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Separation Science and Technology Semiannual Progress Report

October 1992–March 1993

by G. F. Vandegrift, S. Betts, D. L. Bowers,
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SEPARATION SCIENCE AND TECHNOLOGY
SEMIANNUAL PROGRESS REPORT

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Chemical Technology Division

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	1
I. INTRODUCTION	3
II. TRUEX TECHNOLOGY DEVELOPMENT	4
A. Validation of the Generic TRUEX Model	4
B. Application and Modification of Generic TRUEX Model	7
1. Evaluation of Neodymium Runs	7
2. Changes to Model	9
3. Model Needs	9
4. Changes to Solvent Loading Module	11
C. Bismuth Extraction Behavior	11
D. Centrifugal Contactor Development	14
E. Combined TRUEX-SREX Processing	15
1. Solvent Properties	15
2. Aqueous Sampling from the Bottom of a Stage	17
3. Titration Techniques	18
F. Treatment of Plutonium-Containing Waste	19
1. Analysis of Plutonium from Batch 1	19
2. Analysis of Plutonium from Batch 2	19
III. DEVELOPMENT OF ADVANCED EVAPORATOR TECHNOLOGY	20
A. Tests of Laboratory-Scale Evaporator	20
1. Distilled Water Tests	20
2. Feed Simulation Tests	24
3. Determination of Evaporator Decontamination Factors	27
B. Vapor-Liquid Equilibrium Data	34
1. Nitric Acid-Water System	34
2. Nitric Acid-Sulfuric Acid-Sodium Nitrate System	37
IV. TECHNICAL SUPPORT FOR WASTE MANAGEMENT OPERATIONS	46
A. Preliminary Waste Segregation and Treatment Schemes	46

TABLE OF CONTENTS (contd)

B.	Treatment Plan for NonTRU Aqueous Mixed Waste.....	46
1.	Chemical Treatment/Precipitation	50
2.	Filtration	55
C.	Compliance with Hanford Waste Acceptance Criteria	55
D.	Evaluation of Horizontal Agitated Film Evaporation Technology	57
E.	Treatment of Liquid Scintillation Cocktail Wastes	59
REFERENCES		61

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Distribution Ratios for Forward Extraction of ^{210}Bi between $\text{HNO}_3/\text{NaNO}_3$ Solutions and TRUEX/NPH as a Function of Nitric Acid Concentration at 25°C	12
2.	Distribution Ratios for First Back Extraction of ^{210}Bi between $\text{HNO}_3/\text{NaNO}_3$ Solutions and TRUEX/NPH as a Function of Nitric Acid Concentration at 25°C	13
3.	Distribution Ratios for Second Back Extraction of ^{210}Bi between $\text{HNO}_3/\text{NaNO}_3$ Solutions and TRUEX/NPH as a Function of Nitric Acid Concentration at 25°C	13
4.	Schematic of Laboratory-Scale Evaporator Including Location of Sensors	21
5.	Temperature of Major Process Streams vs. Time for Distilled-Water-Feed Run	23
6.	Temperature of Major Heating- and Cooling-Water Streams vs. Time for Distilled-Water-Feed Test	23
7.	Comparison of Calculated Samarium Concentrations by NAA with As-Prepared Samarium Concentrations	32
8.	Schematic of Laboratory Still	35
9.	Boiling Temperature versus Nitric Acid Concentration in Liquid Phase	36
10.	Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase	36
11.	Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase for 0.09M NaNO_3	41
12.	Equilibrium Temperature versus Nitric Acid Concentration in the Liquid Phase for 0.09M NaNO_3	41
13.	Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase for 0.92M NaNO_3	42
14.	Equilibrium Temperature versus Nitric Acid Concentration in the Liquid Phase for 0.92M NaNO_3	42
15.	Sample Calibration Curve for the Sodium Ion Selective Electrode	43
16.	Segregation Scheme for ANL and NBL Liquid Radioactive Waste	47
17.	Preliminary Treatment Scheme for All-Organic Wastes	48
18.	Preliminary Treatment Scheme for Organic/Aqueous Mixtures and Aqueous Wastes	49
19.	Overall Scheme for Treatment of Mixed Wastes Containing Toxic Metals	50
20.	Flowsheet for Alkaline Sulfide Flocculation/Precipitation Vessel	53

LIST OF FIGURES (contd)

<u>No.</u>	<u>Title</u>	<u>Page</u>
21.	Piping and Instrumentation Diagram for the WMO Filtration Skid	56
22.	Schematic Drawing of Rototherm Evaporator.....	58

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Initial Aqueous Composition of Neutralized Cladding Removal Waste Sludge	5
2.	Species Concentrations and Distribution Ratios (D) after TRUEX Processing of Neutralized Cladding Removal Waste Sludge.....	6
3.	Distribution Ratios for ^{210}Bi between $\text{HNO}_3/\text{NaNO}_3$ and TRUEX/NPH Solutions as a Function of HNO_3 Concentration at 25°C	12
4.	Viscosity and Density for Several Solvents.....	16
5.	Dispersion Numbers over a Range of Conditions for Several Solvents	17
6.	Data Time Line for Evaporator Run Using Distilled H_2O Feed	22
7.	Composition of Simulated WMO Evaporator Feed	25
8.	Aluminum Concentrations in the Feed and Concentrate Samples of Run 2 Determined by Titration with 0.512M NaOH	29
9.	Percentage of Gamma Ray Attenuation for the Feed and Concentrate Samples from Evaporator Run 2 Compared to Deionized (DI) Water.....	29
10.	Actual and Experimental Concentrations of Samarium.....	31
11.	Concentration of Samarium Determined by NAA for the Feed and Concentrate Samples from Evaporator Run 1	32
12.	Concentration of Samarium Determined by NAA for the Feed and Concentrate Samples from Evaporator Run 2	33
13.	Samarium Concentrations Determined by NAA for the Feed and Concentrate Samples from Evaporator Run 1	33
14.	Corrected Samarium Concentrations from NAA and ANL Calculated Concentrations for the Feed and Concentrate Samples from Evaporator Run 2	33
15.	Decontamination Factor for the LICON Laboratory-Scale Evaporator.....	33
16.	Resolution and Accuracy of Data Acquisition Card for J-type Thermocouple	34
17.	Vapor-Liquid Equilibrium Data for the Binary $\text{HNO}_3\text{-H}_2\text{O}$ System.....	36
18.	Composition of Prepared Solutions and Equilibrium Solutions as well as Equilibrium Temperatures for Solutions Containing 0.09M NaNO_3	40
19.	Composition of Prepared Solutions and Equilibrium Solutions as well as Equilibrium Temperatures for Solutions Containing 0.93M NaNO_3	40
20.	Sample Calibration Data for the Sodium ISE	43

LIST OF TABLES (contd)

<u>No.</u>	<u>Title</u>	<u>Page</u>
21.	Ratio of Sodium Concentration in the Liquid and Initial Samples with the Same Ratio for Sulfuric Acid for Equilibrium Solutions of Approximately 0.09M NaNO ₃	44
22.	Ratio of Sodium Concentration in the Liquid and Initial Samples with the Same Ratio for Sulfuric Acid for Equilibrium Solutions of Approximately 0.92M NaNO ₃	45
23.	Experimental Results for Treatment of Simulated Waste Containing RCRA Metals	54
24.	Synthetic Feed Solution for the Concentrator	57

SEPARATION SCIENCE AND TECHNOLOGY
SEMIANNUAL PROGRESS REPORT
October 1992—March 1993

ABSTRACT

This document reports on the work done by the Separations Science and Technology Section of the Chemical Technology Division, Argonne National Laboratory, in the period October 1992—March 1993. 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) evaporation technology for concentrating radioactive waste and product streams such as those generated by the TRUEX process and (2) treatment schemes for liquid wastes stored or being generated at Argonne.

SUMMARY

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

The objectives of TRUEX processing are to recover valuable TRU elements and to lower disposal costs for the nonTRU waste product of the process. A 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.

Calculations with the GTM were compared with literature data on TRUEX processing of sludge waste at the Hanford site. Two observations were made: (1) the measured and calculated distribution ratios for Am and Pu agreed within the experimental error, and (2) the measured extraction of zirconium and fluoride was much higher than that calculated by the GTM. New models are thus being developed for zirconium and fluoride extraction. The GTM is also being used to design a flowsheet for recovering TRU elements from aluminum-clad PuO₂ targets for Oak Ridge National Laboratory.

During this period, new features were added to the GTM so that it could reroute an effluent from one section of the process to a section other than the normal one, account for the effects of high solvent loading, and handle extraction efficiencies of less than 100% at each stage. Also, experiments were conducted on the extraction behavior of bismuth—an important component in the Hanford nuclear waste storage tanks. These data will be incorporated into the data base generated for the GTM.

An effort is underway to demonstrate the new TRUEX-SREX process, which is a combination of the TRUEX process and a recently invented SREX (strontium extraction) process. Both these processes were invented in the ANL Chemistry Division. The GTM was used to develop a TRUEX-SREX flowsheet that will handle the expected range of feed compositions for dissolved sludge waste from the Hanford site. A solvent with the desired dispersion number for this process has been identified. Work is underway to experimentally verify the operation of the TRUEX-SREX flowsheet with a 20-stage centrifugal contactor.

A multi-year project on using the TRUEX process for treating plutonium-containing waste from ANL and the New Brunswick Laboratory is nearing completion. The test results have demonstrated (1) the ability of the GTM to design workable flowsheets based on waste feed compositions and (2) the use of the TRUEX process for treating real waste streams.

An effort has been initiated to develop evaporator technology for concentrating radioactive waste and product streams such as those generated by the TRUEX process. A laboratory-scale evaporator fabricated by LICON, Inc., was tested with distilled water (to establish baseline operational parameters) and an evaporator feed tank sample. The information from these tests will help in the future processing of acidic solutions in the evaporator. Experiments were also done to determine the evaporator decontamination factors and vapor-liquid equilibrium data.

A substantial effort involved support to ANL Waste Management Operations. Activities included assisting them in determining the optimum treatment schemes (including automated systems where practical) for radioactive liquid wastes, specifying treatment processes and appropriate equipment for carrying out those processes, and generating needed documentation (permit applications, safety reviews, operations manuals, etc.).

I. INTRODUCTION

(G. F. Vandegrift)

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

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

Two other projects have recently been initiated in separation science and technology. The objectives of these projects are (1) to develop evaporation technology for concentrating radioactive waste and product streams such as those generated by the TRUEX process and (2) to assist ANL Waste Management in treating radioactive and hazardous waste generated as a result of research activities at ANL.

II. TRUEX TECHNOLOGY DEVELOPMENT

A. Validation of the Generic TRUEX Model (M. C. Regalbuto)

Data on TRUEX processing of real waste have been extracted from a Pacific Northwest Laboratory report by J. L. Swanson¹ to compare with GTM predictions. The sludge is currently being stored at Hanford site (Richland, Washington). This sludge contains large amounts of Zr and Na compounds, primarily hydroxides and fluorides. It also contains U, Pu, Am, and a mixture of fission products typical of those present in irradiated reactor fuel. The bulk of the sludge was first dissolved in nitric acid, then Am and Pu were extracted from Zr and other inert components by the TRUEX solvent at appropriate extraction and scrubbing conditions. Tables 1 and 2 summarize Swanson's results.

Important conclusions of this comparison between measured and GTM-predicted results are

- (1) Americium and plutonium distribution ratios were found to be in agreement. Some values were higher and some were lower, but differences were within experimental error by Swanson.²
- (2) The measured distribution ratios of zirconium and fluoride were much higher than calculated by the GTM. These differences were beyond experimental error and, therefore, are due to zirconium/fluoride extraction not being accounted for accurately in the GTM.

Equilibrium speciation calculations were performed using Swanson's data for aqueous feed compositions. As a result of these calculations, we concluded that Zr/F extraction could be accounted for by assuming the extractability of ZrF_4 , which was the dominant species present for the different feeds given by Swanson. The value for the distribution ratio of ZrF_4 was obtained by fitting the distribution ratios measured by Swanson for zirconium and fluoride. As suggested by Swanson, more weight was put on the fluoride extraction data.²

The modified model was then tested using zirconium tracer data collected at Argonne National Laboratory (ANL). However, the calculated extractability of ZrF_4 was not consistent with our own distribution ratio data for zirconium and fluoride. This discrepancy could be explained if Swanson's feed compositions, used to calculate the thermodynamic speciation, were perhaps not for equilibrium conditions but a metastable mixture of hydrolyzed zirconium species. Evidence for this are: (1) some of the solutions formed precipitates on standing and (2) interfacial crud formed for certain extractions. Since the speciation calculations used to determine the dominant species (ZrF_4) assume thermodynamic equilibrium, an inconsistency exists.

To establish a correlation to calculate distribution ratios for zirconium and fluoride, more information is needed about which zirconium species are present. We are currently concentrating our efforts in this area. A series of Zr/F/NO_3 solutions with high zirconium concentrations has been prepared. These solutions are being contacted with the TRUEX solvent, and both organic and aqueous phases for zirconium concentration are being determined using neutron activation analysis. These results will be used to upgrade the model in the GTM that calculates distribution ratios for zirconium and fluoride. We will also assume that a fraction of the zirconium in solution is present as a $(\text{ZrO}_2 \cdot n\text{H}_2\text{O})_m$ species that was not complexed by fluoride (thus, giving more free fluoride than calculated assuming all zirconium species were monomers) and that was somewhat extractable.*

*As will be reported in the following semiannual reports, ZrF_2 is now assumed to be the extractable species.

Initial Aqueous Composition in Molar units

Exp. No.	Na	Zr	H	H *	NO3	F-	C2O4	Al	Cr	Fe	U	Pu	Am	O/A	Notes
34 a	9.00E-01	1.30E-01	5.30E-01	9.14E-01	1.30E+00	5.10E-01		2.94E-02	4.36E-03	1.19E-03	4.80E-03	3.93E-06	1.45E-08	3.30E-01	
34 e	9.00E-01	1.30E-01	5.30E-01	9.14E-01	1.30E+00	5.10E-01		2.94E-02	4.36E-03	1.19E-03	4.80E-03	3.93E-06	1.45E-08	1.10E+00	
34 h	9.00E-01	1.30E-01	5.30E-01	9.14E-01	1.30E+00	5.10E-01		2.94E-02	4.36E-03	1.19E-03	4.80E-03	3.93E-06	1.45E-08	1.10E+00	
37 a	1.60E+00	2.20E-01	3.80E-01	1.04E+00	2.00E+00	8.40E-01		5.48E-02	9.64E-03	2.25E-03	1.10E-02	7.27E-06	2.89E-08	3.30E-01	
37 k	1.52E+00	2.10E-01	3.62E-01	9.92E-01	1.90E+00	1.44E+00		5.22E-02	9.18E-03	2.14E-03	1.05E-02	6.92E-06	2.75E-08	3.10E-01	The composition shown in table one was changed by adding enough HF to increase its concentration to 0.6M; this diluted the sample by 5%.
37 m	1.58E+00	2.18E-01	3.76E-01	1.03E+00	1.98E+00	8.32E-01	5.00E-03	5.43E-02	9.54E-03	2.22E-03	1.09E-02	7.19E-06	2.86E-08	3.30E-01	The composition in table one was changed by adding enough H2C2O4 to increase its concentration to 0.005M; this diluted the sample by 1%.
37 o	8.00E-01	1.10E-01	9.00E-01	1.23E+00	1.71E+00	4.20E-01	2.50E-03	2.74E-02	4.82E-03	1.12E-03	5.49E-03	3.63E-06	1.45E-08	1.60E-01	Diluted 100% while adding H2C2O4 to 0.0025M and HNO3 to increase the acidity to 0.9M.
37 r	8.00E-01	1.10E-01	1.90E-01	5.21E-01	1.00E+00	4.20E-01	2.50E-03	2.74E-02	4.82E-03	1.12E-03	5.49E-03	3.63E-06	1.45E-08	5.00E-01	Diluted 100% while adding H2C2O4 to 0.0025M.
46 a	1.50E+00	1.20E-01	3.70E-01	9.21E-01	2.10E+00	5.80E-01		7.68E-02	1.16E-02	2.34E-03	1.95E-02	7.20E-06	2.65E-08	5.00E-01	
46 c	1.36E+00	1.09E-01	4.70E-01	9.71E-01	2.04E+00	5.27E-01	4.50E-03	6.98E-02	1.05E-02	2.13E-03	1.77E-02	6.55E-06	2.41E-08	2.50E-01	Diluted 10% while adding H2C2O4 to 0.0045M and adding HNO3 to increase the acidity to 0.47M.
46 e	1.45E+00	1.16E-01	4.10E-01	9.44E-01	2.08E+00	5.61E-01	1.60E-03	7.43E-02	1.12E-02	2.27E-03	1.89E-02	6.97E-06	2.57E-08	5.00E-01	Diluted 3.3% while adding H2C2O4 to 0.0016M and adding HNO3 to increase the acidity to 0.41M.
47 c	1.10E+00	1.50E-01	5.50E-01		1.60E+00	5.50E-01						5.40E-06	1.33E-08	5.00E-01	
41 c	8.00E-01	1.30E-01	6.20E-01	1.02E+00	1.60E+00	4.40E-01		3.84E-03	5.04E-03	1.17E-02	1.60E-02	9.80E-06	1.08E-07	5.00E-01	
34 d	8.90E-01	1.17E-01	3.40E-01	5.74E-01								2.40E-07	1.57E-09	3.30E-01	Second extraction; aqueous phase was raffinate from contact of solution 34a with the TRUEX solvent.
37 b	1.60E+00	1.79E-01	1.90E-01	5.48E-01		5.60E-01						1.60E-07	2.53E-09	3.30E-01	Second extraction; aqueous phase was raffinate from contact of solution 37a with the TRUEX solvent.
47 d				3.98E-07								9.88E-08	9.52E-10	5.00E-01	Second extraction; aqueous phase was raffinate from contact of solution 47c with the TRUEX solvent. Also, diluted 1.2% while adding HNO3 to increase the acidity by 0.19M.
41 d	8.40E-01	1.15E-01	4.60E-01	6.90E-01		5.80E-01						6.67E-08	2.05E-09	5.00E-01	Second extraction; aqueous phase was raffinate from contact of solution 41c with the TRUEX solvent.

