction of VOC

H = Henry's law constant, dimensionless

R = universal gas constant, L-atm/mol-K

T = absolute temperature, K

P = reactor gas pressure, atm

G = gas flow, mol/s

Integration of Eq. 23 with the initial conditions $t = 0$ and $C_0 = C$ gives

$$\ln \frac{C}{C_0} = - \frac{GHRT}{PV} t \quad (24)$$

A plot of $\ln C/C_0$ vs. t will give a slope equal to $GHRT/PV$; thus, H can be calculated from the slope for each desorption test for all the VOCs in the test mixture (methylene chloride, cis-1,2-dichloroethylene, trans-1,1-dichloroethylene, trichloroethylene, tetrachloroethylene, chloroform, and benzene).

The early experiments using the sparged reactor produced inconsistent results, caused by poor dispersion of the introduced VOCs in the reactor at the start of a stripping run. A plot of $\ln C/C_0$ vs. time did not produce a straight line. In addition, the early samples had area counts indicative of a concentration of 10 ppm, which was impossible since only enough VOCs were added to produce 1 ppm (1000 ppb).

By macroscopically mixing the VOCs at the start of the sparging experiment, we found that a plot of $\ln C/C_0$ vs. time produced a straight line through the origin at $\ln C/C_0 = 1.0$ and $t = 0$, as the material balance predicts for Henry's law controlled stripping. The Henry's law results are summarized in Table 35. The results of the experiment for carbon tetrachloride (which are typical for our system) are shown in Fig. 32. At a gas flow of 2.505 mL/s, the mixing in the reactor is poor, and the results do not plot as a straight line owing to the introduction of dead spots in the reactor. At a gas flow of 3.125 mL/s, the plot is a straight line, and the Henry's law constant was found to be 0.0099. At the higher gas flow of 7.01 mL/s, the plot is also a straight line, but the data indicate that the exiting gas is not as close to equilibrium as the results at 3.125 mL/s. This is due to the higher velocity of the gas bubbles at this higher superficial velocity, resulting in less contact time and reducing the mass transfer to the gas phase. If the gas were at equilibrium at 7.01 mL/s, the plotted lines for both 3.125 and 7.01 mL/s would be identical. For some of the VOC species, this was the case. A mixer will be added to verify these results in future experiments.

Table 35. Henry's Law Constants at 50°C of Various Volatile Organics in Sunflower Oil

Component	Henry's Law Constant		Boiling Pt., °C
	PID	ELCD	
Methylene Chloride	-	0.0210	40.0
Trans-1,1-Dichloroethylene	0.0204	0.0179	47.0
Cis-1,2-Dichloroethylene	0.0138	0.0119	60.0
1,1,1-Trichloroethane	-	0.0102	74.1
Benzene	0.0102	-	80.0
Chloroform	-	0.0099	61.7
Carbon Tetrachloride	-	0.0099	76.54
Trichloroethylene	0.0069	0.0062	87.0
Tetrachloroethylene	0.0024	0.0035	121.0

Fig. 32. Semilog Plot of C/C_0 vs. Gas Purged at 50°C for Carbon Tetrachloride in Sunflower Oil

C. Mass Transfer in a Hollow Fiber

Based on the early concept of a Newtonian fluid, the equations for laminar flow in cylindrical tubes were first worked out in the mid-nineteenth century. For a Newtonian fluid, the shear stress at any point in the fluid is directly proportional to the velocity gradient, and the proportionality constant is the viscosity. This simple relationship between stress (force/unit area) and velocity gradient can be used to determine the velocities at any point in space by integrating the gradient with respect to the external forces that define the stress on the fluid. For hollow fiber membranes, the fluid inside the fiber is subject to the same type of stress field as a fluid inside any cylindrical tube, and the mathematical description of the velocity profile is easily derived.