* H concentration considering no hydrolysis

Table 1. Initial Aqueous Composition of Neutralized Cladding Removal Waste Sludge. Data from Ref. 1, Tables 2 and 3.

Exp. No.	Na		H		Pu		Am			Zr			F		
	Aq. Conc.	Aq. Conc.	Org. Conc.	Aq. Conc.	D value	Org. Conc.	Aq. Conc.	D value	Org. Conc.	Aq. Conc.	D value	Org. Conc.	Aq. Conc.	D value	
34 a	0.89	0.34		1.3E-05	2.4E-07	60	4.9E-08	1.6E-09	30	0.04	0.12	0.3	0.05		
34 e	0.98			3.9E-06	3.3E-08	100	1.2E-08	7.2E-10	20	0.02	0.11	0.2			
34 h	0.97	0.0		4.6E-06	6.7E-08	70	1.9E-08	2.4E-10	90	0.03	0.11	0.3	0.05		
37 a	1.60	0.19		2.1E-05	1.6E-07	100	4.9E-08	2.5E-09	20	0.05	0.18	0.3	0.10	0.56	0.17
37 k	1.06			6.9E-06	2.3E-07	30				≤0.15	0.05	≤0.3			
37 m	1.56	0.20		3.7E-05	1.6E-07	200	1.0E-07	2.5E-09	40	0.05	0.17	0.3	0.09	0.59	0.15
37 o	0.80	0.83		3.2E-05	2.4E-07	100	6.0E-08	1.6E-09	40	0.02	0.09	0.2	0.06	0.36	0.16
37 r	0.80	0.12		1.1E-05	8.7E-08	100	2.2E-08	6.0E-10	40	0.02	0.08	0.3	0.10	0.30	0.32
46 a	1.55	0.19		2.1E-05	5.3E-08	400	6.5E-08	4.8E-10	200	0.03	0.10	0.3	0.07	0.47	0.14
46 c	1.42	0.31		2.1E-05	1.6E-07	100	6.3E-08	1.8E-09	30	0.02	0.10	0.2			
46 e	1.54	0.69		1.6E-05	1.0E-07	200	6.5E-08	4.8E-10	100	0.03	0.08	0.3	0.06	0.40	0.14
47 c				1.4E-05	1.0E-07	200	4.0E-08	9.6E-10	40				0.08		
41 c	0.84	0.46		1.8E-05	6.7E-08	300	1.7E-07	2.0E-09	80	0.02	0.12	0.2	0.06	0.58	0.10
34 d	0.88	0.23		5.4E-07	6.0E-08	9	4.3E-09	1.4E-10	30	0.04	0.11	0.3			
37 b	1.55	0.18		3.3E-07	5.3E-08	6	≤6.02E-09	≤3.61E-10	≥20	0.07	0.16	0.5	0.12	0.74	0.16
47 d				1.9E-07	≤6.7e-9	≥30	2.0E-09	≤1.20E-10	≥20				0.08	0.47	0.17
41 d	0.84	0.35		1.4E-07	≤1.3e-9	>100	4.1E-09	2.4E-11	200	0.02	0.10	0.2	0.07	0.58	0.12

Table 2. Species Concentrations and Distribution Ratios (D) after TRUEX Processing of Neutralized Cladding Removal Waste Sludge. Data from Ref. 1, Table 3.

B. Application and Modification of Generic TRUEX Model

(R. A. Leonard, J. M. Copple, M. C. Regalbuto, and G. F. Vandegrift)

The SASSE worksheet was developed for detailed evaluation of proposed TRUEX flowsheets in conjunction with distribution ratios calculated by the SASPE worksheet. It works for any amount of other-phase carryover and gives the steady-state concentration profile for each feed component without requiring any iterations. When SASSE is used independently, the appropriate distribution-ratio (D) values or equations must be supplied by the user. When it is used within the Generic TRUEX Model, these ratios are calculated by SASPE. All worksheets were developed using the Microsoft Excel spreadsheet.

The SASSE_Generator macro is being revised so that we can use the SASSE worksheet and the GTM to develop a TRUEX flowsheet for processing Mark 42 targets (aluminum-clad PuO_2 irradiated at Savannah River Plant to high burnup) at Oak Ridge National Laboratory (ORNL). Before irradiation, each target consisted of three concentric hollow cylindrical tubes that were 4.06 m (160 in.) long. The outside diameter of the outer tube was 102 mm (4 in.). The amount of aluminum in the target tubes was 28 kg, with 3.3 kg of plutonium, mostly as ^{239}Pu , embedded in the aluminum during fabrication. After irradiation, the amount of plutonium left in the target is only 0.3 kg and most of the plutonium mass is ^{242}Pu . The rest of the plutonium is now present either as the higher actinide elements, mainly Am and Cm, or as fission products. A target is cut up into eight segments, each 508 mm (20 in.) long. Before TRUEX processing of a target segment in the three mini-mixer-settlers (16 stages each) at ORNL, the target must be dissolved. Aluminum cladding is first removed by a caustic leach process. The remaining solids are dissolved in 7M HNO_3 . The resulting solution is concentrated by evaporation so that the final solution volume is greatly reduced. While nitric acid concentrations as low as 0.5M can be achieved if they are desired, concentrations after fuel dissolution and evaporation in the range of 1 to 2M are typical. Based on the feed tanks available at ORNL, the volume of the aqueous feed for the Mark 42 TRUEX flowsheet should be no more than 15 L.

Work has been focused on the following: (1) evaluating two neodymium runs to determine the extraction efficiency for the mini-mixer-settlers, (2) making changes to SASSE and the GTM to help develop the Mark 42 TRUEX flowsheet, and (3) identifying and implementing needed GTM changes.

1. Evaluation of Neodymium Runs

In 1990, two cold runs, an extraction/scrub run and a stripping run, were done at ORNL using acidic neodymium nitrate as the feed. We evaluated the data using the GTM to see if we could determine the stage efficiency (E_a) of the 16-stage mini-mixer-settler at ORNL.

a. Extraction/Scrub

For the extraction/scrub run, the aqueous (DF) feed to the mixer-settler was at a flow rate of 0.98 L/h. It contained 0.123M neodymium and 2.2M HNO_3 . The organic (DX) feed was at a flow rate of 1.8 L/h. The solvent was the standard TRUEX NPH formulation, with 0.2M CMPO and 1.4M TBP diluted by NPH. Using this neodymium concentration and the expected loading of one neodymium per three CMPO, we calculated the solvent loading to be close to 200%. Since essentially all of the neodymium was contained in the organic (DP) effluent, this indicates that the neodymium loading mechanism changes at high solvent loadings such that one neodymium is extracted by less than three CMPO. The temperature for the stripping run was 45°C. This is

probably the temperature for the extraction/scrub run as well. At this high temperature, that is, above 30°C, one does not have to worry about a second organic phase forming at high solvent loadings. The high temperature was used in the cold tests to simulate conditions in the ORNL shielded cell facility, which operates at about 40°C.

Using the GTM to analyze this flowsheet, we found that not much HNO_3 will be scrubbed out of the organic (DP) effluent. Since this effluent was used for the organic feed for the strip test, we were not surprised to learn that the aqueous (EW) effluent from the strip test had a high concentration of HNO_3 . Since essentially all of the neodymium goes through the scrub section and out the DP effluent, the stage efficiency has essentially no effect on the concentration of neodymium in the scrub section, and so, cannot be calculated from the scrub data. Although the GTM works for neodymium concentrations of 0.00123M and 0.06M in the DF feed, it does not work when the concentration is 0.123M. As a result, we were not able to determine the stage efficiency that would be required to match the calculated neodymium concentration profile in the extraction section with the measured profile. However, based on preliminary GTM calculations at related conditions, some of which suggest that E_a is greater than 1.0 (100%), the stage efficiency for the mini-mixer-settler appears to be good, 0.8 (80%) or higher.

Work is underway to improve the loading module so that the GTM is more realistic at high solvent loadings (see Sec. II.B.4). When that work is complete, we should be able to analyze the neodymium data in the extraction section and derive an appropriate E_a for the mini-mixer-settlers.

b. Strip

For the strip run, the organic (EX) feed was at a flow rate of 1.4 L/h. This feed was a composite of all the organic (DP) effluent from the extraction/scrub run and had a neodymium concentration of 0.058M. Its acid concentration was not measured. The aqueous (EF) feed had a flow rate of 1.07 L/h and contained 0.054M HNO_3 . The aqueous (EW) effluent had a neodymium concentration of 0.075M and an acid concentration of 0.59M.

The data from the neodymium stripping test were evaluated using the GTM to estimate the stage efficiency in the mixer-settlers. This analysis was thwarted because of two problems that developed in running the GTM. First, the GTM-calculated D values did not converge at an E_a of 1.0 (100%) because of apparent interactions with the D values and the concentrations for neodymium and HNO_3 . This is a continuing problem when using the GTM at high loadings. Second, the GTM broke down even sooner at E_a values less than 1.0, that is, 0.8 and 0.6. This is a problem that we had not encountered before, since we had not been using the E_a version of the SASSE worksheet. An analysis of this worksheet showed that the S_i term needs to be isolated from the full iterative loop of the Excel calculation, or the convergence of the SASSE worksheet can become unstable. This S_i term is $y_{i,j-1}/x_{i,j}$, where x is the molar concentration in the aqueous phase, y is the molar concentration in the organic phase, i is the component number, and j is the stage number. When E_a is 1.0, the S_i term is no longer a part of the calculation, so convergence of the worksheet is no problem. These results showed that some further changes are needed in the GTM so that it can be used at high loadings and at E_a values less than 1.0.

2. Changes to Model (R. A. Leonard)

Changes have been made to SASSE and the GTM so that the user can specify an extraction efficiency for each stage, define a fixed effluent flow rate for either the organic or aqueous phase at any process stage, and reroute an effluent from one section to a section other than the one to which it would normally go. This reroute feature is crucial if we are to evaluate flowsheets for the Mark 42 TRUEX process using the GTM.

a. Extraction Efficiency and Sampling Flows

Equations for the SASSE worksheet have been revised so that the user can specify an extraction efficiency for each stage and a fixed effluent flow rate for either phase at any stage in the SASSE worksheet, that is, sampling flows. These changes have been incorporated into the SASSE_Generator macro, with corresponding changes in other GTM files, and will be available as we develop a flowsheet for processing Mark 42 targets.

b. Reroute Macro

To purify the americium/curium/rare-earth product from plutonium ($\leq 0.1\%$ of plutonium in this product), a solvent scrub of this product stream is necessary. Therefore, the GTM needs to be able to introduce some of the organic solvent at the strip aqueous-scrub section and to have the interstage organic liquid skip over several processing stages (for example, the stages of the strip aqueous-scrub section) before it is reintroduced into the contactor. These changes were developed, tested, and incorporated into the SASSE_Generator macro and other GTM files in a general way so that a user can reroute an effluent (either aqueous or organic) from one section to a section other than the normal one.

In debugging the reroute macro, we found an error in the current SASSE_Generator macro. If the fraction of organic phase exiting from stage i that is taken as effluent (FEOI) is 1.0 for any stage except the last stage, that is, stage n , then the SASSE algorithm will fail because of divide-by-zero errors. This can be corrected if FEOI is made just slightly less than 1.0, for example, $1.0 - 1.0 \times 10^{-9}$. The amount subtracted from the 1.0, which is the value of FEOI_min, is enough to allow the SASSE algorithm to work correctly. Changes have been made to the SASSE_Generator macro so that the value of FEOI will always be slightly less than 1.0. This change fixes the problem. (This problem had not been seen up to now, as we had only taken organic effluent from the last stage.) With the reroute algorithm, organic effluent is now being taken at stages other than stage n and reintroduced as an external feed at some third stage. Hence, it was important to change the SASSE algorithm.

At present, the reroute feature is not accessible from the front end of the GTM. However, it is available if the FE_Loop of the GTM is used instead. This FE_Loop is what we are using to develop the Mark 42 TRUEX flowsheet.

3. Model Needs

Running the GTM with the new reroute macro and E_a for the first time resulted in the need for some minor adjustments, including transferring the E_a values and all the concentrations of the organic feed components from the export file to the SASSE worksheet. In addition, the SASPE worksheet was modified so that a single temperature correction factor controls the D values for

americium, curium, plutonium(III), and the rare earths. The default D values at 25°C are reduced by a factor of 0.621 to estimate the D values for 45°C. The factor is in the formula:

$$=EXP(2258*((1/(proc_temp + 273.2)) - 0.0033534))$$
 where proc_temp is the process temperature in degrees centigrade. This formula should work over process temperatures from 10 to 70°C.

The need for the GTM to handle higher solvent loadings has been recognized for some time and is being developed. However, it will not be available in time to use as we develop the Mark 42 TRUEX flowsheet.

To gain control over the convergence of D values from SASPE during the SASSE/SASPE iterations of the GTM calculations, we plan to implement the following two changes:

- Have a complete set of initial D values loaded for each feed component from the export file to the SASSE worksheet. If no D values are given, the default initial values supplied by the GTM will be used.*
- Be able to specify in the export file the number of previous D values that will be shown for each feed component at each stage. At the present time, the last two D values are shown. Having values from even earlier iterations should allow one to estimate more accurately the D values to use when restarting the calculation so that D values will, in fact, converge during the GTM iterations between SASSE and SASPE. Having more former D values present will allow new extrapolation routines to be developed that may facilitate convergence during normal GTM iterations.

To better control the convergence of the SASSE worksheet during the GTM calculations when E_a is less than 1.0, we plan to implement two other changes:

- The SASSE worksheet structure and procedure will be changed. The structure is changed so that a key row, which contains a ratio of two component concentrations, is repeated twice. This ratio is used only if E_a is less than 1.0. The procedure is changed so that, while the ratios are calculated by the first row, they can only be used when these values are copied and pasted to the second row. While these ratios are typically a minor part of the worksheet calculation, they destabilize it. By using a double row where the values are copied and pasted in a controlled manner (that is, by the user or by a macro) between worksheet iterations, this ratio is taken out of the iterative worksheet loop, and worksheet calculations are stabilized. The copy-and-paste transfer step is done as often as is needed to achieve convergence. Initial tests suggest that only one or two transfers will be needed.
- The basic GTM macro will be changed so that it uses this procedure when E_a is less than 1.0.

*These values are used in SASSE for the first interaction before SASPE is used to calculate D values for each component for each stage, based on the aqueous-phase composition for each stage.

4. Changes to Solvent Loading Module

The GTM's solvent loading module was upgraded to help generate TRUEX flowsheets for processing the Mark 42 targets. The upgrade consisted on making n_i , the extractant dependence for a given component i (moles of extractant/moles of component i), a function of free CMPO (CMPO_f).^{*} The following equations are used:

$$n_3 = 1 + \frac{2(1+C)\left(\frac{\text{CMPO}_f}{\text{CMPO}_o}\right)}{1+C\left(\frac{\text{CMPO}_f}{\text{CMPO}_o}\right)} \quad (1)$$

$$n_2 = 1 + \frac{(1+C)\left(\frac{\text{CMPO}_f}{\text{CMPO}_o}\right)}{1+C\left(\frac{\text{CMPO}_f}{\text{CMPO}_o}\right)} \quad (2)$$

Equation 1 is used when a feed component has a third-order dependence on CMPO in the old module and Eq. 2 when it has a second-order dependence. The value of the constant C was set equal to 2. This value was obtained after completing several runs using the GTM and comparing by how much the distribution ratio changed in going from unloaded to loaded solvent. So far these equations are empirical, and the value of C is based on "what looks about right." Further improvements are planned.

C. Bismuth Extraction Behavior (J. Sedlet)

Distribution ratios were measured for bismuth with the use of ^{210}Bi as the radioactive tracer. The method is described in the previous report (ANL-94/29, pp. 15-17). Previous measurements involving contacts with aqueous phases containing nitric acid concentrations below 0.5M HNO_3 have given variable results, even in the presence of high concentrations of nitrate ion. It has been suggested that this problem could be caused by (1) the presence of variable amounts of a higher oxidation state of bismuth, Bi(V) , rather than the normal Bi(III) or (2) the presence of small particles to which ions of ^{210}Bi attach themselves. The latter possibility is the result of two factors: (1) the ^{210}Bi has a short half-life (5 days), which means relatively few bismuth atoms are present, and (2) the ^{210}Bi is eluted from a crown ether/resin column each time it is used, and resin particles may be removed at the same time. The following experiments were performed to test these assumptions.

Three sets of distribution ratio measurements for bismuth were performed. Four different nitric acid concentrations (0.02, 0.10, 0.05, and 1.0M) were used, each containing 3.2M NO_3^- . The nitrate ion was kept constant by adding the appropriate amount of sodium nitrate. With one set, the usual extraction procedure was performed as follows. An aliquot of the freshly prepared ^{210}Bi tracer solution was added to 3-mL portions of the aqueous phase, mixed briefly, and the aqueous phase was contacted with 3 mL of TRUEX/NPH solvent for three 20-s periods at 25°C . The phases were

^{*} Amount of CMPO that is not loaded by metal, i.e., initial CMPO (CMPO_o) minus loaded CMPO.

separated by centrifuging, aliquots were taken for counting, and 2 mL of the organic phase was contacted for three 20-s periods with fresh aqueous solutions. This procedure was repeated with 1 mL of solvent and 1 mL of fresh aqueous phase. Thus, each set of extractions consisted of one forward and two back extractions.

This procedure was repeated, but to ensure that higher oxidation states of bismuth were not present, the tracer solution was made 0.05M in $\text{NH}_2\text{OH}\cdot\text{HNO}_3$ before evaporation to dryness, as was each aqueous phase before extraction. The ability of $\text{NH}_2\text{OH}\cdot\text{HNO}_3$ to reduce Bi(V) was tested with 100 mg of NaBiO_3 . This compound is brown, and its reduction to the colorless Bi(III) ion can be followed visually. To reduce or eliminate the possibility that particulate ^{210}Bi was present, the prepared ^{210}Bi tracer was passed through a 0.02- μm filter before use. The same distribution ratio measurements described above were performed with this tracer solution.

The results are given in Table 3 and plotted in Figs. 1-3. The data show considerable variability at the two lowest acid concentrations, but the reproducibility was much improved at the two highest concentrations. This is more apparent in the back extractions than in the forward, although some improvement is apparent in the forward also.

Table 3. Distribution Ratios for ^{210}Bi between $\text{HNO}_3/\text{NaNO}_3$ and TRUEX/NPH Solutions as a Function of HNO_3 Concentration at 25°C

Conc., M			D Value, Forward			$[\text{HNO}_3]$, M ^b	D Value, BACK-1			$[\text{HNO}_3]$, M ^b	D Value, BACK-2		
$[\text{NaNO}_3]$	$[\text{HNO}_3]^a$	$[\text{HNO}_3]^b$	A	B	C		A	B	C		A	B	C
3.18	0.02	0.00478	248	18	22	0.00858	1570	730	1170	0.0115	2100	1250	846
3.10	0.10	0.0272	141	79	54	0.0509	1300	1200	920	0.0686	1780	1220	451
2.70	0.50	0.208	448	568	158	0.372	445	408	386	0.451	327	312	385
2.20	1.0	0.534	239	253	163	0.851	153	163	159	0.957	132	138	137

^aInitial concentration, aqueous phase.

^bEquilibrium concentration, aqueous phase. These concentrations were calculated from the Generic TRUEX Model by Monica C. Regalbuto, CMT Division.

Fig. 1.

Distribution Ratios for Forward Extraction of ^{210}Bi between $\text{HNO}_3/\text{NaNO}_3$ Solutions and TRUEX/NPH as a Function of Nitric Acid Concentration at 25°C. The nitrate ion concentration was maintained constant at 3.2M; A = normal procedure, B = reducing agent present, and C = ^{210}Bi filtered through 0.02- μm filter.

Fig. 2. Distribution Ratios for First Back Extraction of ^{210}Bi between $\text{HNO}_3/\text{NaNO}_3$ Solutions and TRUEX/NPH as a Function of Nitric Acid Concentration at 25°C . The nitrate ion concentration was maintained constant at 3.2M ; A = normal procedure, B = reducing agent present, and C = ^{210}Bi filtered through $0.02\text{-}\mu\text{m}$ filter.

Fig. 3. Distribution Ratios for Second Back Extraction of ^{210}Bi between $\text{HNO}_3/\text{NaNO}_3$ Solutions and TRUEX/NPH as a Function of Nitric Acid Concentration at 25°C . The nitrate ion concentration was maintained constant at 3.2M ; A = normal procedure, B = reducing agent present, and C = ^{210}Bi filtered through $0.02\text{-}\mu\text{m}$ filter.

In general, the back extractions fall on a smooth curve, with the ratios decreasing with increasing acid concentration. The decrease is attributed to the high extraction of nitric acid in the presence of large nitrate ion concentrations, and the resulting decrease in free CMPO due to its association with nitric acid. There is no striking improvement in reproducibility from the two back extractions used. The tracer appears to have different properties each time it is prepared, and bismuth tends to hydrolyze in dilute nitric acid solution. These two possible reasons for the lack of reproducibility will be examined by repeating the normal runs with the use of long-lived ^{207}Bi , which has become available recently, and by converting some of the bismuth tracer to an acid chloride medium. Hydrolysis in hydrochloric acid solution is inhibited by the formation of a chlorobismuth complex and by the increased strength of HCl over HNO_3 .

D. Centrifugal Contactor Development

(R. A. Leonard, D. B. Chamberlain, and G. F. Vandegrift)

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 an effort to clean up the solvent so that it can be recycled and the solvent inventory minimized, we examined the possible use of an Argonne 4-stage minicontactor for TRUEX solvent cleanup as an integral part of the Mark 42 TRUEX process (Sec. II.B). However, the design and operation of the hot cell facility at ORNL are such that operations in the cell must be very simple. Also, there are only two pumps inside the cell, and they are needed for the main aqueous and organic feeds. Thus, even though there are three 16-stage mini-mixer-settlers already in the ORNL cell, because of the way they are connected, the addition of those four minicontactor stages would be very difficult.

In other contactor work (not directly related to TRUEX work), R. A. Leonard talked with D. J. Chaiko (Chemical Technology Division of ANL) about his problems with using aqueous biphasic systems as a separation technology in, for example, treating contaminated soil. These problems include: (1) phase densities that are 10% or less in difference, (2) one phase, the polyethylene glycol (also called the PEG or less-dense) phase, that has a high viscosity, (3) low interfacial tension between the two aqueous phases, and (4) the need to deal with solids during processing. The high viscosity and the low interfacial tension can be dealt with, to some extent, by varying the composition of the PEG phase. A Karr column appears adequate for some applications. However, because of its height, it cannot be used in radioactive work in gloveboxes or shielded cell facilities. A static mixer, the Kenics mixer, has worked well for mixing the two phases prior to phase separation. We also considered the possible use of centrifugal contactors with the aqueous biphasic systems.

For the aqueous biphasic systems, Leonard proposed a novel multistage unit using a Kenics mixer at each stage. Two pumps will be needed at each stage, one for each phase. The separating zone for each stage will need two weirs, one for the more-dense phase and one for the less-dense phase. This will allow for changes in the volume of the two phases from stage to stage and for slight changes in the pumping rates at various stages. The settler can be either a gravity settler or a centrifugal settler. In one version of this design, we would feed the output from the mixer to the bottom of the centrifugal settler and so avoid the mixing zone of the contactor, which may be a problem because of its high mixing intensity. If the annular mixing zone of the centrifugal contactor is not a problem, then the Kenics mixers can be eliminated along with the interstage pumps, and a much simpler design can be realized. Each of these process steps needs to be evaluated individually,

and based on tests of each step, the mechanical components will be combined so that they work together in the most effective way.

Chaiko reported that batch centrifuge tests of the aqueous biphasic system indicate low g forces, in the range from 2 to 19 g's. This allows for separation of the two aqueous phases in less than a minute while keeping the solids in the less-dense PEG phase. Based on these observations, Leonard designed a 4-cm contactor that would operate at 5 g's and so should allow continuous separation while keeping the solids that distribute to the less-dense phase in that phase. To test this concept, a special more-dense-phase weir could be built for an old one-stage 4-cm contactor, which has removable weirs. The rotor speed of the contactor would be 600 rpm rather than the normal 3600 rpm. However, even at this low rotor speed, the annular mixing zone has a Reynolds number that is about 100 times higher than that of the Kenics mixer. Thus, the annular mixer will give much better mixing than the Kenics mixer. Because the rotor is not self-pumping at this low rotor speed, there will always be a significant liquid head in the mixing zone.

E. Combined TRUEX-SREX Processing

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

The Chemistry Division (CHM) at Argonne has developed a new solvent extraction process that will selectively extract and partition U, Sr, Bi, the TRU elements such as Am and Pu, the lanthanides, and most of the Tc from dissolved sludge wastes (DSW) at the Hanford site. This process is a combination of the TRUEX process and the recently developed SREX (StRontium EXtraction) process. We are providing support for this effort by designing flowsheets and demonstrating the combined TRUEX-SREX process on a laboratory scale using the centrifugal contactor. This effort is being carried out in cooperation with E. P. Horwitz and H. Diamond of the CHM Division. In previous work (ANL-94/29, pp. 55-57), we measured dispersion numbers for the new solvent, developed a flowsheet for the process, and set up to verify experimentally the nitric acid portion of the flowsheet in the ANL minicontactor (2-cm centrifugal contactor). The actual test with nitric acid was put on hold because of difficulties in acquiring sufficient crown ether from the supplier (Parish Chemical Co., Orem, UT).

In FY 1993, we had planned to complete the nitric acid test, that is, the cold test of the combined TRUEX-SREX flowsheet, and then conduct a radioactive test of the process flowsheet. The required crown ether has been received and tested. However, because of funding delays, it appears that only the cold test will be completed. The radioactive test would be completed in FY 1994. In this report, we discuss several issues that support the flowsheet tests: solvent properties, aqueous sampling from the bottom of a stage, and titration techniques.

1. Solvent Properties

The composition of the combined TRUEX-SREX solvent was to have been 0.2M CMPO, 0.2M crown ether [4,4'(5')-di-t-butylcyclohexano-18-crown-6, referred to here as CE], and 1.2M diamyl amylphosphonate (usually written as DA[AP] or DAAP) in Isopar M. This combined solvent is referred to here as PS 9. Its use was abandoned after the dispersion number (N_{Di}) for the solvent was found to be too low. The search for a new solvent is reported here. The final choice, PS 12, is similar to PS 9, except that the diluent is Isopar L rather than Isopar M.

*Co-op student from University of Evansville, Evansville, IN.

a. Density and Viscosity

To determine the effect of density and viscosity on N_{Di} , we measured these properties for several solvents, as listed in Table 4. The density measurements, determined by weighing the solvent in a 250-mL volumetric flask, are accurate to within ± 1.0 g/L. The viscosity measurements, determined using a Brookfield Viscometer model LVF with an ultra-low adapter, are accurate to within ± 0.1 mPa·s. Note that the various solvent viscosities correlate most strongly with their diluent; that is, normal dodecane (nDD) solvents have viscosities in the range from 2 to 3 mPa·s; Norpar 12, 3 to 5 mPa·s; Isopar L, 4 to 6 mPa·s; and Isopar M, 8 to 9 mPa·s. For a given diluent, density increases as the amount and type of extractant and modifier increase.

Table 4. Viscosity and Density for Several Solvents

Solvent Name	Composition, M				Diluent	Viscosity, ^a mPa·s	Density, ^a g/L
	CMPO	CE	TBP	DA[AP]			
PS 6	0.2	0.2	1.2	-	Isopar L	4.5	871
PS 9	0.2	0.2	-	1.2	Isopar M	8.4	875
PS 10 w/o CE	0.2	-	-	1.2	Norpar 12	3.0	827
PS 10	0.2	0.2	-	1.2	Norpar 12	4.3	855
PS 12	0.2	0.2	-	1.2	Isopar L	5.4	865
T 1 ^b	-	-	1.47	-	nDD	2.2	838
T 2 ^c	-	-	2.33	-	nDD	2.7	891

^aMeasured at room temperature (23.5-25.0°C).

^bT 1 is 40.3% TBP in normal dodecane (nDD).

^cT 2 is 63.8% TBP in nDD.

b. Dispersion Number Measurements

The N_{Di} values for these solvents are listed in Table 5 for a range of process conditions. The measurement of N_{Di} was expanded to include the movement of the final interface between the two phases. When the movement of this interface has essentially stopped (i.e., there is no movement after successive 2- or 3-min intervals), the position of the interface relative to the position before shaking the 100-mL cylinder is used to determine the amount of A in O or O in A. The time to reach this position determines the N_{Di} value. The amount of A in O or O in A gives the other-phase carryover expected during contactor processing at this N_{Di} value. An N_{Di} value of 8×10^{-4} is typical of 30% TBP in dodecane and gives satisfactory performance in most solvent extraction equipment; other-phase carryover less than 1% is likewise acceptable.

No correlation was found between the dispersion numbers in Table 5 and the solvent densities in Table 4. In fact, solvent T 2, which has the highest density, has one of the highest dispersion numbers with one of the lowest other-phase carryovers. However, a reasonable correlation was found between the dispersion numbers in Table 5 and the solvent viscosities in Table 4. Both Isopar L and Norpar 12 acted to reduce the viscosity of the solvent, increase N_{Di} , and decrease other-phase carryover. As a result, both PS 10 and PS 12 looked to be borderline acceptable solvents for the combined TRUEX-SREX process. The PS 12 solvent has been chosen as the new process solvent because Isopar L gives a higher uranium loading in the solvent without third-phase formation than does the Norpar 12. In either case, the diluent should have little effect on the distribution ratios for metal ions to be extracted and, thus, on the process flowsheet.

Table 5. Dispersion Numbers over a Range of Conditions for Several Solvents

Solvent Name	Aqueous Phase	O/A = 0.33		O/A = 1.0		O/A = 3.0		Notes
		$N_{Di} \times 10^4$	Max. A in O, %	$N_{Di} \times 10^4$	Max. A in O, %	$N_{Di} \times 10^4$	Max. A in O, %	
PS 6	0.25M Na_2CO_3	7.7	3	5.1	4	1.4	25	
	0.1M HNO_3	16.7	2	5.1	2	4.2	2	
PS 9	0.25M Na_2CO_3	8.1	5	6.3	5	1.5	10	
	0.01M HNO_3	8.3	4	4.3	4	4.0	6	
	0.1M HNO_3	9.3	8	2.5	7	1.6	7	a
	0.1M HNO_3	7.4	9	2.7	3	2.6	4	
	0.1M HNO_3	12.4	3	9.2	1	3.6	1	b
	3.0M HNO_3	7.0	3	4.3	4	2.9	5	
	0.2M THFTCA	5.0	1 ^c	3.5	4	4.0	6	
PS 10 w/o CE	0.25M Na_2CO_3	9.9	2	7.4	3	8.7	3	
	0.1M HNO_3	7.9	1	7.1	1	7.1	1	
PS 10	0.25M Na_2CO_3	7.1	4	6.5	4	4.2	4	
	0.1M HNO_3	13.2	0.4	5.1	1	4.6	2	
PS 12	0.25M Na_2CO_3	11.6	4	8.3	6	3.7	3	
	0.1M HNO_3	13.4	2	4.5	1	4.1	4	
T 1	0.25M Na_2CO_3	7.1	1	7.1	1	6.4	1	
	0.1M HNO_3	13.2	0	16.2	0.4	15	0.4	
T 2	0.25M Na_2CO_3	11.6	1	6.4	1	5.8	1	
	0.1M HNO_3	22.9	0.4	6.8	0	6.9	0.8	

^aThe solvent was not contacted with sodium carbonate solution before this test.

^bThese dispersion tests were done at $48 \pm 5^\circ\text{C}$. All others were done at $24.3 \pm 0.8^\circ\text{C}$.

^cThis case gives max. O in A; max. A in O was less. Aqueous phase was the continuous phase.

2. Aqueous Sampling from the Bottom of a Stage

Aqueous sampling from the bottom of selected minicontactor stages is done on a continuous basis at a low flow rate through a low-volume sampling system. In preliminary work using a 20-stage 2-cm contactor for the combined TRUEX-SREX flowsheet (ANL-94/29, pp. 52-57), two of the eight stages where we had sampled the aqueous phase from the bottom of the stage contained large amounts of organic phase in what we expected to be organic-free aqueous samples. The solvent used was 40% TBP in nDD (Solvent T 1). Investigation into possible sources of the contamination revealed no obvious problems, although the two affected stages (stages 1 and 12) had swelling of the Viton sampling tubes near the end that connects to the capillary tube extending down from the bottom of the stage. These two swelled sections of tubing were removed. However, it was not known if this swelling was the cause or the result of the organic phase in the bottom sample.

To investigate further, a single-stage sampling test was performed on stage 1 of the 2-cm contactor used in the preliminary test. This single-stage sampling test was conducted by taking samples from the mixing zone at O/A flow ratios of 0.5, 1.0, and 2.0 for both organic- and aqueous-continuous operation; that is, flow through the stage was started with only organic or aqueous phase initially in the mixing zone, respectively. The organic flow rate remained constant at 9 mL/min for all of the O/A flow ratios, and the aqueous flow rates were 18 mL/min for the O/A flow ratio of 0.5, 9 mL/min for the O/A flow ratio of 1.0, and 4.5 mL/min for the O/A flow ratio of 2.0. Sampling from the bottom of the mixing zone was done using a 1.60-m length of Viton tubing with an inside

diameter of 0.8 mm. This tubing was fed through a standard Masterflex peristaltic pump head and driver. The sampling rate was 0.3 mL/min, and samples were collected for 10 min at a time. The organic phase for these tests was the solvent T 1 listed in Table 4.