A free body diagram for a cylindrical element of fluid is shown in Fig. 33. The fluid velocity is increasing from zero at $r = R$ at the wall (radius, cm) to its maximum value at the centerline of the tube. The fluid momentum is in the positive z direction. A shearing force is created at the wall of the tube, and the momentum of the fluid near the wall is reduced and is transferred to the wall; thus, z momentum is transferred in the r direction. As shown in Fig. 33, τ_{zr} (z momentum flux in

Fig. 33. Cylindrical Fluid Element in Tube with Laminar Flow Velocity Profile

r direction, g/cm-s^2) is positive; as r increases, z momentum flux increases (i.e., z velocity is reduced and momentum is transferred through each adjacent fluid layer to the wall). As r is increased from 0 to R , each successive layer of fluid has a lower z velocity, and that velocity reduction is transferred as z momentum toward the wall. Pressure forces P_1 and P_0 (dyn/cm^2) act on the fluid element at each end of the cylindrical element; P_1 is greater than P_0 for flow in the positive z direction in this tube.

Bird et al.³⁰ report the following force balance for this fluid element in dynamic equilibrium:

$$2\pi r \Delta L \tau_{zr} \Big|_r - 2\pi r \Delta L \tau_{zr} \Big|_{r+\Delta r} + (P_1 - P_0) 2\pi r \Delta r = 0 \quad (25)$$

where ΔL = length of fluid element, cm

$2\pi r \Delta L$ = area of cylinder surface on which τ_{zr} acts

$2\pi r \Delta r$ = area of base of fluid segment on which the pressure acts

Dividing Eq. 25 by the cylinder element volume, $2\pi r \Delta L r$, gives

$$\frac{r \tau_{zr} \Big|_r - r \tau_{zr} \Big|_{r+\Delta r}}{r \Delta r} + \frac{(P_1 - P_0)}{\Delta L} = 0 \quad (26)$$

By taking the limit as Δr approaches zero,

$$-\frac{dr \tau_{zr}}{r dr} + \frac{(P_1 - P_0)}{\Delta L} = 0 \quad (27)$$

This equation can be integrated using the boundary condition at $r=0$, where τ_{zr} is finite, to give

$$\tau_{zr} = \frac{(P_1 - P_0)}{\Delta L} \left(\frac{r}{2} \right) \quad (28)$$

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For a Newtonian fluid,

$$\tau_{zr} = -\mu \frac{dv_z}{dr} \quad (29)$$

In Eq. 29, μ is the viscosity in poise (P). Equation 29 can be equated to Eq. 28 and integrated with the boundary condition that $v_z = 0$ at $r = R$,

$$v_z = \frac{(P_1 - P_0)R^2}{4\mu\Delta L} \left(1 - \frac{r^2}{R^2}\right) \quad (30)$$

Equation 30 indicates that the maximum velocity occurs at $r = 0$, the tube center. Thus Eq. 30 can be rewritten as

$$v_z = v_{\max} \left(1 - \frac{r^2}{R^2}\right) \quad (31)$$

The maximum velocity depends on the pressure drop, tube length, fluid viscosity, and tube radius. Equation 30 is the Hagen-Poiseuille parabolic velocity profile for laminar flow of a Newtonian fluid in a tube.

To find the average fluid velocity, Eq. 30 is substituted for v_{avg} in the double integral in the numerator below and integrated to give the following result:

$$v_{\text{avg}} = \frac{\int_0^{2\pi} \int_0^R v_z r \, dr \, d\theta}{\int_0^{2\pi} \int_0^R r \, dr \, d\theta} = \frac{(P_1 - P_0)R^2}{8\mu\Delta L} \quad (32)$$

where θ = angle in radians. Thus $v_{\max} = 2v_{\text{avg}}$, and the fully developed velocity profile for a tube with the origin at the center is given by

$$v_z = 2 v_{\text{avg}} \left(1 - \left(\frac{r}{R}\right)^2\right) \quad (33)$$

where v_z = local liquid velocity, cm/s

v_{avg} = average liquid velocity, cm/s

r = position along tube radius away from origin at tube center, cm

R = radius of tube wall, cm

The average velocity only depends on the tube geometry, external pressure drop, and the physical properties of the fluid, as shown by Eq. 32.