The detailed procedure for sampling the mixing zone was as follows for the aqueous-continuous tests. First, the contactor motor and the aqueous feed pump were turned on. After the aqueous phase began to flow from the aqueous exit port, the organic feed pump was turned on. When the organic phase flowed from the organic exit port, the system was allowed to operate normally for about 1 min. Then, the sampling pump was turned on and allowed to run for about 4 min to clear the line of the water used to fill the tubing before the test. Next, three 10-min samples were collected from the bottom of the stage over a period of 30 min. The samples were then poured into a graduated 15-mL centrifuge tube (accurate to 0.1 mL) and examined to determine the amount of sample collected and the amount of organic phase present. The procedure was the same for the organic-continuous tests, except that the organic pump was turned on first (the rotor was still filled with aqueous phase from the previous test), and the aqueous pump was switched on after the organic phase began to exit the organic exit port. In no case was organic phase found in the samples drawn from the bottom of the stage.

Since the organic and aqueous feed rates used during the single-stage tests were lower than those used during the preliminary tests, two additional tests were made to try to match the aqueous and organic flow rates encountered in stages 1 and 12 of the preliminary test. The first test duplicated the flows encountered in stage 12, which had an organic flow rate of 12 mL/min and an aqueous flow rate of 12 mL/min. The second test had an organic flow rate of 12 mL/min and an aqueous flow rate of 20 mL/min. The maximum flow rate for the aqueous phase in the second test should have been 24 mL/min; however, 20 mL/min was the highest rate that we could attain with the available pump. It is not known if this small change in flow rate affected the results of the test. Each test was conducted for aqueous- and organic-continuous operation following the procedure given above. These tests also showed no sign of organic phase in the samples drawn from the bottom of the mixing zone.

In summary, it appears that our low-flow bottom sampling system will take aqueous phase samples from the mixing zone under the contactor stage. However, these tests used solvent T 1. The actual TRUEX-SREX tests will use solvent PS 12. Because PS 12 has a viscosity twice that of T 1, its behavior may be different from any of the results seen to date. Thus, this aqueous sampling system should also be tested with the solvent PS 12.

3. Titration Techniques

An automatic titrator, the Brinkmann Metrohm 670 Titroprocessor, which is used to titrate HNO_3 , was evaluated for measuring the concentration of tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) in aqueous samples containing HNO_3 . This was done so that we could measure the concentrations of both HNO_3 and THFTCA in the strip section of the TRUEX-SREX tests. When both HNO_3 and THFTCA are present, the titrator does not work, since the neutralization of THFTCA is masked by the neutralization endpoint of HNO_3 . To determine both endpoints, it is necessary to titrate the sample in an organic medium, isopropyl alcohol, where the difference in acid strengths of HNO_3 and THFTCA is far larger than in water. This is done with a second automatic titrator, the Brinkmann Metrohm 636 Titroprocessor. The aqueous sample containing both acids is mixed with isopropyl alcohol and titrated with 0.1M tributyl ammonium hydroxide (TBAOH) in

isopropyl alcohol. Thus, when both THFTCA and HNO_3 are in the process samples, they will be titrated in isopropyl alcohol.

After these acid concentrations are measured for a TRUEX-SREX contactor test, the results will be compared with the concentrations predicted by the GTM so that the ability of the GTM to model the combined TRUEX-SREX flowsheet can be evaluated.

F. Treatment of Plutonium-Containing Waste

(D. B. Chamberlain, D. L. Bowers, C. J. Conner, J. C. Hutter, R. A. Leonard, J. Sedlet, D. G. Wygmans, and G. F. Vandegrift)

The TRUEX process was used to treat plutonium-residue solutions (total of 200 L) generated by the New Brunswick Laboratory (NBL). These solutions, generated from the analysis of plutonium samples, have accumulated over the past several years at NBL and Argonne National Laboratory (ANL). These residues contained varying concentrations of nitric, sulfuric, phosphoric, and hydrochloric acids, plus U, Pu, Np, and Am. The TRUEX process was used to generate a nonTRU waste stream (≤ 10 nCi/mL) and recover the plutonium from the NBL waste. This processing was carried out in a 20-stage centrifugal contactor installed in a glovebox, with an organic solvent of TRUEX-nDD.

1. Analysis of Plutonium from Batch 1

The plutonium product stream generated during the processing of Batch 1 (ANL-94/29, p. 58) was evaporated and calcined. Two batches of oxide were produced from the calcination process: Batch 1a weighed 6.4 g and contained 6.2 g plutonium, while Batch 1b weighed 21.2 g and contained 3.4 g plutonium. Based upon analysis by inductively coupled plasma/atomic emission spectroscopy, Batch 1b was contaminated with sodium and potassium oxides. Because of the presence of these metals, it appears that some of the solution calcined was a carbonate wash solution and not a plutonium product stream. To remove these metals, the oxide product was washed several times with water--the sodium and potassium oxides should be soluble in water, while plutonium oxide should be relatively insoluble. Subsequent analysis, after washing, indicated that most of the Na and K had been successfully removed. For Batch 1, 11.69 g of oxide remains (after washing and analysis), containing 9.04 g of plutonium. The material was retained for use in future laboratory experiments.

2. Analysis of Plutonium from Batch 2

The plutonium product solution generated during the processing of Batch 2 (ANL-94/29, pp. 59-80) was calcined, generating 30.8 g of oxide containing 13.17 g of plutonium and 10.28 g of uranium. This material was disposed of as solid radioactive waste. Originally, the oxide product was to be assigned a batch number, converted to metal, and shipped to Idaho. However, the logistics in returning the recovered plutonium has proven to be costly, difficult, and time consuming. Therefore, to continue processing additional waste from NBL this year, we were forced to dispose of the oxide as solid waste. Even though this material was returned as waste, there was a significant reduction in TRU waste volume as a result of the TRUEX process.

III. DEVELOPMENT OF ADVANCED EVAPORATOR TECHNOLOGY

(D. B. Chamberlain, S. Betts,* S. Landsberger,* C. Conner, D. Taylor, and D. G. Wygmans)

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 concentrating radioactive waste streams and recycling the decontaminated condensates. A technology that shows a great deal of potential for this application is an evaporator being developed by LICON Inc. (Pensacola, Florida).

Initial studies will evaluate this technology for concentrating specific process streams in terms of (1) economic and institutional 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 ANL will work together to (1) design an evaporator specifically for remote operation and (2) in a hot facility at ANL, test the remote operability and maintenance of this evaporator and other equipment in glovebox, shielded-cell, and canyon facilities. In later stages of the program, this equipment will be installed in a DOE processing/production plant for actual in-plant demonstration.

A. Tests of Laboratory-Scale Evaporator

A laboratory-scale evaporator has been purchased from LICON, delivered to ANL, and installed. This evaporator is designed for processing 0.19 L/min (3 gal/h) and will be used to gather preliminary experimental data that will aid in eventual designs of a plant-scale evaporator and to gain experience in operating the LICON evaporator.

Two tests were completed to gain more information about the operation of the laboratory-scale evaporator with various feed solutions. These tests included (1) a test using distilled water as feed to establish baseline operational parameters and (2) a test with a simulated ANL Waste Management Operations (WMO) feed. The latter test was done to gain information about the problems that WMO may encounter with the LICON evaporators (5.7 L/min, 90 gal/h), which are planned for installation at ANL.

1. Distilled Water Tests

To establish baseline operational data for the evaporator, a test was completed using distilled water as the feed (Fig. 4) with electric heaters 1 and 2 set for 71°C (160°F) and heater 3 set for 69°C (157°F). The heating temperatures were the same as the previous two runs using salt-solution feeds, which are reported in the previous semiannual (ANL-94/29, p. 84). The results of this test can be used as a baseline for comparison with the previous salt-solution tests or with future tests.

A time line of data gathered during the test is given in Table 6, and some of the data are plotted in Figs. 5 and 6. For reasons cited below, efforts during the first section of the test were focused on taking temperature data; data for vacuum, distillate conductivity, and tank volumes (from which distillate production rate is calculated) were not taken at the same rate. This accounts for the many blank spaces in Table 6. As can be seen in that table, the distillate production rate for this run

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Fig. 4. Schematic of Laboratory-Scale Evaporator Including Location of Sensors

was about 0.22 L/min (3.5 gph). This is slightly higher than the 0.19 L/min (3.0 gph) stated capacity of the evaporator.

Note from Table 6 that the system vacuum decreased from 71 cm Hg (28 in. Hg), measured shortly after startup, down to 61 cm Hg (24 in. Hg) at steady state. These data, however, are suspect due to a problem with water vapor condensing in the vacuum-gauge line throughout the run, generating a hydraulic pressure head (about 2.5 cm Hg or 1 in. Hg) at the gauge by the end of the test. (This line had been emptied prior to the run, and condensation and water buildup in the line began almost immediately after the start of the run.) Since the vapor should be saturated steam, the system pressure at a given vapor temperature should be obtainable from tabulated data for steam. Such tabulated data show that, at the measured vapor temperature, the initial pressure was actually 73.7 cm Hg (29 in. Hg), instead of the 71 cm Hg (28 in. Hg) measured. The tabulated data also

Table 6. Data Time Line for Evaporator Run Using Distilled H₂O Feed

Elapsed Time, min	Temperatures, ^a °F									Vacuum, in. Hg	Distillate Conductivity, µS/cm	Distillate Production Rate, L/min	Concentrate & Feed Reduction Rate, L/min
	Cond. Water In, TC-1	Cond. Water Out, TC-2	Evap. Water Out, TC-3	Evap. Water In, TC-4	Dist., TC-5	Vapor, TC-6	Conc., TC-7	Feed, TC-10	Heater Tank Water, TC-11				
0	73	73	73	73	73	72	73	73	66	25.0	8.8	0.00	0.00
7	64	64	75	75	73	72	73	73	72	28.0			
16	63	64	89	91	72	78	73	73	94				
18	73	76	106	108	74	83	73	73	112				
20	80	83	114	119	77	93	95	86	120	27.5			
22	85	88	118	123	81	98	100	92	125				
24	90	93	123	128	86	103	105	98	131	27.0			
27	94	98	129	134	92	108	109	103	137	26.5			
30	98	102	133	139	98	112	114	108	142	26.0			
32	100	105	136	142	101	115	116	110	144	26.0			
34	103	107	139	144	105	117	119	114	147	26.0			
36	104	108	141	146	107	119	121	116	150	25.5			
38	106	110	143	149	110	121	123	119	152	25.0			
40	108	112	145	151	113	123	125	121	154	25.0	7.2	0.13	0.16
45	111	116	147	153	118	127	128	126	157	24.5			
48	112	117	148	153	120	127	128	127	155				
52	112	117	147	151	121	127	128	128	156		6.3	0.25	0.25
55	113	117	147	152	122	128	129	128	156	24.0	6.0		
66	111	115	146	151	122	126	127	120	155	24.0			
72	111	116	147	153	121	127	128	124	156	24.0			
90	112	117	146	151	123	127	129	128	156	24.0	4.1	0.22	0.21
115	112	116	146	150	122	127	129	128	155	24.0	3.4	0.20	0.20

^aT_{0C} = (T_{0F} - 32)/1.8.

Fig. 5. Temperature of Major Process Streams vs. Time for Distilled-Water-Feed Run

Fig. 6. Temperature of Major Heating- and Cooling-Water Streams vs. Time for Distilled-Water-Feed Test

suggest that the vapor pressure at steady state was probably 65 cm Hg (25.7 in. Hg), instead of the 61 cm Hg (24 in. Hg) measured. These adjustments are reasonable given the water problem in the vacuum-gauge line and the coarse graduations on the vacuum gauge scale (5.1 cm Hg or 2 in. Hg).

Temperature data were taken about every two minutes at the beginning of the run to establish the time needed to reach steady state. The temperatures of the three major process streams are plotted vs. running time in Fig. 5. As can be seen, steady state was reached about 50 min after startup. The feed temperature is the temperature of the concentrate entering the evaporator shell, as measured by TC-10. The vapor temperature is measured by TC-6, and the distillate temperature is measured by TC-5.

As seen in Fig. 5, each stream's temperature taken at about 65 min was slightly lower than the data before and after that time, with the feed temperature dropping the most. This drop in temperature occurred because the external feed pump filled the concentrate tank just prior to 60 min of running time. The external feed pump comes on when the liquid level in the concentrate tank is low. The concentrate tank is then filled from 9 L up to 14 L with relatively cool (ambient temperature) feed, thus dropping the temperature of the feed to the evaporator shell considerably. The temperatures of the vapor and the distillate were only slightly affected by this drop in feed temperature.

This filling of the concentrate tank with cold feed also occurred at about 20 min and 95 min of running time. The first filling, at 20 min, is not noticeable in Fig. 5 because it occurred as the system was warming up, before the concentrate in the tank was very warm. The last filling of the concentrate tank, at 95 min, is also not noticeable as a drop in temperatures because temperature data were not taken until about 25 min later, and the system, by then, had time to recover.

Three major operating streams are plotted vs. running time in Fig. 6. As expected, these streams reached steady state at about the same time, 45 min of running time. Also note a slight temperature drop in the heating water streams at about 60 min. This is most likely due to the addition of the cold feed to the concentrate tank, as noted above. Since the heating water stream operates in full solution recycle, a decrease in concentrate temperature will decrease the heating water temperature.

This base-case test was made with water as feed and cannot be used to predict all operating trends experienced during runs using salt- or acidic-solution feeds. For example, the fairly stable steady-state temperatures in all streams seen in Table 6 and Figs. 5 and 6 are not expected when high-salt solutions are used.

2. Feed Simulation Tests

A second set of tests, using the laboratory-scale evaporator to evaporate a simulated WMO feed, was completed to gather information regarding operating conditions and problems that WMO may encounter in the two LICON evaporators being planned for purchase. Two major items of concern in the testing were scaling and solids-handling capability.

The ionic composition of the feed for the first portion of the tests, shown in Table 7, was based on an Evaporator Feed Tank sample collected in December 1992 (ACL Sample No. 93-0090-01). Before the tests started, we prepared 100 L of this feed, which contained about 2300 mg/L dissolved solids. Throughout the tests, the electric heaters were used as the heat source. No concentrate product was drawn off.

During the first day of testing, over about 6 h of running time, the 100 L of feed was concentrated to about 11.75 L, for a concentration factor of about 8.5. Solids began forming almost immediately after the test began. This was expected, since some of the species were already saturated in the feed.

At the outset of the test, a set point of 88°C (190°F) was used for heaters 1 and 2, and 86°C (187°F) for heater 3. The distillate production rate during this time was about 0.27 L/min (4.3 gph). This is above the evaporator's stated capacity of 0.19 L/min (3 gph). Even so, the distillate produced during this time was apparently very clean, as evidenced by the conductivity being around 4 μ S/cm, about the same as the building's deionized water.

Table 7. Composition of Simulated WMO Evaporator Feed

Cations		Anions	
Ion	Conc., mg/L	Ion	Conc., mg/L
Ca ²⁺	7.62	F ⁻	17
Cu ²⁺	0.27	Cl ⁻	204
K ⁺	21.8	SO ₄ ²⁻	362
Li ⁺	1.75	NO ₂ ⁻	130
Mg ²⁺	16.0	NO ₃ ⁻	129
Mn ²⁺	0.019	HCO ₃ ⁻	683
Na ⁺	630.	SiO ₃ ²⁻	2.7
Ni ²⁺	0.574	B ₄ O ₇ ²⁻	2.5
		H ₂ PO ₄ ⁻	77

Foaming in the form of large bubbles was observed in the evaporator shell at the beginning of the test and continued throughout the test. The bubbles associated with this foam were up to about 5 cm (2 in.) across, large enough to fill the vapor space in the evaporator shell and carry liquid into the separator. On three occasions, this liquid carryover to the separator led to an automatic shutdown because the concentrate pump clearing the separator of liquid caused a high liquid level. To rectify these problems and lower the liquid level in the evaporator shell, a number of valves were adjusted. Also, the heating water temperatures were lowered to produce less-vigorous boiling. The heater set points were adjusted to 71°C (160°F) and 69°C (157°F). This lowered the distillate production rate, from 0.22 to 0.26 L/min (3.5 to 4.1 gph), over the remainder of the tests. Although neither of these adjustments eliminated the foaming, they allowed processing to continue without tripping the high-liquid-level alarm.

Although no suspended solids were visible in the original feed, a fluffy white precipitate was observed in the concentrate almost immediately after tests began. This was expected, since some of the components in the feed were at their solubility limit. After the first day, a white scale was visible on the tubes, and the tube bundle weight had increased by 1.3 g. A similar scale was visible on the inside of the evaporator shell.

During the second day, the 11.75 L of concentrate from Day 1 processing was concentrated down to about 5 L, for a total concentration factor of 20. Distillate conductivity during this time ranged between 3.7 and 4.8 µS/cm. Once a concentration factor of 20 was reached and the distillate tank was full, the distillate product was set to recycle back to the concentrate tank. Under these operating conditions, the feed to the evaporator shell (i.e., the contents of the concentrate tank) cycled between concentrations of about 10.5 and 20 times the original feed. Seven cycles were completed, and running time for the second day was about 6 h. Distillate conductivity during this time dropped slowly, starting at about 4.2 and ending at about 2.8 µS/cm.

The evaporator-shell tube bundle increased by 0.5 g after the second day. Before tests began on the third day, the tube bundle was cleaned of scale by scrubbing it with 2M HNO₃.

On the third day the 20X concentrate, along with an additional 10 L solution prepared at 20X the original feed composition, was concentrated to about 60X the original feed composition. We then cycled between concentration factors of 30 and 60. Total running time for the third day was about 2.4 h.

A frothy, small-bubble foam was observed in the evaporator shell toward the end of the run, when the concentration factor was about 30X. This frothy foam had bubbles of about 0.3-cm (1/8-in.) diameter or less and was never more than about 0.6-cm (1/4-in.) thick on top of the concentrate in the evaporator shell. Dow Chemical's Polyglycol, an anti-foaming agent, was then added to the concentrate in a ratio of 1 volume of agent to 100 volumes of concentrate. This eliminated the frothy foam altogether and decreased the large bubbles to about one-half their former size.

Solids appeared to continue forming as concentration factors increased. A concentrate sample taken at about 20X concentration had about 0.1 mL of solid in 12 mL of liquid. These solids were easily dispersed in the liquid, and buildup of solids within the evaporator shell was not a problem.

A scale buildup of 1.8 g was measured on the evaporator tube bundle over the third day. The greater scaling rate seen the third day may be due as much to difficulties keeping the tubes submerged as to the amount of solids present in the concentrate. With the foaming that was experienced, keeping the topmost heat exchanger tube submerged in liquid was difficult. The liquid level in the evaporator shell must be kept low enough so that foaming does not carry excessive amounts of liquid into the separator.

Overall, the tests yielded valuable information about the operating conditions and problems that WMO may encounter in processing similar feeds. It would appear that WMO can concentrate similar feeds considerably beyond the present 20X goal, provided scaling, foaming, and sedimentation problems can be minimized. Careful control of both evaporation rate and evaporator-shell liquid level appears necessary to control scaling and foaming. The operational parameters influencing these items are many, including evaporator-heating temperature, condenser-cooling temperature, feed-flow rate, and concentrate-recirculation rate.

Because of the higher scaling rates seen on the heat-exchanger tube not submerged in liquid, the liquid level in the evaporator shell must be kept high, but the foaming put limits on the level that could be maintained without flooding the separator. Scaling was always more pronounced on the top tube of the bundle, which, unlike the bottom tubes, is not fully submerged in liquid. Furthermore, scaling was heaviest in places where the liquid velocity across or along the tubes was lowest (e.g., at the ends of the tube bundle where the concentrate-recirculation flow is low).

Attempts to dissolve the scale on the tubes included (1) soaking in the original feed solution, (2) soaking overnight in 0.1M HNO_3 , (3) scrubbing with 0.1M HNO_3 , and (4) scrubbing with 2M HNO_3 . The feed had no effect on the scale. Soaking in 0.1M HNO_3 overnight appeared to clean all scale from the tubes, but a quick scrubbing with this dilute acid seemed to dissolve only about half of the scale. A quick scrubbing with the 2M HNO_3 appeared to dissolve all the scale deposit.

After all tests were completed, a section of concentrate-recycle plumbing was disassembled. A sticky sediment was observed in a pipe in which the flow was intermittent. No sedimentation was evident in piping in which flow was constant.

A test strip of Type 304 stainless steel (SS), approximately 18 gauge, was placed in the concentrate tank at the beginning of the tests to allow monitoring of the effects of the concentrate on this material. (The 304 SS was chosen because of its ready availability in small sizes. The

evaporators will be constructed of 316L SS, but corrosion of 304 SS is expected to be greater than 316L. Therefore, this simple test should indicate a worst-case scenario for corrosion.) At the end of the tests, we observed that the test strip appeared shinier than it had at the beginning. Otherwise, no noticeable pitting or scaling seemed to have occurred. The weight of this small strip of material (about 1/4 x 6 in.) increased from 7.0329 to 7.0344 g over the first two days of testing. Over the third day the weight decreased to 7.0337 g.

Design changes that may help minimize problems in WMO's evaporators include: (1) moving the evaporator shell feed and recirculation connections as close to the end of the shell as possible to eliminate dead spaces, (2) increasing the size of the concentrate pump to allow for higher recirculation rates, (3) lowering the heating tubes in the evaporator shell to allow all tubes to be submerged, and (4) adding an overhead-spray feed to the evaporator shell to ensure that the tubes stay wet. Consideration should also be given to changes that would facilitate scale-removal and flushing operations. Appropriate flushing solutions and procedures to dissolve the scale need further study.

Steps necessary to allow for the processing of acidic solutions in the laboratory-scale evaporator are continuing. Besides the plans to gather data on the evaporation of acids, the ability to process acidic solutions will allow the testing of appropriate flushing and scale-removal techniques. Once the evaporator, hood, and support systems are modified, a second safety review covering the evaporation of acidic solutions will be undertaken. The operating procedures are being updated in preparation for the acid runs. These procedures will cover neutralizing acidic wastes, cleaning up spills, and maintaining the evaporator after acidic solutions have been processed. Appropriate labeling of acid-carrying piping must be completed before the next safety review.

In addition to the above, a data acquisition system is being designed for monitoring the laboratory-scale evaporator. The system will employ LabView software running on a Macintosh computer. The acquisition system will monitor all of the parameters currently recorded by hand, including temperatures, pressures, flow rates, tank levels, and distillate conductivity. Additionally, other sensors will be included to monitor certain parameters not currently measured. A detailed model of the evaporator can then be created and verified. The data acquisition system will transfer information to Microsoft Excel spreadsheets, where calculations can be made and reports generated.

3. Determination of Evaporator Decontamination Factors

Two evaporator runs were completed with the laboratory-scale evaporator to determine the decontamination factors that can be achieved. For the first run, the feed was $6.7 \times 10^{-4} \text{ M Sm(NO}_3)_3$. The concentration of samarium was measured in the distillate and concentrate by neutron activation analysis (NAA). The feed for the second run was $0.5 \text{ M Al(NO}_3)_3$ and $6.7 \times 10^{-3} \text{ M Sm(NO}_3)_3$. Aluminum was added to increase the salt concentration and to determine the effect of aluminum on NAA. Argonne sent three samples of both the distillate and concentrate, as well as one sample of the feed, to the University of Illinois for NAA.

Before the evaporator runs were completed, a concentration vs. density correlation for an $\text{Al(NO}_3)_3$ solution at 35°C was derived at Argonne:

$$[\text{Al(NO}_3)_3] = \frac{\rho(35^\circ\text{C}) - 0.99473}{0.1486} \quad (3)$$

where $\rho(35^\circ\text{C})$ is the density (g/mL) of the solution at 35°C . By measuring the density of the samples collected during the run, the aluminum nitrate concentration was calculated. The calculated aluminum concentrations could then be used to check the NAA results.

Normally, liquid samples in NAA should have a pH close to 1. This prevents the metal ion from adhering to the plastic vial and thus allows complete transfer of the ion from the irradiated vial to a non-irradiated vial for analysis. When the pH of the samples received from ANL was checked using litmus paper, the distillate samples from both runs and the feed and concentrate samples from run 1 had a pH of 5, while the feed and concentrate samples from run 2 had a pH of 1. In an attempt to obtain reproducible data, the pH of the samples received from ANL was adjusted to 1 by adding 20 μL of concentrated HNO_3 , then the NAA procedure was completed.

Initial NAA results for aluminum did not agree with the aluminum concentrations predicted by the density equation. To verify these aluminum concentrations with a third technique, a titration method was used. Therefore, all the samples were titrated using 0.512M NaOH. According to Brinkmann Application Bulletin No. 89e, when titrating a solution of nitric acid and aluminum with NaOH, the first endpoint occurs when all the acid has been neutralized. A second endpoint will occur when all the aluminum has precipitated as aluminum hydroxide. For the feed and concentrate samples from evaporator run 2, there was no acid originally present. However, before NAA was performed, 20 μL of nitric acid was added. This small amount of acid is much lower than the aluminum concentration and can be neglected. Thus, when titrating these samples, we used the first endpoint to determine the aluminum concentration. The molar concentration of aluminum was determined from

$$[\text{Al}] = \frac{(\text{Endpoint 1}) (0.512)}{(\text{Sample Size}) (3)} \quad (4)$$

Both endpoint 1 and sample size are in milliliters. The factor of 3 is in the denominator because 3 moles of NaOH are required to react completely with 1 mole of Al^{3+} . The results of titrating the feed and concentrate samples of run 2 are given in Table 8.

In the titration, NaOH was initially added to approximately 1 mL less than theoretically required to fully react with the aluminum. Then the NaOH was added at 0.02 mL/step until the solution pH was between 10.5 and 11.5. In Table 8, the titration data agree fairly well with the aluminum concentration determined at ANL for all the samples. Therefore, the NAA results were suspect.

Since the aluminum concentrations determined by NAA were considered incorrect, it was also assumed that the samarium concentrations were incorrect. Further studies were conducted to resolve this problem. We found three factors which may have contributed to the discrepancy: production of another gamma ray close to the 103.2-keV samarium peak, self-absorption of the gamma ray, and neutron self-shielding in the sample during irradiation. Each of these is discussed below.

a. Production of a Second Gamma Ray

The first factor could be the production of another gamma ray with an energy close to the 103.2-keV gamma peak of samarium. A closer look at the table of isotopes showed that ^{155}Sm gives off a 104.3-keV gamma ray with a half-life of 22 min. This gamma ray falls within the

Table 8. Aluminum Concentrations in the Feed and Concentrate Samples of Run 2 Determined by Titration with 0.512M NaOH

Sample	End Point l, mL	Sample Size, mL	Aluminum Conc., M		% Diff.
			Analysis by Titration	Analysis by Density	
0.559M Al	3.076	1	0.525	-	6.08
F-2-1	2.678	1	0.457	0.50	-9.40
C-2-2	4.891	1	0.835	0.85	-1.83
C-2-4	7.147	1	1.220	1.31	-7.73
C-2-7	5.848	0.5	1.996	2.15	-7.81

103.2-keV gamma-ray photopeak and adds a significant number of counts to samples analyzed within the first half-hour to hour after irradiation. This can be avoided by counting all samples and standards 13,200 s (220 min, or 10 half-lives) after irradiation.

b. Self-Absorption

The second factor could be the self-absorption of the gamma ray by the sample. As the aluminum nitrate concentration increases, it appears that the differences in the aluminum concentration between NAA and density increase. Jaegers and Landsberger³ developed a computer code to determine self-absorption of gamma rays in high Z materials. The concentrations of aluminum nitrate determined from the density correlation and the density of the solutions were used to calculate the weight fractions of aluminum, nitrogen, hydrogen, and oxygen present in the samples. The data were entered in the self-absorption code along with counting geometry information. This analysis showed only a 3% absorption of the 103.2-keV gamma peak from samarium; and the absorption for the 1.7787-MeV gamma peak from the aluminum was less than 2%. These findings suggest that self-absorption does not account for the discrepancy. To further clarify this issue, an experiment was conducted to determine the self-absorption of the 103.2 keV gamma ray in the evaporator samples. Small quantities, 100 μ L, of an irradiated atomic absorption standard of 1000-ppm Sm were added to 0.5 mL of non-irradiated feed and concentrate samples from run 2, as well as a 0.5-mL sample of deionized water. These spiked samples were then counted on the 13% efficient gamma-X ray detector in position 1. The results are given in Table 9. These results indicate that the percentage of gamma-ray attenuation for the 103.2-keV gamma peak is small. It does, however, contribute to the error in the original results of the samarium concentration determined by NAA.

Table 9. Percentage of Gamma Ray Attenuation for the Feed and Concentrate Samples from Evaporator Run 2 Compared to Deionized (DI) Water

Sample	Net Counts	Transition Coefficient	% Gamma Attenuation
DI Water	8735	1.0000	0.003
F-2-1 1H	8696	0.9955	0
C-2-2 1H	8349	0.9558	4.42
C-2-4 1H	8295	0.9496	5.04
C-2-7 1H	8124	0.9301	6.99

c. Neutron Self-Shielding

The third possible factor for this error may be due to neutron self-shielding of the sample during irradiation. When no self-shielding of neutrons occurs in a sample, there is a first-order linear relationship between the count rate and the sample concentration. When neutron self-shielding is present, as with samples containing cadmium with concentrations greater than 1 mg, the relationship is not linear. At the higher concentrations, the curve flattens out. If NAA is used to determine the concentration of a sample containing a few milligrams of samarium by using a sample containing a few tenths of a milligram of samarium as a standard, then the calculation will under-predict the concentration of the sample. Since samarium has a large cross section for neutron absorption and is present in relatively large quantities in the feed and concentrate samples, neutron self-shielding may occur in these samples.

To determine if neutron self-shielding is a problem, samarium standards ranging from 0.01 to 10 mg of samarium were prepared. The samples from 0.5 to 10 mg were prepared by pipetting samarium NIST* standard at 10.0 mg/mL. The 0.01-0.1 mg standards were prepared by diluting 0.1 to 1 mL of the same samarium NIST standard in a 100-mL volumetric flask. New feed and concentrate samples, from both evaporator runs (Sec. III.A.2), were also prepared for irradiation. All samples and standards were prepared in duplicate. These samples and standards were then irradiated at 500 kW for 6.2-6.3 s. They were allowed to decay for at least 13,200 s and then counted. The 0.01-mg standard was used as a reference to calculate the concentration of samarium in the other standards. The results are given in Table 10 and plotted in Fig. 7. The data were fit with a second-order linear curve, which is given in Fig. 7. An equation was also determined which relates the actual sample concentration to the concentration determined by NAA. The relation is as follows:

$$[\text{Sm}] = 1.044 \cdot \left(\frac{[\text{Sm}]_{\text{NAA}}}{T} \right) + 0.062 \cdot \left(\frac{[\text{Sm}]_{\text{NAA}}}{T} \right)^2 \quad (5)$$

where [Sm] is the Sm concentration in milligrams per liter, and T is the transmission coefficient. For the standards, the transmission coefficient was assumed to be 1. The transmission coefficients for the feed and concentrate samples are given in Table 9.

The concentrations of the feed and concentrate samples from both evaporator runs were determined by NAA using the 0.01-mg NIST standard as a reference. The results are given in Tables 11 and 12. The samarium concentrations listed in Tables 11 and 12 were averaged for each duplicate and then used in Eq. 5. The results of the calculation are given in Tables 13 and 14. The molar concentration of samarium was found using

$$([\text{Sm}], \underline{M}) = ([\text{Sm}], \text{Corrected}(\text{mg})) (6.65 \times 10^{-3}) \quad (6)$$

The decontamination factors for the evaporator were then calculated using the corrected samarium concentrations in Tables 13 and 14 and are shown in Table 15. These decontamination factors are higher than expected for the pilot-scale evaporator. Decontamination factors in the range of 10^6 are excellent; larger-scale LICON evaporators should have similar if not better decontamination factors.

* NIST = National Institute of Standards and Technology.

Table 10. Actual and Experimental Concentrations of Samarium

Sample	Actual [Sm], mg	Sample Mass, g	Irradiation Time, s	Decay Time, s	NAA [Sm], mg
1	10	1.0371	6.2	168,179	6.94
2	10	1.0448	6.2	167,944	6.88
3	9	0.9426	6.3	157,970	5.97
4	9	0.9438	6.3	157,871	6.30
5	8	0.8364	6.2	157,797	5.70
6	8	0.8344	6.3	157,719	5.73
7	7	0.7232	6.3	157,660	5.20
8	7	0.7299	6.2	157,647	5.39
9	6	0.6255	6.3	90,615	4.08
10	6	0.6240	6.3	90,580	4.57
11	5	0.5157	6.3	90,525	3.84
12	5	0.5192	6.2	90,446	3.92
13	4	0.4153	6.3	90,379	3.30
14	4	0.4152	6.3	90,337	3.31
15	3	0.3039	6.3	89,378	2.35
16	3	0.3085	6.2	90,453	2.61
17	2	0.1999	6.3	89,065	1.752
18	2	0.2077	6.3	89,006	1.811
19	1	0.0924	6.2	88,672	1.025
20	1	0.1040	6.2	88,617	0.899
21	0.9	0.0932	6.3	88,352	0.883
22	0.9	0.0941	6.3	95,133	0.869
23	0.8	0.0829	6.4	94,840	0.789
24	0.8	0.0831	6.3	94,686	0.758
25	0.7	0.0719	6.2	87,315	0.680
26	0.7	0.0721	6.3	93,922	0.692
27	0.6	0.0613	6.3	94,118	0.595
28	0.6	0.0135	6.3	93,438	0.497
29	0.5	0.0509	6.3	93,368	0.502
30	0.5	0.0512	6.2	85,114	0.495
31	0.1	1.0074	6.2	103,433	0.1065
32	0.1	0.9962	6.2	104,099	0.0994
33	0.08	1.0041	6.2	104,791	0.0851
34	0.08	0.9986	6.2	105,676	0.0791
35	0.06	0.9984	6.2	107,128	0.0615
36	0.06	0.9929	6.3	0	
37	0.05	0.9979	6.3	101,034	0.0507
38	0.05	0.9945	6.2	102,496	0.0497

Fig. 7. Comparison of Calculated Samarium Concentrations by NAA with As-Prepared Samarium Concentrations

Table 11. Concentration of Samarium Determined by NAA for the Feed and Concentrate Samples from Evaporator Run 1^a

Sample No.	Sample Mass, g	Irradiation Time, s	Decay Time, s	[Sm], mg
F11-1	1.0057	6.2	38,484	0.0931
F11-2	1.0001	6.2	38,610	0.0949
C12-1	0.9774	6.3	38,835	0.1735
C12-2	0.9400	6.3	39,056	0.1824
C14-1	1.0085	6.3	39,244	0.2362
C14-2	1.0033	6.2	39,340	0.2401
C16-1	1.0047	6.2	39,512	0.4470
C16-2	1.0045	6.2	39,703	0.4660

^aSamples not corrected for gamma ray self-absorption or neutron self-shielding.