The above equations can be used to determine the flow inside the hollow fiber membrane. Typical velocities in the membrane extractor hollow fibers approach 3 cm/s. The velocity profile for a 200- μm dia hollow fiber with an average fluid velocity of 2.8 cm/s is shown in Fig. 34.

Fig. 34.
Laminar Flow Velocity Profile Inside a
200- μm Dia Fiber

Using the above velocity profile, we calculated the diffusion of VOCs through the flow field to the wall of the fiber. We also used a differential material balance solved in the tube volume for the appropriate boundary conditions. This type of problem has been investigated for heat transfer from the fluid to the tube wall.³¹⁻³⁴ The equations for mass transfer are similar. A volume element for this situation is given in Fig. 35.

Fig. 35. Volume Element for Mass Transfer with Laminar Flow

As in the previous case for momentum transfer, the following incremental mass balance for each individual VOC component can be written:

$$2\pi r \Delta z J_r \Big|_r - 2\pi r \Delta z J_r \Big|_{r+\Delta r} + 2\pi r \Delta v_z C \Big|_z - 2\pi r \Delta v_z C \Big|_{z+\Delta z} = 0 \quad (34)$$

where J_r = Diffusive flux in the r direction, $\text{mg}/\text{cm}^2\text{-s}$

$2\pi r \Delta v_z$ = Volumetric flow rate through volume element in z direction, cm^3/s

C = local concentration, mg/cm³

z = axial position in tube ($z = 0$ at entrance) cm

The first two terms in Eq. 34 account for the diffusion of the VOC toward the wall; the next two terms account for the bulk flow in the z direction.

By dividing by the incremental volume, $2\pi r\Delta r\Delta z$, and taking the limit as both Δr and Δz approach zero, Eq. 34 becomes

$$-\frac{\partial r J_r}{r \partial r} - v_z \frac{\partial C}{\partial z} = 0 \quad (35)$$

By introducing Fick's Law,

$$J_r = -D_{ab} \frac{\partial C}{\partial r} \quad (36)$$

where D_{ab} is the diffusivity of the VOC in the liquid phase, cm²/s. Equation 36 can then be written as

$$-D_{ab} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) - v_z \frac{\partial C}{\partial z} = 0 \quad (37)$$

To solve Eq. 37, v_z as a function of r must be known (v_z is independent of z since the flow is fully developed). The laminar flow velocity profile can be inserted into Eq. 37 since in the hollow fiber membrane the flow is known to be laminar.

Using the laminar flow velocity profile for this mass transfer case, the following equation applies:

$$2 v_{avg} \left(1 - \left(\frac{r}{R} \right)^2 \right) \frac{\partial C}{\partial z} = D_{ab} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) \quad (38)$$

The boundary conditions for Eq. 38 are for the case:

- at $r = 0$ $C = \text{finite}$
- at $r = R$ $C = C_W$, a constant
- at $z = 0$ $C = C_E$, a constant for all r

For Eq. 38, the diffusion in the z direction along the tube axis has been neglected compared to the bulk flow in the z direction. This is not a valid assumption for low velocities in the tube (v_{avg}), where the velocity and diffusion velocity are similar. However, in the cases we are interested in, the velocity is large compared to the diffusion rate, so diffusion can be neglected.

The solution to Eq. 38 for these boundary conditions is³⁵

$$\frac{C_W - C}{C_W - C_M} = \sum_{n=0}^{\infty} K_{2n} \left(\frac{r}{R} \right)^{2n} \quad (39)$$

where CM is the mixed point concentration, and the coefficient K_{2n} is given by

$$K_0 = 1 \quad (40)$$

$$K_2 = -\frac{\lambda_0^2}{2^2} = -1.828397 \quad (41)$$

$$K_{2n} = \frac{\lambda_0^2}{(2n)^2} (K_{2n-4} - K_{2n-2}) \quad (42)$$

$$\lambda_0 = 2.7043644199 \quad (43)$$

where λ_0 is a constant determined by solving Eq. 38. The sum of the coefficients given by Eq. 42 must be zero. In addition, r/R is bound by $0 \leq r/R \leq 1$. Both of these constraints ensures that the infinite series given by Eq. 39 converges. The sum of the coefficients of Eq. 42 rapidly approaches zero and is considered convergent for $n = 10$.

The bulk fluid mixing concentration is given by the following asymptotic formula for $z^* > 0.0335$ (z^* is a dimensionless position coordinate):

$$\frac{CW - CM}{CW - CE} = 0.819046 \exp(-\lambda_0^2 z^*) \quad (44)$$

where

$$z^* = \frac{z/D_{hyd}}{ReSc} \quad (45)$$

$$Re = \frac{2 R \rho v_{avg}}{\mu} \quad (46)$$

$$Sc = \frac{\mu}{\rho D_{ab}} \quad (47)$$

$$D_{hyd} = \frac{\text{cross sectional area}}{\text{wetted perimeter}} \quad (48)$$

In the above,

- D_{hyd} = hydraulic radius, cm
- Re = Reynold's number
- Sc = Scmitt number
- ρ = density, g/cm³
- μ = viscosity, g/cm-s

The Reynold's number is a dimensionless ratio of inertia forces to viscous forces, and the Scmitt number is the ratio of momentum diffusivity (viscosity) to molecular diffusivity (mass diffusion).

The dimensionless concentration given by Eq. 44 is only a function of the radial position, just like the velocity. The mixing cup concentration or flow average concentration is defined by

$$CM = \frac{1}{A_c v_{avg}} \int_0^{A_c} v C dA \quad (49)$$

where A_c is the cross-sectional area (cm^2), and A is the area (cm^2). A FORTRAN program was written to evaluate the solution to the concentration profiles numerically. The results for a 200- μm dia fiber with $CE = 1000$ ppb, $CW = 0$ ppb, and $v_{avg} = 2.8$ cm/s for water at 25°C are shown in Fig. 36.

The concentration profiles were calculated using the published diffusivity of chloroform in water at 25°C, $1.01 \times 10^{-5} \text{ cm}^2/\text{s}$.³⁶ As shown in Fig. 36, parabolic concentration profiles are calculated for this laminar flow case, as expected. By the end of the 10 cm fiber, the maximum concentration decreases from 1000 ppb at the fiber inlet to 200 ppb at the fiber exit. These results are consistent with those of Zander et al.³⁶ By changing the boundary conditions and physical properties and operating parameters of the system, one should be able to accurately model the performance of this system.

Fig. 36. Concentration Profiles Inside a Hollow Fiber

D. Optimal Configurations of Hollow Fiber Modules

Hollow fiber modules are usually assembled in the countercurrent shell-and-tube configuration. This configuration gives the largest integrated concentration gradient for mass transfer, as is well documented in standard textbooks.^{30,37} Other configurations, such as 1-2 (1-shell pass, 2-tube passes), 2-4, 1-4, or cross-flow configurations, are not as efficient, and the driving force must be adjusted by an appropriate log-mean correction factor. Despite the fact that the standard 1-1 configuration is the best in terms of the integrated driving force, the compact packing in the shell-and-tube hollow fiber module promotes substantial bypassing of the shell-side fluid, limiting effectiveness of this 1-1 design.³⁸ Prototype radial cross-flow modules which overcome these problems are under development by Hoechst Celanese.