Table 12. Concentration of Samarium Determined by NAA for the Feed and Concentrate Samples from Evaporator Run 2^a

Sample No.	Sample Mass, g	Irradiation Time, s	Decay Time, s	[Sm], mg
F21-1	1.0818	6.2	94,567	0.937
F21-2	1.0892	6.2	94,585	0.971
C22-1	1.1402	6.2	91,516	1.601
C22-2	1.1461	6.2	91,578	1.501
C24-1	1.1995	6.3	92,746	2.235
C24-2	1.2007	6.2	93,159	2.290
C27-1	1.3143	6.3	93,769	3.230
C27-2	1.3150	6.3	93,819	3.360

^aSamples not corrected for gamma ray self-absorption or neutron self-shielding.

Table 13. Samarium Concentrations Determined by NAA for the Feed and Concentrate Samples from Evaporator Run 1

Sample No.	Density, g/mL	Sm Conc.			Concentration Factor
		NAA, mg	Corr., mg	NAA, <u>M</u>	
F-1-1	1.003	0.0940	0.099	6.56E-04	1
C-1-2	0.9587	0.1780	0.188	1.25E-03	1.91
C-1-4	1.006	0.2382	0.252	1.68E-03	2.56
C-1-7	1.005	0.4565	0.489	3.25E-03	4.95

Table 14. Corrected Samarium Concentrations from NAA and ANL Calculated Concentrations for the Feed and Concentrate Samples from Evaporator Run 2

Sample No.	Density, g/mL	Sm Conc.				% Diff.	Concentration Factor
		NAA, mg	Corr., mg	NAA, <u>M</u>	ANL, <u>M</u>		
F-2-1	1.0860	0.954	1.057	7.03E-03	6.70E-03	-4.93	1
C-2-2	1.1430	1.551	1.857	1.23E-02	1.14E-02	-7.89	1.76
C-2-4	1.2000	2.263	2.839	1.89E-02	1.76E-02	-7.39	2.69
C-2-7	1.3150	3.295	4.474	2.98E-02	2.88E-02	-3.47	4.23

Table 15. Decontamination Factor for the LICON Laboratory-Scale Evaporator

Samples	[Sm], ^a <u>M</u>	Decontamination Factor
C-1-2/D-1-2	2.65E-09	4.71E+05
C-1-4/D-1-4	2.13E-09	7.87E+05
C-1-6/D-1-5	1.86E-09	1.75E+06
C-2-2/D-2-2	7.08E-09	1.74E+06
C-2-4/D-2-4	2.67E-09	7.07E+06
C-2-7/D-2-6	4.02E-09	7.40E+06

^aIn the vapor phase.

B. Vapor-Liquid Equilibrium Data

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

1. Nitric Acid-Water System (S. Betts)

Experiments have been conducted to reproduce literature data for the binary nitric acid-water system. The experiments were carried out in a circulation type equilibrium still (Fig. 8) developed by Altsheler et al.,⁴ which was purchased from LUREX Scientific. The still was modified to measure equilibrium temperatures by replacing the glass stopper in the top of the still with an adapter which accepts two J-type thermocouples. One thermocouple measured the liquid temperature, and one the vapor temperature above the entrainment separator. The thermocouples were coated with perfluoroalkoxy (PFA) Teflon to protect them from the corrosive acid environment. The temperature resolution and accuracy of the data acquisition card for a J-type thermocouple are given in Table 16.

Table 16. Resolution and Accuracy of Data Acquisition Card for J-type Thermocouple

Temperature, °C		
Range	Resolution	Accuracy
-80 to 100	0.3	±1.6
100 to 760	0.2	±1.2

To verify operation of the still and to develop laboratory techniques for collecting and analyzing acidic solutions, experimental data on nitric acid and water at atmospheric pressure were collected and compared with literature data.

Nitric acid solutions were prepared close to the desired equilibrium concentrations from 15.8M HNO_3 and deionized water. In the first experiment, 444 mL of solution was placed in the still. For all subsequent experiments, 500 mL of solution was used. The stopcock at the bottom of the still was adjusted to allow fluid flow from the reflux line to the heating section. The vapor sample began to collect in the vapor phase reservoir after 20-30 min of heating. Another 30 min was required before the vapor phase reservoir was filled and circulation began. The system was allowed to run for at least another hour. Temperature data were collected every 5 s. The equilibrium temperature was determined by averaging the temperatures from 1 h to the end of heating. After the

Fig. 8. Schematic of Laboratory Still

heating was shut off, the solution was cooled in the still for approximately 15 h. When collecting samples from the still, the first few milliliters of each phase was discarded. The concentration of the sample was determined by titrating with 0.5M NaOH. The concentration of the NaOH was standardized by titrating with potassium hydrophthalate, $2-(\text{HO}_2)\text{C}_6\text{H}_4\text{CO}_2\text{K}$ (KHP). Again, three titrations were performed. The average concentration was $0.498 \pm 0.0012\text{M}$, with a percent error of 2.3%. Before the last sample was analyzed, a new solution of NaOH was prepared and standardized with KHP. The average concentration was $0.512 \pm 0.0006\text{M}$. The density of the samples was found by weighing 5 mL of sample. From the density and molar concentration of acid, the wt% of HNO_3 , wt% H_2O , and mol% HNO_3 were calculated. The results are presented in Table 17.

The data in Table 17 were plotted in Figs. 9 and 10 with literature data. It can be seen from the figures that our data ("Betts") agree very well with the literature data.

Table 17. Vapor-Liquid Equilibrium Data for the Binary $\text{HNO}_3\text{-H}_2\text{O}$ System

[HNO_3], M		Density, g/mL		wt% HNO_3		wt% H_2O		mol% HNO_3		Temp., °C
Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	
3.56	0.139	1.106	1.066	1.12	0.04	4.41	5.24	6.78	0.24	104.2
5.15	0.48	1.16	1.03	1.62	0.15	4.18	5.00	9.99	0.86	106.9
6.55	1.20	1.185	1.029	2.06	0.38	3.86	4.77	13.24	2.22	108.5
8.78	2.69	1.270	1.094	2.77	0.85	3.58	4.62	18.07	4.98	111.8
12.84	9.89	1.352	1.288	4.04	3.12	2.72	3.32	29.83	21.14	119.01
14.92	13.81	1.410	1.390	4.70	4.35	2.35	2.60	36.37	32.35	120.9

Fig. 9. Boiling Temperature versus Nitric Acid Concentration in Liquid Phase

Fig. 10. Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase

The temperature data reported in Table 17 were taken only from the thermocouple that was submerged in the liquid. For the first five runs, the other thermocouple, a 6-in. (15-cm) thermocouple, recorded temperatures closer to 100°C. In the last run, a 15-in. (38-cm) thermocouple measured the liquid temperature and a 12-in. (30-cm) thermocouple, the vapor phase. In this run, the difference in equilibrium temperature between the two thermocouples was only 0.9°C, the liquid phase having the higher temperature.

2. Nitric Acid-Sulfuric Acid-Sodium Nitrate System

The results from the binary nitric acid-water system show that the experimental procedure for operating the equilibrium still, as well as collecting and analyzing samples, gave results that agreed well with literature. The next step then is to study a system for which data are not available in the literature. No data were available for multiple acid-salt systems. A second acid likely to be present in solutions to be processed in the evaporator is sulfuric acid. Furthermore, sodium nitrate solutions have been studied extensively and present little difficulty to model thermodynamically. Therefore, it was decided to study the nitric acid-sulfuric acid-sodium nitrate system. Sodium nitrate was chosen as the salt because it has been studied extensively and presents little difficulty to model thermodynamically.

We studied solutions with both low and high salt concentrations over a large range of nitric acid concentrations. While working with these solutions, we had to ensure that the salts remained soluble at room temperature, since samples were collected and analyzed at this temperature. The solubility data presented in Appendix A of Ref. 9 indicate that 2M NaNO₃ is soluble up to 6M HNO₃. We then experimentally determined that the salt would remain completely soluble in a solution containing 5M HNO₃-1.5M H₂SO₄-2M NaNO₃, while some solid would form in a solution containing 5M HNO₃-2M H₂SO₄-2M NaNO₃. Therefore, we decided that the following solution compositions would be studied: [HNO₃] = 1, 2, 4, 5 M; [H₂SO₄] = 0.5, 1, 1.5 M; [NaNO₃] = 0.1, 1, and 2 M.

Sodium nitrate concentrations are determined by two methods: (1) final concentrations are estimated by determining the volume of solution present in the portion of the still which contains the liquid sample and dividing this volume into the number of moles of sodium added to the initial solution, and (2) after collecting samples from the equilibrium still, the sodium concentration is determined using a sodium ion selective electrode. This may be done by preparing a calibration curve of millivolts versus sodium ion concentration of known standards or by known addition methods.

Before testing could begin, it was necessary to ensure that titrations would be performed to determine accurate nitric and sulfuric acid concentrations in multiple acid systems. A titration procedure for that purpose was received from Metrohm, Application Bulletin No. 39/1 e.¹⁰ The procedure calls for an organic titration using 0.5M cyclohexylamine in methanol. According to Metrohm's procedure, titrating sulfuric-nitric acid mixtures gives two endpoints. Based upon normality, the first endpoint corresponds to the sum of HNO₃ + 1/2 H₂SO₄, and the difference between the first and second endpoints corresponds to the remaining half of the sulfuric acid. The bulletin points out that various titrating reagents, such as piperidine, alcoholic KOH, potassium methylate, and tetrabutylammonium hydroxide, have been used in the literature. Except for piperidine, which is difficult to use, all the others are affected by atmospheric CO₂, which can cause difficulties in titration as well as produce serious errors in the results. As a titrating reagent, cyclohexylamine maintains a constant concentration, because it is unaffected by atmospheric CO₂. Methanol usually gives a zero result on a blank control sample.

The titrating reagent is standardized by titrating 2 mL of 1M H_2SO_4 in 90 mL of methanol. From this titration two factors are calculated:

$$t_1 = \frac{4.000}{\text{EP1}} \quad (7)$$

$$t_2 = \frac{4.000}{\text{EP2} - \text{EP1}} \quad (8)$$

where t_1 = reagent consumption up to the first endpoint (EP1)

t_2 = the difference between reagent consumption at the first endpoint (EP1) and the second endpoint (EP2).

An unknown sample is prepared in the same manner as the standard by placing a small quantity of the sample in a beaker and adding 90 mL of methanol. The concentrations of sulfuric and nitric acids are then found using the following equations:

$$[\text{H}_2\text{SO}_4, (\text{g/kg})] = \frac{(\text{EP2} - \text{EP1}) \cdot C_1 \cdot t_2}{C_3} \quad (9)$$

$$[\text{HNO}_3, (\text{g/kg})] = \frac{\text{EP1} - (\text{EP2} - \text{EP1}) \cdot C_2 \cdot t_1}{C_3} \quad (10)$$

where C_1 = equivalent weight of sulfuric acid = 49038.8 mg/L

C_2 = equivalent weight of nitric acid = 31506.5 mg/L

C_3 = mg of titration sample

The molar concentration of each acid may be found using these equations:

$$[\text{H}_2\text{SO}_4, (\text{M})] = [\text{H}_2\text{SO}_4, (\text{g/kg})] \frac{\rho}{98.0776} \quad (11)$$

$$[\text{HNO}_3, (\text{M})] = [\text{HNO}_3, (\text{g/kg})] \frac{\rho}{63.0130} \quad (12)$$

where ρ is the density of the solution in g/mL.

This procedure was tested by titrating a mixture of 3.6M H_2SO_4 and 1.58M HNO_3 , which was prepared by placing 25 mL of 15.8M HNO_3 and 50 mL of 18M H_2SO_4 in a 250-mL volumetric flask and adding distilled water. One milliliter of this mixture was placed in 20 mL of water and 80 mL of methanol. The mass of the sample placed in the beaker was 1.249 mg, and the solution density was 1.25 g/mL. Ten milliliters of this solution was pipetted into another flask, and 90 mL of methanol was added. Therefore, the solution mass which was finally titrated was 124.9 mg.

The endpoints from the titration were EP1 = 1.062 mL and EP2 = 1.805 mL. A 1M H_2SO_4 standard was also titrated, with the endpoints EP1 = 4.086 mL and EP2 = 8.199 mL. Using the endpoints from the standard in Eqs. 7 and 8, we obtained $t_1 = 0.979$ and $t_2 = 0.9725$. The concentrations of sulfuric and nitric acid (in g/kg) were found using t_1 and t_2 with the endpoints from the sample titration in Eqs. 9 and 10. This gave 283.47 g/kg H_2SO_4 and 78.72 g/kg HNO_3 . The molar concentrations were found, using Eqs. 11 and 12, to be 3.61M H_2SO_4 and 1.56M HNO_3 . They agree very well with the actual concentrations.

Solutions were prepared such that the equilibrium concentration of each component would be close to that listed above. Initially, 500 mL of solution was placed into the equilibrium still. At equilibrium, about 400 mL of solution will remain in the liquid phase. To ensure that all the salt remains in solution, we assumed that this number could be as low as 390 mL. Since the activity of sulfuric acid is extremely low, virtually none is transferred to the vapor phase. Similarly, sodium nitrate should also remain completely in the liquid phase. Therefore, the volume of concentrated (18.0M) sulfuric acid and mass of sodium nitrate needed to prepare one liter of solution that will result in the desired equilibrium composition can be found using the following equations:

$$\text{Volume (mL) of } \text{H}_2\text{SO}_4 = [\text{FINAL } \text{H}_2\text{SO}_4] \left(\frac{0.390}{0.5} \right) \left(\frac{1000}{18} \right) \quad (13)$$

$$\text{Mass (g) of } \text{NaNO}_3 = [\text{FINAL } \text{NaNO}_3] \left(\frac{0.390}{0.5} \right) 84.99 \quad (14)$$

Using the above equations and the desired final solution compositions, we determined that solutions would be prepared in the following combinations: 60, 125, 250, and 315 mL of 15.8M HNO_3 with 22, 44, and 66 mL of 18.0M H_2SO_4 , and 6.65, 66.5, and 135.0 g of NaNO_3 .

Temperature data for the liquid and vapor phases were recorded during the experiment using two J-type thermocouples. Approximately one hour was required for the solutions to reach equilibrium. The system was run for another two hours to allow sufficient reflux of the vapor phase. After the heating was shut off, the system was cooled for approximately 15 h. At that time, liquid and vapor samples were collected from the still and analyzed.

As mentioned above, virtually no sulfuric acid or sodium nitrate will be transferred to the vapor phase. Therefore, the vapor phase should consist of only nitric acid and water. The concentration of nitric acid in the vapor phase was determined by titration with 0.512M NaOH .

To date, solutions containing 0.09 and 0.93M NaNO_3 have been studied. The results are given in Tables 18 and 19. The data are plotted in Figs. 11-14. (The convention used for the sample name is as follows. The number before the first M corresponds to the approximate equilibrium concentration of nitric acid in the liquid phase. The number between the first M and the second M corresponds to the approximate equilibrium concentration of sulfuric acid in the liquid phase. And the number between the second and the third M corresponds to the approximate equilibrium concentration of sodium nitrate in the liquid phase. Where the two numbers are used, a decimal place should be placed between them. For example, the sample name 5M15M1M means that the equilibrium composition of the solution should be approximately 5M HNO_3 -1.5M H_2SO_4 -1M NaNO_3 .)

Table 18. Composition of Prepared Solutions and Equilibrium Solutions as well as Equilibrium Temperatures for Solutions Containing 0.09M NaNO₃

HNO ₃ -H ₂ SO ₄ - NaNO ₃ Sample	Density of Liquid Phase, g/mL	[H ₂ SO ₄], M		[HNO ₃], M		Vapor Phase [HNO ₃], M	Temp., °C
		Prepared	Liquid Phase	Prepared	Liquid Phase		
1M05M01M	1.064	0.39	0.45	0.94	1.05	0.014	102.4
2M05M01M	1.112	0.39	0.46	2.00	2.30	0.081	104.2
4M05M01M	1.178	0.39	0.46	3.90	4.47	0.446	107.4
5M05M01M	1.227	0.39	0.47	5.09	5.81	0.870	109.2
1M1M01M	1.100	0.79	0.96	0.95	1.14	0.030	102.9
2M1M01M	1.138	0.80	0.95	1.94	2.26	0.103	104.9
4M1M01M	1.203	0.79	0.93	3.90	4.47	0.593	108.6
5M1M01M	1.234	0.79	0.92	4.93	5.59	1.101	110.6
1M15M01M	1.130	1.19	1.38	0.97	1.10	0.038	103.9
2M15M01M	1.164	1.20	1.40	1.98	2.30	0.148	106.1
4M15M01M	1.235	1.20	1.39	3.97	4.46	0.804	110.0
5M15M01M	1.246	1.17	1.37	4.89	5.34	1.432	111.9

Table 19. Composition of Prepared Solutions and Equilibrium Solutions as well as Equilibrium Temperatures for Solutions Containing 0.93M NaNO₃

HNO ₃ -H ₂ SO ₄ - NaNO ₃ Sample	Density of Liquid Phase, g/mL	[H ₂ SO ₄], M		[HNO ₃], M		Vapor Phase [HNO ₃], M	Temp., °C
		Prepared	Liquid Phase	Prepared	Liquid Phase		
1M05M1M	1.148	0.39	0.46	0.95	1.16	0.029	103.9
2M05M1M	1.151	0.39	0.45	1.99	2.31	0.116	105.6
4M05M1M	1.218	0.40	0.46	4.04	4.53	0.606	109.0
5M05M1M	1.239	0.39	0.45	5.05	5.57	1.117	110.8
1M1M1M	1.142	0.80	0.93	0.96	1.11	0.049	104.3
2M1M1M	1.178	0.79	0.93	1.97	2.29	0.169	106.3
4M1M1M	1.236	0.78	0.92	3.95	4.42	0.778	110.1
5M1M1M	1.258	0.79	0.92	4.94	5.46	1.390	112.0
1M15M1M	1.167	1.19	1.40	0.95	1.12	0.078	105.1
2M15M1M	1.192	1.18	1.38	1.97	2.26	0.244	107.0
4M15M1M	1.257	1.17	1.38	3.88	4.36	0.998	110.5
5M15M1M	1.286	1.17	1.39	4.93	5.40	1.752	112.8

Fig. 11. Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase for 0.09 M NaNO_3

Fig. 12. Equilibrium Temperature versus Nitric Acid Concentration in the Liquid Phase for 0.09 M NaNO_3

Fig. 13. Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase for 0.92M NaNO₃

Fig. 14. Equilibrium Temperature versus Nitric Acid Concentration in the Liquid Phase for 0.92M NaNO₃

It can be seen from the figures that the data follow expected trends. That is, the equilibrium composition of the vapor phase and the equilibrium temperature increase with increasing concentrations of nitric acid, sulfuric acid, or sodium nitrate in the liquid phase.