VIII. DEVELOPMENT OF 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 radioactive streams such as those generated by the TRUEX process. Minimizing waste generation requires that equipment be installed for (1) concentrating radioactive waste streams and (2) 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 advantages and disadvantages, (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. In a collaborative effort, LICON and Argonne will work together to (1) design an evaporator specifically for remote operation and (2) in a mock-up facility at Argonne, test the remote operability and maintenance of this evaporator and other equipment in glovebox, shielded-cell, and canyon environments. 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 will be undertaken in cooperation with the University of Illinois (UI) Nuclear Engineering Department. The UI researchers will initially focus on completing a literature survey, covering work on mixed-phase equilibria (vapor/liquid and vapor/liquid/solid) of aqueous solutions of HNO_3 (possibly HF as well) in the presence of metal nitrate salts. The most important measurements needed are the concentrations of water and nitric acid in the liquid and vapor phases as a function of temperature, pressure, and composition of the aqueous solution (i.e., effects of metal nitrate salts on the volatilities of water and nitric acid). A second need is the composition of the solids that precipitate as these mixed-acid/metal-salt solutions are concentrated (again as a function of temperature, pressure, and composition). Analysis of these data is needed for 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 being undertaken to collect data not available in the literature.

A. Neutron Activation Analysis

To measure decontamination factors (DFs) in evaporators, radioactive tracers can be used. Since detection limits for tracers are typically very low, DFs of 10^4 to 10^5 are easily measured. The problem with tracers, however, is that the equipment would be contaminated following their use. This complicates future work with the evaporator and increases the cost associated with future tests. In addition, use of radioactive materials at LICON is prohibited. Therefore, an element that is not radioactive but can be detected at low concentrations is needed. An analytical procedure called "neutron activation" is one method that can be used to measure the concentration of an element at low concentrations.

Neutron activation is simply the creation of a radioactive element as a result of neutron interaction with a stable isotope. When a neutron collides with a nucleus, the following reactions may occur: elastic scattering (n,n), inelastic scattering (n,n'), radiative capture (n,g), charge-particle reaction

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(n,a) or (n,p), neutron-producing reaction (n,2n), and fission (n,f). The most useful reaction in neutron activation is radiative capture, which can be denoted as

where ${}^{A+1}_Z^*$ is called the "compound nucleus," which is usually in an excited state. It can de-excite with the emission of a gamma-ray called a "prompt gamma." In many cases, the ${}^{A+1}_Z$ also decays by emitting gamma rays called "delayed gammas." These delayed gammas can be detected using a high-resolution, gamma-sensitive detector.

Neutron activation analysis (NAA) will be performed in the operating TRIGA reactor at the University of Illinois (Champaign-Urbana), using the "lazy-susan" facility, which can provide a thermal flux of $3.3 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ at 1.5 MW and is capable of irradiating up to 80 samples simultaneously. For higher neutron fluxes, an in-core facility for thermal ($1.2 \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ at 1.5 MW) and epithermal ($1.0 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ at 1.5 MW) irradiation positions is also available. This neutron activation facility is equipped with three separate counting systems: a 19%-efficient germanium detector in conjunction with a Compton Suppression system, a 13%-efficient Gamma-X detector capable of detecting both X-rays and gamma-rays, and a 24%-efficient germanium detector in conjunction with a sample changer.

To use neutron activation for measuring decontamination factors in the evaporator, it is necessary to find a stable, inexpensive element with a large cross section for radiative capture. Therefore, a review of elements was initiated. Based on this review, we determined that samarium may be suitable for our application. Samarium-152 has a radiative capture cross section of 208 b. The radiative capture reaction produces ${}^{153}\text{Sm}$, which has a half-life of 1.929 days and emits a 103.2 keV gamma ray. The half-life of nearly 2 days allows sufficient time for analysis, and the relatively rapid decay lessens the concern of radioactive waste production. Tests will be completed to determine the applicability of using samarium for this measurement.

B. Laboratory-Scale Evaporator

A laboratory-scale evaporator, the FRIDGEVAP FVP-C3, has been ordered from LICON, where final design and fabrication work is being done. This evaporator will be useful in verifying materials compatibility, gathering data on the evaporation process, and assessing solids handling and maintenance needs. This knowledge will aid in the eventual design of pilot- and plant-scale evaporators. The major portion of experimental work done using this evaporator will involve evaporating liquid from solutions containing high concentrations of salts and acids. These tests will (1) gain knowledge regarding boiling-point elevations caused by the presence of the salts, (2) begin to establish the range of DFs that can be attained in the evaporator, and (3) gain further experience that will aid in establishing the experimental plan and the hazards that may be posed by the presence of acids in the feed.

The evaporator being purchased is a single-effect vacuum evaporator that is driven by a heat pump, employs horizontal tubes, and has a capacity of about 11.5 L/h (3 gal/h) distillate output. A basic flow diagram for this FRIDGEVAP is presented in Fig. 37. The general specifications for the evaporator are summarized in Table 36.

Because the system operates under a vacuum (~100 mm Hg absolute pressure), water will boil at temperatures below 43°C (110°F). The evaporation section will normally run at temperatures around 60°C (140°F), and the condenser section, around 38°C (100°F). An auxiliary electric heating

Fig. 37. Flow Diagram for FRIDGEVAP FVP-C3 Evaporator

system is being incorporated into the system by LICON because of the higher boiling points foreseen when using a high-salt feed. This will allow evaporation temperatures around 82°C (180°F.) System vacuum is provided by hydraulic jet eductors driven by pumps.

Major plumbing components of the FVP-C3 are constructed of PVC and chlorinated PVC tubing, with the high-temperature sections being the latter. Significant softening of PVC begins around 60°C (140°F), and CVPC begins to soften at around 93°C (200°F). A limit switch is built into the system to shut it down should the temperature in the evaporator section (made of CPVC) exceed 88°C (190°F). Thus, softening of the PVC and CPVC piping due to high temperatures will not be a problem.

Table 36. General Specifications for FRIDGEVAP FVP-C3

Overall Dimensions	81 x 168 x 188 cm (32 x 66 x 74 in.)
Estimated Dry Weight	544 kg (1200 lb)
Electrical Connection Required	208 V/one phase/60 cycle, 11 kW maximum
Cooling Water Required	9.5 L/min (2.5 gpm) maximum
Heat Pump Medium	Freon 22
Heat Pump Heating Capacity	8.8 kW (30,000 Btu/h)
Electric Heater Heating Capacity	5.5 kW (18,800 Btu/h) each heater, 16.5 kW (56,300 Btu/h) total
Evaporator and Condenser Heat-Exchanger Tube Bundles	Three 2.54 cm (1 in.) OD titanium tubes
Concentrate Tank Volume	28.4 L (7.5 gal)
Distillate Tank Volume	28.4 L (7.5 gal)
Evaporator And Condenser Shells	Schedule 80 chlorinated PVC tubing, 1-m long (3 x 40 in.) and 7.6-cm dia
Separator Shells	Schedule 80 CPVC, 7.6 cm (3 in.) dia Schedule 80 CPVC, 10.2 cm (4 in.) dia Schedule 80 CPVC, 15.2 cm (6 in.) dia
Vapor Uptakes	Twin 5.1-cm (2 in.) dia Schedule 80 CPVC tubes
Evaporator and Condenser Pressure	100 mm Hg (2 psia)

The evaporator will sit inside a 7.6-cm (3-in.) deep stainless steel pan. This pan will form a secondary container for the evaporator and will be able to hold the total liquid contents of the evaporator and tanks (about 75 L total) should a major leak occur.

The eventual use of concentrated acids as feeds requires that key parts of the evaporator be enclosed in a hood. Feeds containing mixtures of nitric, phosphoric, sulfuric, oxalic, and possibly hydrofluoric acids are anticipated in the experimental work involving acids. Because experimental goals include evaporation of acidic solutions, acids in the separator and condenser sections (as distillate) must be anticipated.