Since neither sulfuric acid nor sodium nitrate transfer from the liquid to the vapor phase, the ratio $([\text{H}_2\text{SO}_4]_{\text{L}})/([\text{H}_2\text{SO}_4]_{\text{I}})$ should equal the ratio $([\text{Na}]_{\text{L}})/([\text{Na}]_{\text{I}})$. Here L and I stand for the liquid and initial (prepared) samples, respectively. Comparing these ratios requires a means of measuring the sodium ion concentration, which we determined using a Ross Sodium Ion Selective Electrode (ISE). The electrode was calibrated by obtaining millivolt readings from standard solutions of known sodium concentrations. The data were plotted on a semi-log scale with the molar concentration of the standard on the log axis. The data were fit using

$$\text{mV} = A + B \ln([\text{Na}], \text{M}) \quad (15)$$

where A and B are fit constants.

Three known sodium concentrations were used: 0.001, 0.005, and 0.01M. These were prepared by placing 0.1, 0.5, and 1.0 mL of 1M Na standard, purchased from Orion, and 10 mL of Ionic Strength Adjustor (ISA) into 100-mL volumetric flasks and filling with deionized water. The ISA, consisting of 4M NH_4OH and 4M NH_4Cl , is used to adjust the pH of the sample to between 9 and 10. This is required for proper operation of the electrode. An example of calibration data is given in Table 20. These data were fit using Eq. 15 and are shown in Fig 15. The fit constants were $A = 71.150$ and $B = 24.772$, with $R^2 = 0.9999$.

Table 20. Sample Calibration Data for the Sodium ISE

Standard [Na], M	mV
0.001	-100
0.05	-60
0.01	-43

Fig. 15.

Sample Calibration Curve for the Sodium Ion Selective Electrode

Samples were prepared by placing a small amount of solution, from 0.25 to 3 mL, in a 100-mL volumetric flask, adding 10 mL of ISA, and filling with deionized water. The volume of solution used was chosen such that the concentration of sodium, in the diluted sample, would fall between the high and low points on the calibration curve. The concentration of sodium in the sample was obtained by solving the calibration curve for the sodium concentration as a function of millivolts and multiplying by a term to correct for the dilution:

$$[\text{Na}, \underline{\text{M}}] = \exp\left(\frac{\text{mV } A}{B}\right) \cdot \frac{100}{\text{Vol.}} \quad (16)$$

where A and B are the fit constants, and Vol. is the volume (mL) of solution placed in the 100 mL volumetric flask. The data for samples containing equilibrium concentrations of approximately 0.09 and 0.93M NaNO_3 are given in Tables 21 and 22.

The data indicate that $[\text{Na}]_I$ and $[\text{Na}]_L$ are less than they should be, probably due to the inaccuracy of the ISE. It was assumed that this error would be approximately the same for both the initial and liquid samples. If this assumption is true, then the ratio $[\text{Na}]_L/[\text{Na}]_I$ should be accurate. A comparison of the ratios for $[\text{Na}]_L/[\text{Na}]_I$ and $[\text{H}_2\text{SO}_4]_L/[\text{H}_2\text{SO}_4]_I$, listed in Tables 21 and 22, showed the percent difference to be less than 4%. As expected, the sulfuric acid and sodium have concentrated by the same factor.

Table 21. Ratio of Sodium Concentration in the Liquid and Initial Samples with the Same Ratio for Sulfuric Acid for Equilibrium Solutions of Approximately 0.09M NaNO_3

Sample	Vol., mL	mV		A	B	Conc., M		$[\text{Na}]_L/$ $[\text{Na}]_I$	$[\text{H}_2\text{SO}_4]_L/$ $[\text{H}_2\text{SO}_4]_I$	% Diff.
		Init.	Liquid			$[\text{Na}]_I$	$[\text{Na}]_L$			
1M05M01M	5	-69	-65	71.150	24.772	0.070	0.082	1.18	1.173	-0.209
2M05M01M	3	-82	-77	71.150	24.772	0.069	0.084	1.22	1.180	-3.670
4M05M01M	3	-82	-78	71.150	24.772	0.069	0.081	1.18	1.180	0.412
5M05M01M	3	-82	-78	71.150	24.772	0.069	0.081	1.18	1.200	2.080
1M1M01M	2	-90	-86	71.150	24.772	0.075	0.088	1.18	1.212	3.020
2M1M01M	2	-91	-87	71.150	24.772	0.072	0.084	1.18	1.184	0.745
4M1M01M	2	-91	-88	71.150	24.772	0.072	0.081	1.13	1.176	4.051
5M1M01M	2	-92	-89	71.150	24.772	0.069	0.078	1.13	1.167	3.258
1M15M01M	2	-92	-88	71.150	24.772	0.069	0.081	1.18	1.153	-1.920
2M15M01M	2	-91	-88	72.489	25.130	0.075	0.084	1.13	1.167	3.473
4M15M01M	2	-92	-88	72.489	25.130	0.072	0.084	1.17	1.155	-1.491
5M15M01M	2	-92	-88	72.489	25.130	0.072	0.084	1.17	1.171	-0.129

Table 22. Ratio of Sodium Concentration in the Liquid and Initial Samples with the Same Ratio for Sulfuric Acid for Equilibrium Solutions of Approximately 0.92M NaNO₃

Sample	Vol., mL	mV		A	B	Conc., M		[Na] _L / [Na] _I	[H ₂ SO ₄] _L / [H ₂ SO ₄] _I	% Diff.
		Init.	Liquid			[Na] _I	[Na] _L			
1M05M01M	0.5	-68	-64	72.489	25.130	0.747	0.875	1.17	1.187	1.251
2M05M01M	0.5	-68	-64	72.489	25.130	0.747	0.875	1.17	1.160	-1.058
4M05M01M	0.5	-68	-64	72.489	25.130	0.747	0.875	1.17	1.143	-2.625
5M05M01M	0.5	-68	-64	72.489	25.130	0.747	0.875	1.17	1.139	-2.975
1M1M01M	0.4	-74	-70	71.489	25.130	0.765	0.897	1.17	1.158	-1.222
2M1M01M	0.4	-74	-70	71.489	25.130	0.765	0.897	1.17	1.172	-0.065
4M1M01M	0.4	-74	-70	71.489	25.130	0.765	0.897	1.17	1.177	0.412
5M1M01M	0.4	-72	-68	73.489	25.130	0.765	0.897	1.17	1.162	-0.948
1M15M01M	0.3	-80	-75	73.489	25.130	0.742	0.905	1.22	1.179	-3.509
2M15M01M	0.3	-80	-76	73.489	25.130	0.742	0.870	1.17	1.170	-0.187
4M15M01M	0.3	-81	-77	73.489	25.130	0.713	0.836	1.17	1.173	0.061
5M15M01M	0.25	-85	-80	73.489	25.130	0.730	0.890	1.22	1.185	-2.955

IV. TECHNICAL SUPPORT FOR WASTE MANAGEMENT OPERATIONS

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The Separation Science and Technology Section is cooperating with Argonne National Laboratory (ANL) Waste Management Operations (WMO) to develop treatment schemes for all liquid wastes stored or being generated at ANL or New Brunswick Laboratory (NBL). Liquid wastes are defined as solutions, slurries, or sludges of low-level, transuranic (TRU), or mixed wastes. The liquid phase is aqueous and/or organic. The Section's work for WMO includes conducting studies to determine the optimum treatment schemes (including automated systems where practical), specifying treatment processes and appropriate equipment for carrying out those processes, and generating needed documentation (e.g., permit applications, safety reviews, operations manuals).

A. Preliminary Waste Segregation and Treatment Schemes

Early work was directed toward characterizing the radioactive liquid wastes and generating preliminary schemes for segregation and treatment. The compositions of wastes generated at ANL are highly variable, but in most cases a large volume reduction is possible through appropriate segregation followed by chemical/physical treatment. Figure 16 shows the scheme generated for segregation of liquid radioactive wastes. As seen in Fig. 16, segregation of the TRU waste streams into hazardous and nonhazardous portions is not being considered. This segregation will not be made because strict regulatory restrictions on TRU waste disposal make the distinction of hazardous and nonhazardous almost meaningless.

Using the waste-segregation scheme shown in Fig. 16, preliminary treatment schemes were generated for each category of waste. Figures 17 and 18 show the schemes in their present state. These treatment schemes are being used as general guides, and refinement will be necessary as work progresses. Calculational and experimental studies will be used to refine the preliminary treatment schemes, after which treatment scenarios and processing equipment will be developed and specified for use by WMO. [Since the treatment and disposal of hazardous materials are regulated under the Resource Conservation and Recovery Act (RCRA), the terms "hazardous" and "RCRA" are used interchangeably in the figures and in this report when referring to such materials.] In Fig. 18, the TRU, nonTRU RCRA, and nonTRU non-RCRA branches are combined, for simplicity's sake, to show one treatment scheme instead of three. This is true for both the aqueous/organic mixture and the inorganic main streams. Generally the same overall treatment scheme, with minor differences in details, will be followed for all three branches, although completely separate equipment will be required for each.

The first two categories of waste receiving attention were the nonTRU aqueous mixed wastes and the scintillation cocktail wastes. Details of the current status of these efforts are reported below.

B. Treatment Plan for NonTRU Aqueous Mixed Waste

One of the first categories to be dealt with in detail was the nonTRU mixed radioactive inorganic liquid wastes that contain toxic metals and/or hazardous acid. Toxic metals (such as Ag, Pb, Hg, and Cd) and hazardous acid concentrations ($2.5 < \text{pH} < 12$) are defined and regulated by the

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Fig. 16. Segregation Scheme for ANL and NBL Liquid Radioactive Waste

Fig. 17. Preliminary Treatment Scheme for All-Organic Wastes. Following separation of "other organics," the segregated streams will undergo basically the same type of treatment, as shown, with some minor differences. The segregated streams will be treated in completely separate equipment to avoid cross-contamination.

Radioactive Liquid Waste

^a Following this separation the segregated streams will undergo basically the same type of treatment, as shown, with some minor differences. The segregated streams will be treated in completely separate equipment to avoid cross-contamination.

^b This segregation will not be necessary for the TRU stream. The reasons are explained in the text.

Fig. 18. Preliminary Treatment Scheme for Organic/Aqueous Mixtures and Aqueous Wastes

RCRA. A waste treatment plan for these wastes was developed. The plan focuses on reducing the volume of mixed waste in a four-step process: (1) chemical treatment/precipitation in an automated system where the pH would be adjusted and the toxic metals would be precipitated, (2) filtration of the toxic metals from the bulk of the treated liquid using both recoverable and disposable filter media, (3) evaporation of the filtrate (now a low-level waste), and (4) concentration by evaporation of the high-solid slurries resulting from the treatment step and the back-flushing of filters. A schematic overview of the treatment plan is shown in Fig. 19. Because of high decontamination factors available in the evaporator, the liquid portion of the waste should be disposable as waste water, while the mixed-waste product will be a solid.

Fig. 19. Overall Scheme for Treatment of Mixed Wastes Containing Toxic Metals
(M = mixer, LLW = low level waste)

A report explaining the preliminary plans for treatment of the inorganic mixed wastes containing toxic metals and/or hazardous acid concentrations has been published.¹¹ A brief overview, summarizing the chemical treatment and filtration systems specified in the report, is given below, along with a summary of work done subsequent to the writing of the report. This subsequent work concentrated on (1) establishing the chemistry, equipment, and control scheme for the chemical treatment/precipitation system and (2) completing the design of the filtration system.

1. Chemical Treatment/Precipitation

a. Overview

The plan for chemical treatment uses pH adjustment of the solution and preliminary precipitation of the metals by addition of a calcium hydroxide slurry. Sodium sulfide solution will then be added to convert the generally amorphous hydroxide solids to crystalline sulfide salts and to precipitate most of the remaining dissolved metals. Additions will be monitored and controlled by titration using pH and sulfide ion-selective electrodes. In general, radioactive components will be found in both the solution and the precipitate fractions of the effluent. Filtration will follow to separate these two fractions. The use of back-flushable filters, where practical, will minimize waste volumes. Following filtration, the filtrate can go to the LLW evaporator for concentration. The slurry of metal salts back flushed from filters will go directly to the mixed-waste drums, which will be shipped to Hanford. Eventually, a mixed-waste concentrator will be used to further concentrate the slurry of filtered solids before they are placed in the mixed-waste drums.

Not all wastes in this category can be treated in precisely the same fashion; some metals, such as chromium, will require special treatment. However, by dividing the wastes into groups based on the hazardous metals they contain, we obtained a standard treatment plan that should apply to more than 95% of the nonTRU inorganic mixed wastes at ANL.

The Waste Treatment Plan report specifies the general scenario for treatment of waste containing mineral acids and toxic metals. According to the plan, neutralization of acidic mixed-waste solutions will be accomplished by pumping the calcium hydroxide slurry into the treatment vessel already containing the acidic mixed waste. A slight modification to this scenario is being pursued. Instead of titrating a slurry into the waste, we will add the slurry of calcium hydroxide to the empty vessel and pump the waste into the tank with a metering pump. The subsequent sulfide addition will follow according to the Waste Treatment Plan.

b. Mixed-Waste Treatment Chemistry

Removal of the RCRA metals (Cd, Cr, Pb, Hg, Se, Ag) from wastewater is readily accomplished using chemical precipitation. The metals are converted to an insoluble form and can be removed by clarification/filtration. Precipitation processes are conventional technologies. The lime-soda softening process is a precipitation process for removing calcium and magnesium divalent ions from groundwater prior to its use in public drinking water supplies.

By adding slaked lime, Ca(OH)_2 , to water containing a divalent ion, the following chemical reaction will occur:

Any of the RCRA divalent metals listed above will form an insoluble metal hydroxide precipitate, M(OH)_2 . The degree of removal depends on the metal used (some are amphoteric), the final pH, the temperature, and the presence of any complexants (which cause interference). Typical operations result in metal concentrations of 0.1-1.0 ppm; for some metals the ppb theoretical equilibrium solubilities can be achieved after filtration to remove all the suspended particles.

Each of the RCRA metals has a minimum solubility at a different pH. If a wastewater mixture of metals is processed, the optimum pH for removal of one metal can be quite different from the optimum pH for another metal. Thus, a pilot study is required to find the best pH for a given mixture. Often, a staged precipitation process is used, and the pH is adjusted in each stage to precipitate one of the targeted metals. In the lime soda softening process, the lime addition stage is followed by a sodium carbonate addition at a more basic pH to optimize the removal of both calcium and magnesium.

To avoid this complexity due to staging, a much more robust precipitating agent can be used. For the removal of the targeted RCRA metals, we employ sodium sulfide precipitation at a pH of 9. The sodium sulfide should be added to the precipitation tank only if the pH exceeds 8 to avoid the formation of H_2S gas. The following stoichiometry applies to the precipitation of the RCRA metals by sodium sulfide:

Metal sulfides are much less soluble than the comparable metal hydroxides. Thus, the precipitation treatment step removes a significantly larger fraction of the hazardous metals from the aqueous phase. In addition, the sulfides are not amphoteric, and the metal sulfide solubilities only monotonically decrease with increasing pH. An excess of 0.5 ppm free sulfide is added to the precipitation tank to ensure that the precipitation reaction goes to completion in a reasonable amount of time. The excess sulfide improves the kinetics of Eq. 18 and also shifts the equilibrium to the right, the insoluble metal sulfide form.¹²⁻¹⁴

Metal hydroxides are also precipitated by sodium hydroxide, although this method requires the addition of a flocculant to remove the particles. In general, polymer-based flocculants are used to coagulate the gelatinous precipitate.^{15,16} After flocculation, sedimentation and/or filtration can be used to recover the precipitated metals. Other flocculants such as alum or iron chlorides often are not robust enough to remove all the metals in a given waste stream. These flocculants can be used only in limited cases with well-known chemistry.

c. Equipment Description for Alkaline Sulfide Precipitation

The apparatus to treat mixed waste is shown in Fig. 20. The flocculation/precipitation tank is 36-cm dia and 69-cm high, and it has a capacity of 2.2 L. Since the tank is made of polyethylene, it is resistant to both acids and bases. To promote flocculation, a blade turbine mixer impeller (8-cm dia, 45° pitch) was selected to attain a high pumping capacity at a low shear rate. It has a low solidity ratio (ratio of impeller projected area to the impeller swept area), which will allow a high flow to be induced in the tank. When operated at low speed (30 rpm), both solids suspension and blending are readily accomplished. Since the tank is not baffled, the impeller shaft was inserted at an angle of 15° off the center vertical axis of the tank. The impeller was rotated so that it pumped downward, the most efficient way to operate this impeller as a blending device.¹⁷ There are two feedback control loops in the tank. The pH control loop consists of a pH electrode, proportional controller, analog-digital converter, and a diaphragm metering pump. The pH control loop activates the diaphragm metering pump to feed either waste acid or the 0.1M nitric acid stock used for pH adjustment. The sulfide control loop consists of a sulfide electrode and a reference electrode, proportional controller, analog-digital converter, and a diaphragm metering pump. The sulfide control loop activates the diaphragm metering pump to feed the 1.9M sodium sulfide solution. The tank has a high flow capacity pump, which can be used to rapidly fill or empty the tank when the batch process is completed. Not shown in the figure is a temperature feedback loop, which can be used to shut down all the system feed pumps in case the exothermic neutralization reactions cause an unacceptably high temperature (45°C). This safety feature will prevent mechanical failure of the polyethylene tank, which has a glass transition temperature near 110°C.¹⁸

d. Laboratory Experiments

Laboratory experiments were carried out using simulated acidic waste solutions; no radioactive nuclides were present in the simulated waste solutions. In these experiments, the acidic waste solution was added to calcium hydroxide slurry to neutralize the acid, followed by addition of sodium sulfide solution to obtain the insoluble sulfides of RCRA metals. The two main goals of the laboratory experiments are (1) to demonstrate that RCRA metals in acid solutions could be precipitated, leaving the filtrate with metals below regulatory levels, and (2) to establish that pH and sulfide-ion electrodes can be used to monitor and control the neutralization and precipitation reactions. The electrodes will be used as process controllers in the actual treatment of mixed wastes.