Under normal operation, the evaporator, separator, and condenser sections, which will contain the acids, are not open to the atmosphere. Maintenance and design-change operations, however, will require disassembly of these sections at key points. Most important, the heat-exchanger tube bundles in both the evaporator and condenser shells will need to be pulled out on occasion. These bundles are pulled out with the water boxes, that is, with the headers that feed the heating and cooling water to the tube bundles (see Fig. 38). Therefore, the flanges at which these water boxes connect to the respective shells need to be contained within a hood.

A Vac-Frame hood has been put in and is being modified for use with the LICON FVP-C3. Plumbing complexities necessitated joining the hood with the evaporator. For the evaporator design, LICON has incorporated an end plate for the hood into the evaporator plumbing, as shown in Fig. 38; the existing hood end plate is being modified accordingly. Installation of the evaporator will involve sliding the evaporator and hood together and bolting the new end plate onto the hood.

The drawing consists of two views: a side elevation at the top and a front elevation below it.

Side Elevation (Top): Shows a rectangular duct with a height of 92 cm. A label 'Duct' is inside. On the right side, there are two horizontal pipes labeled 'Cond.' (top) and 'Evap.' (bottom).

Front Elevation (Bottom): Shows the hood's profile with a total height of 213 cm (84"). The top section is the 'Hood End Plate' (91 cm x 37 cm / 36" x 14 1/2") with a '3.8 cm x 7.6 cm (1 1/2" x 3") Rib, both ends'. Below this is the 'Hood Base' (56 cm / 22" high). The 'Drip Pan' is located between the end plate and the base. On the right side, there are two horizontal pipes labeled 'Cond.' and 'Evap.', with 'Water Boxes' indicated. The 'Hood End Plate' is made of 0.32 cm (1/8") Aluminum (6061), 91 cm W x 173 cm H (36" x 68 1/8"), with a 56.7 cm (22 15/16") off pad supplied by LICON. The 'existing top plate' is 91 cm x 37 cm (36" x 14 1/2"). The 'existing bottom plate' is 91 cm x 31.8 cm (36" x 1 1/4"). The 'Load distribution pad' is 0.95 cm (3/8") thick, plus a 0.32 cm (1/16") thick drip pan. The 'Evaporator Frame' is at the bottom. The total width is 213 cm (84").

Fig. 38. Orientation of Hood and Evaporator

REFERENCES

1. K. S. Bhatki, *Radiochemistry of Bismuth*, NAS-NS-3061, published by Energy Research and Development Administration (1977).
2. P. J. Durrant and B. Durrant, *Introduction to Advanced Inorganic Chemistry*, John Wiley and Sons, New York, pp. 789-795 (1970).
3. J. D. Smith, *Comprehensive Inorganic Chemistry*, Ed., J. C. Bailar et al., Pergamon Press, London, Vol. 2, pp. 547-683 (1973).
4. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed., Interscience Publishers, New York (1972).
5. R. M. Smith and A. E. Martell, *Critical Stability Constants*, Vol. 4, *Inorganic Complexes*, Plenum Press, New York (1976).
6. F. Nelson, T. Murase, and K. A. Kraus, *J. Chromat.* 13, 503 (1964).
7. F. W. E. Strelow, R. Rethemeyer, and C. J. C. Bothma, *Anal. Chem.* 37, 106 (1965).
8. F. Nelson and K. A. Kraus, *J. Am. Chem. Soc.* 76, 5916 (1954).
9. A. K. De, S. M. Khopkar, and R. A. Chalmers, *Solvent Extraction of Metals*, Van Nostrand Reinhold, London (1970).
10. S. Kitahara, *Bull. Inst. Phys. Chem. Res. Tokyo* 24, 454 (1948).
11. H. M. Irving and F. J. C. Rossotti, *Analyst* 77, 801 (1952).
12. B. Z. Iofa and V. N. Vysotskii, *Radiokhimiya* 4, 238 (1962).
13. G. W. C. Milner, G. A. Barnett, and A. A. Smales, *Analyst* 80, 380 (1955).
14. R. Bock and E. Bock, *Z. Anorg. Allge. Chem.* 263, 147 (1950).
15. J. C. Sheppard, *J. Inorg. Nucl. Chem.* 29, 848 (1967).
16. J. Marechal-Cornill and E. Picciotto, *Bull. Chem. Soc. Belges* 62, 372 (1953).
17. J. C. Sheppard, *The Extraction of Polonium(IV) and Bismuth(III) from Nitric Acid by Several Organic Solvents*, U. S. Atomic Energy Commission Report HW-83226 (1964).
18. F. Aoki and H. Tamioka, *Bull. Chem. Soc. Japan* 38, 1557 (1965).
19. D. H. Templeton and L. G. Bassett, *Analytical Chemistry of the Manhattan Project*, Ed., C. J. Rodden, McGraw-Hill Book Co., New York, pp. 321-338 (1950).

20. L. Meites, *Handbook of Analytical Chemistry*, McGraw-Hill Book Co., New York, pp. I-14 to I-15 (1963).
21. E. P. Horwitz, M. D. Deitz, and R. Chiarizia, accepted for publication in *Solvent Extraction and Ion Exchange*.
22. W. D. Fairman and J. Sedlet, *Anal. Chem.* 40, 2004 (1968).
23. H. C. Paxton, J. T. Thomas, D. Callihan, and E. B. Johnson, "Critical Dimensions of Systems Containing U^{235} , Pu^{239} , and U^{233} ," U.S. Atomic Energy Commission Report TID-7028 (1964).
24. "American National Standard for Nuclear Criticality Safety in Operations with Fissionable Materials Outside Reactors," American Nuclear Society, ANSI/ANS-8.1-1983 (Revision of ANSI N16.1-1975), LaGrange Park, IL (1983).
25. G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters*, Wiley Publishing, New York (1978).
26. John A. Dean, *Lange's Handbook of Chemistry*, McGraw-Hill Book Co., New York (1972).
27. P.-K. Tse, L. Reichley-Yinger, and G. F. Vandegrift, *Sep. Sci. Technol.* 25 (13-15), 1763-1775 (1990).
28. R. Chiarizia and E. P. Horwitz, *Solvent Extrac. Ion Exch.* 8 (6), 907-941 (1990).
29. D. Mackay, W. Y. Shiu, and R. P. Sutherland, *Environ. Sci. Technol.* 13(3), 333-337 (1979).
30. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, John Wiley and Sons, New York (1960).
31. M. Jakob, *Heat Transfer*, Vol. 1, John Wiley & Sons, New York (1949).
32. J. R. Sellars, M. Tribus, and J. S. Klein, *Trans. ASME* 78, 441-448 (1956).
33. R. Siegel, E. M. Sparrow, and T. M. Hallman, *Appl. Sci. Res.* A7, 386-392 (1958).
34. H. J. Hickman, *Trans. ASME, J. Heat Transfer* 96, 354-358 (1974).
35. S. Kakac, R. K. Shah, and W. Aung, *Handbook of Single Phase Convective Heat Transfer*, John Wiley and Sons, New York (1987).
36. A. K. Zander, R. Qin, and M. J. Semmens, *J. Env. Eng.* 115, 768-784 (1989).
37. W. L. McCabe and J. C. Smith, *Unit Operations of Chemical Engineering*, McGraw-Hill Book Co., New York (1976).
38. A. F. Siebert, X. Py, M. Mshewa, and J. R. Fair, "Hydraulics and Mass Transfer Efficiency of a Commerical Scale Membrane Extractor," presented at Sep. Sci. Technol. Meeting, Oak Ridge, TN, October 22, 1991.

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