Fig. 20. Flowsheet for Alkaline Sulfide Flocculation/Precipitation Vessel

The first experiment involved titrating 0.1M $\text{Cd}(\text{NO}_3)_2$, 0.1M $\text{Pb}(\text{NO}_3)_2$, 0.1M AgNO_3 in 2M HNO_3 against 10% $\text{Ca}(\text{OH})_2$ slurry, followed by the addition of 1.9M Na_2S solution. The waste solution (in a burette) was titrated against a known quantity of 10% calcium hydroxide slurry (in a beaker). Upon the first addition of the waste solution, the solution in the beaker developed a yellowish color, changing to brown and finally brownish black, indicative of the formation of oxides and hydroxides of the metals. The acid-base titration was terminated at a pH of 9.8. At this point 1.9M sodium sulfide solution was added to the mixture. Both pH and sulfide concentration in the solution increased. The solution turned black due to the formation of metal sulfides. The addition of both waste solution and sodium sulfide was continued until the pH reached a value of 11, and the sulfide concentration reached a value of about 6 ppm ($\sim 1.9 \times 10^{-4}\text{M}$). (At this point the experimental goal was to reach $\text{pH} = 10$ and $\text{S}^{2-} = 5$ ppm by alternating sodium sulfide addition, which raises the pH, and waste addition, which brings the sulfide concentration down. However, because this goal proved unrealistic, it was changed to $\text{pH} < 12$ and $\text{S}^{2-} = 5$ ppm. This new goal was easily attained.) Both pH and sulfide electrodes responded quickly to changes in the concentrations of H^+ and S^{2-} in the beaker; stable readings were obtained usually within a few minutes following the addition of the waste solution or the sodium sulfide reagent.

The treated waste solution was then filtered through a $0.2\text{-}\mu\text{m}$ membrane filter. The filtrate was acidified with concentrated nitric acid to a pH of 0.9 and analyzed for Cd, Pb, and Ag by ICP/AES. The metal concentrations in the original waste solution and in the filtrate, along

with the RCRA regulatory limits for characterization as hazardous wastes, are shown in Table 23. Also included in Table 23 are the decontamination factors achieved for each of the RCRA metals. The decontamination factor is defined as the metal's concentration in the filtrate divided by its concentration in the original, untreated waste.

Table 23. Experimental Results for Treatment of Simulated Waste Containing RCRA Metals

Metal	Metal Concentration, $\mu\text{g/mL}$		Regulatory Limit	Decontamination Factor
	Untreated Waste	Filtrate		
Cadmium	11,200	<0.05	1.0	>224,000
Lead	20,700	<0.5	5.0	>41,400
Silver	10,800	<0.05	5.0	>216,000

As seen in Table 23, the metal concentrations in the filtrate are much less than the respective regulatory limits, and the decontamination factors are quite high. The volume of filtrate was about three times higher than the original waste volume because of the addition of reagents and water. The decontamination factor is 10^4 or greater, accounting for the dilution.

The above experiment demonstrates that acidic solutions of Cd, Pb, and Ag, each present in 0.1M concentrations, can be effectively removed from the waste solutions through neutralization and precipitation. The experiment also demonstrates that the pH and sulfide electrodes can be adapted for use as process controllers in the scaled-up treatment system.

The filtrate, no longer a hazardous waste, can be disposed in a manner consistent with the disposal practices for nonhazardous liquid wastes. However, in the treatment of actual mixed wastes, some of the radioactive nuclides may not be completely precipitated. The filtrate will then be classified as low-level radioactive waste; further treatments of the filtrate, such as evaporation and concentration, may be necessary before disposal.

The precipitate from the experiment is a mixture of sulfides and hydroxides/oxides of the RCRA metals; insoluble calcium compounds are also present. The original waste volume has been considerably reduced by the neutralization/precipitation treatment. A small volume of precipitate (a few milliliters in the above experiment) was extracted from a large volume of original waste solution (about 75 mL). The precipitate can likely be disposed of as nonhazardous waste. The solid would need to be verified as nonhazardous by the toxicity characteristic leaching procedure. In the actual treatment of mixed wastes, the precipitate is likely to contain some or all of the radioactive nuclides present in the original waste solution; hence, it will be a low-level waste. If the solid were mixed, DOE facilities may use the Hanford solid waste storage site for temporary storage of these wastes.

In a separate experiment, magnesium hydroxide slurry was used instead of calcium hydroxide to neutralize the acid in a simulated waste solution. In place of the RCRA metals, a 0.1M copper sulfate solution in 2M hydrochloric acid was used as the simulated waste solution. Two difficulties were encountered in the use of magnesium hydroxide slurry. Firstly, it was difficult to prepare a sufficiently concentrated slurry (~10%) by reacting magnesium oxide with water. Secondly, the pH electrode responded much more slowly with this slurry compared to calcium

hydroxide. In view of these difficulties, no additional studies were done with magnesium hydroxide. Therefore, calcium hydroxide will be used in all future laboratory experiments, as well as in the actual treatment of mixed wastes.

2. Filtration

A hollow-fiber filter (HFF) skid had been purchased by WMO from the Braidwood Station of Commonwealth Edison. The skid contains a 0.1- μm (nominal size) polyethylene HFF rated for a flow rate of 5 gpm (19 L/min), along with plumbing, instrumentation, and an air-flushing system for the filter. The skid is being modified so it can filter a wide variety of mixed-waste streams.

Because of the wide variety of streams anticipated for filtration, a versatile design, incorporating a number of modules, was pursued. A piping and instrumentation diagram for the filtration system is shown in Fig. 21. As seen in the figure, most modules can either be included in, or isolated from, the flow scheme as desired. The modular design allows the filtration scheme to be varied for research purposes and for treatment of a variety of influents.

The bag filter, using elements with 20- to 60- μm pores, has been included to trap the bulk of the solids. The bag filter combines the advantages of high solids capacity and low disposable-cartridge volume. Plumbing connections in parallel with the bag filter will allow the later addition of a filter press or other pre-treatment option if studies show that it is needed.

Two parallel prefilters, using elements with 1- to 10- μm pores, will protect the HFF from solids loading. One of the prefilter options will be a polypropylene mesh filter; the other will be a sintered-metal, back-flushable filter. Connections between the prefilters and the hollow-fiber filter were included to allow for the possible later addition of a carbon adsorption system to sorb organics which would plug the HFF.

The hollow-fiber filter provides for micro-filtration using a recoverable polyethylene membrane with a pore size of about 0.1 μm . The after-filter, in parallel with the HFF, will include polypropylene disposable elements with 0.1- to 1- μm pores and will be used mainly as a backup for the HFF (for streams such as those containing dissolved organics which cannot be run through the membrane).

C. Compliance with Hanford Waste Acceptance Criteria

Low-level solid wastes generated by Argonne are scheduled to be shipped to Hanford for disposal. The Hanford Site Solid Waste Acceptance Criteria¹⁹ (WAC) was reviewed to determine whether wastes generated following our waste treatment plan will meet these requirements. This report is a very general document which refers to documents from the Washington State Department of Ecology²⁰ and the U. S. Environmental Protection Agency²¹ for many of the details. The waste treatment plan was discussed with ANL-WMO personnel to get their understanding of the Hanford WAC, as well as possible Illinois EPA concerns. It does not appear that we will have any problem satisfying the Hanford WAC or the Illinois EPA concerns. The results of this study are in press.¹¹

TERMINAL CONNECTIONS		
TC1	WASTE FEED IN TO SYSTEM	1" TEFLON
TC2	FILTRATE OUT TO DRAIN	1/2" SS PIPE
TC3	BACKFLUSHING AIR IN	1/2" C.S.
TC4	ELECTRIC POWER TO PUMP	220 V, 25 A

SYMBOLS			
	BALL VALVE, OPEN		FLOW INDICATOR, ROTAMETER
	BALL VALVE, CLOSED		FLOW TRANSMITTER, TURBINE
	BALL VALVE, THROTTLED		FLOW INDICATOR, PANEL-MOUNTED
	PRESSURE RELIEF VALVE		PRESSURE INDICATOR, IN-LINE GAUGE
	CHECK VALVE		PRESSURE TRANSMITTER, DP CELL
	LUB/FILTER/REGULATOR		PRESSURE INDICATOR, PANEL-MOUNTED
	CAPPED TERMINAL		TEMPERATURE INDICATOR, IN-LINE GAUGE
	PULSATION DAMPENER		TERMINAL CONNECTION
			DIAPHRAGM PUMP

	AIR/PRESSURE LINE
	DIRECTION OF FLOW
	ELECTRICAL SIGNAL
	CAPPED CONNECTION

Revision #	Name	Date

Fig. 21. Piping and Instrumentation Diagram for the WMO Filtration Skid

Drawn by: DAVID WYGMANS 2/15/93

D. Evaluation of Horizontal Agitated Film Evaporation Technology

Many radwaste treatment schemes achieve considerable liquid volume reduction using evaporation. Although this step is energy intensive, the decontamination factor achieved is considerable, approaching 10^6 . Forced convection evaporators are designed to evaporate water and reduce the volume of liquid low-level waste streams. The volume reduction achieved in these devices is often a factor of 10-20. Thus, the output concentrate liquor from these evaporators is typically a low-weight-percent slurry. With horizontal agitated-film evaporation technology, this low-weight-percent stream can be concentrated to a high-weight-percent slurry with a volume reduction factor approaching 100.

To evaluate the applicability of horizontal agitated film evaporation technology, the Rototherm manufactured by Artisan Industries, Inc. (Waltham, MA) was tested at their facility using a simulated low-weight-percent solids aqueous waste. The composition of the synthetic feed to the Rototherm is given in Table 24. After 80% boil-up, this feed was found to have a 5°C boiling point elevation; at 90% boil-up, the boiling point elevation was 8°C; and at 70% boil-up, the boiling point elevation was larger than 15°C.

Table 24. Synthetic Feed Solution for the Concentrator

	Conc., mg/L
Cations	
Mn(SO ₄)•H ₂ O	1
Cu(SO ₄)•5H ₂ O	21
Ni(NO ₃) ₂ •6H ₂ O	57
LiNO ₃	350
Ca(NO ₃) ₂ •4H ₂ O	902
Mg(NO ₃) ₂ •6H ₂ O	3374
Anions (Sodium Salts)	
NaHCO ₃	18,818
Na ₂ SO ₄	10,697
NaCl	6721
NaNO ₂	3905
NaNO ₃	184
NaH ₂ PO ₄ •H ₂ O	2191
NaF	752
Na ₂ B ₄ O ₇ •10H ₂ O	123
Na ₂ SiO ₃ •9H ₂ O	202
Total	48,298

A schematic of the Rototherm evaporator is given in Fig. 22. The Rototherm is a horizontal wiped-film evaporator. Feed enters the horizontal heat transfer area and is spread on the heat transfer surface by rotating blades (790 rpm). The blades have an initial tapered region, followed by a straight-edge shape that forces the liquid longitudinally toward the exit at the end of the evaporator body. The evaporator body is heated by an external heat transfer fluid (hot oil or steam) in a jacket which surrounds the main body of the evaporator. The liquid is vaporized in the main body of the evaporator. The vapor flows to a condenser adjacent to the main evaporator body and is recovered. The Rototherm is typically operated at 1 atm pressure, but options are available to operate the device with a vacuum. The Rototherm unit used in the pilot test was also equipped with a double-pipe heat

Fig. 22. Schematic Drawing of Rototherm Evaporator

exchanger preheater, which was used to preheat the feed or boil a small fraction of the feed inside the tube.

Horizontal wiped-film evaporators have several features over other evaporator configurations which make them particularly suitable for high solids evaporation applications. High heat-transfer coefficients occur due to the boiling and agitation at the heat-transfer surface; heat transfer coefficients to liquids without a phase change are typically 50% smaller. Very high liquid rotational speeds are attained at the heat-transfer surface to keep the solids in suspension. There is very little hydraulic pressurizing of the liquid to prevent boiling in the horizontal configuration, so that the temperature to attain boiling is lower than with vertical forced circulation. A disadvantage of this feature is that as water is vaporized, dissolved solids may precipitate from the liquor and foul the heat transfer surface. Other advantages are that the thin film attained in the evaporator reduces the mass-transfer film resistance for evaporation by increasing the liquid surface area. The unit is also operated in a one-pass mode, so that recirculation is not required as in falling-film or other forced-convection devices. The following data were taken during the pilot test:

- Feed flow rate and temperature
- Bottoms flow rate and temperature
- Distillate flow rate and temperature
- Vapor temperature in the tee
- Vapor temperature in the condenser
- Average steam temperature in the heating jacket
- Preheater temperatures
- Condenser cooling water temperatures

The following observations were made during the pilot-plant testing:

- a. Because of the low product rate, typically under 4.54 kg/h, the installed thermocouples cannot accurately determine the bottoms film temperature. This signal had a significant amount of noise and could not be used in a control loop or to derive an accurate heat transfer coefficient from these pilot tests.
- b. Startup was initiated by adding feed first, then turning on the steam supply to both the preheater and Rototherm. Thus, a diverter valve must be installed to return the product obtained during startup back to the feed tank. This can also be used for the rinse solutions.
- c. Independent steam control to both the Rototherm and the preheater is required to adequately adjust product quality.
- d. The distillate, product, and feed flows are not continuous, but are pulsed due to the action of the feed pump and the natural frequency of the Rototherm. On-line metering of these low flows will be difficult to impossible. Control loops on these flows would be of questionable value.
- e. The use of a preheater allows boiling in the preheater tube and, consequently, very high evaporation rates. This could lead to high solids formation in the preheater; if these solids settle, it could lead to clogging.
- f. Because of the high boil-up fraction and low product rates, small changes in the boil-up percentage will produce large changes in the product quality. The boil-up rate must be set high enough to ensure good product quality. The problem of product quality being sensitive to boil-up fraction is generic to this type of continuous or batch operation, and it is a problem which would not be isolated to the agitated-film technology.

The results from the pilot plant tests indicated that the Rototherm could achieve the required 43 kg/h boil-up and produce a consistent high-solids slurry suitable for adsorption.

E. Treatment of Liquid Scintillation Cocktail Wastes

The liquid scintillation cocktail wastes generated from research, development, and service activities at ANL are currently in temporary storage at WMO facilities. The wastes are contained in a number of 55-gal steel drums awaiting proper methods of treatment and disposal. Possible ways to dispose of the wastes were investigated, and a report was prepared and submitted to WMO for further action. This study will be published as an ANL report. The major points of the report are given below:

- Liquid scintillation cocktails that contain radionuclides with $Z \leq 86$ may be sent to a properly licensed facility (for example, Quadrex Corp. in Gainesville, FL) for treatment and disposal. The Quadrex facility will accept both the "old" cocktail wastes resulting from the use of hazardous cocktails with flash points $< 140^\circ\text{F}$ ($< 60^\circ\text{C}$), as well as the "new" cocktail wastes generated from the use of nonhazardous cocktails with flash points $> 140^\circ\text{F}$ ($> 60^\circ\text{C}$).
- At this time liquid scintillation cocktails that contain radionuclides with $Z > 86$ (mostly transuranic nuclides) cannot be sent to a commercial facility for treatment and disposal. The only avenue currently available is the use of the Hanford solid-waste

site for temporary storage, with final disposal at a later time when suitable treatment and disposal facilities become available.

- To use the Hanford Storage facility, users are required to implement a program aimed toward waste reduction (source reduction, volume reduction, etc.). Very little work has been done on treatment of cocktail wastes, especially those containing transuranic nuclides, to achieve volume reduction and/or separation of radionuclides from cocktails. We are planning experimental studies of some of the treatment methods, in particular, the separation of radionuclides from the wastes. If these studies are successful, the organic component of the cocktail wastes, stripped of its radioactivity, can be disposed through commercially available facilities. Experimental studies are expected to begin in summer 1993, in collaboration with the Nuclear Engineering Department of the University of Illinois.

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