CLASSIFICATION CANCELLED

DATE FEB 12 1957 *mol*

For The Atomic Energy Commission

H.B. Cansell

Chief, Declassification Branch

ANL-5213

Photostat Price \$16.80

Microfilm Price \$5.70

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

W.O. 11-187

CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

October, November, and December, 1953

Stephen Lawroski, Division Director
C. E. Stevenson, Associate Division Director

February 1, 1954

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

189-001

Operated by The University of Chicago
under
Contract W-31-109-eng-38

UNCLASSIFIED

1

4814

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	4
I. EXPERIMENTAL BREEDER REACTOR PROGRAM	6
II. SOLVENT EXTRACTION	11
A. Solvent Extraction Processes Using Chloride Systems	11
B. Droplet Settling in Systems of Immiscible Liquids	17
C. Investigation of Stacked Stage Extractor	22
III. FLUORIDE VOLATILIZATION SEPARATION PROCESS	25
A. Laboratory Investigations	25
B. Engineering and Process Development	43
IV. ELEVATED TEMPERATURE SEPARATIONS	51
A. Laboratory Studies of Elevated Temperature Separations	52
B. Semi-Works Studies of High Temperature Processes	68
V. DENITRATION OF URANYL NITRATE IN A FLUIDIZED BED	75
VI. DEVELOPMENT OF ANALYTICAL TECHNIQUES	81
A. Determination of Fluoride, Bromide, and Low Level Plutonium in Fluoride Volatility Samples	81
B. Revised Radiochemical Iodine Analytical Procedure	85
VII. PROCESSING AND UTILIZATION OF RADIOACTIVE WASTES	88
A. Routine Processing of Radioactive Wastes	88
B. Ion Exchange Studies	89
C. Disposal of Sodium-Potassium Alloy	89
D. Electrodeionization of Aqueous Wastes	90
E. Distillation of Acid Wastes	90
F. Preparation of an Experimental Irradiation Source from Waste Fission Products	93
APPENDIX A	98
APPENDIX B	99
LIST OF TABLES	101
LIST OF FIGURES	102

189 002
DECLASSIFIED

CHEMICAL ENGINEERING DIVISION

SUMMARY REPORT

October, November, and December, 1953

I. Experimental Breeder Reactor Program (pages 6 to 10)

The recovery process used in the Argonne analytical facility on unalloyed uranium fuel has been modified to accommodate the 2 per cent zirconium in uranium fuel. Safe procedures for the pickling and dissolving of up to 20 per cent zirconium in uranium alloys have been completed.

II. Solvent Extraction (pages 11 to 24)

Pertinent uranium distribution data have been obtained for hydrochloric acid-tributyl phosphate systems which will be used in the development of a nitrate-free solvent extraction flowsheet. Satisfactory methods for measuring the pertinent physical properties have been found for the investigation of the coalescence of temporary emulsions in immiscible liquid systems.

Two additional runs using the Stacked Stage Extractor are reported.

III. Fluoride Volatilization Separation Process (pages 25 to 50)

Further investigations of the uranium-bromine trifluoride reaction have been made.

The solid-liquid phase diagram of the system bromine pentafluoride-uranium hexafluoride has been completed, and the experimental work on the vapor-liquid equilibrium of the system bromine trifluoride-bromine pentafluoride has been concluded.

Preliminary spectrophotometric studies have been made on the vapors of bromine, bromine trifluoride, and bromine pentafluoride over the range 200 to 800 μ . Research has continued on hydrolyzing and chemically analyzing the interhalogen samples resulting from various laboratory operations.

The status of pilot plant construction is noted, and progress of leak testing and shakedown operations is described. Experiments on uranium hexafluoride purification steps other than distillation are reported.

IV. Elevated Temperature Separations (pages 51 to 74)

Studies on the high temperature distribution of fission products between uranium metal and slag were continued in thoria, urania, alumina, and magnesia crucibles. The redistribution appears to be independent of these crucible materials and was nearly complete after 4 hours.

Work on the electrorefining of uranium using a uranium tetrafluoride-lithium chloride-potassium chloride bath was terminated after it was concluded that the system was not easily adaptable for continuous remote operation.

5

The fundamental program for the determination of thermodynamic data in fused salt systems using crystalline quartz diaphragms in electrochemical cells began to give encouraging results. Stable potentials were obtained for a concentration cell operated at 500°C. with silver electrodes and a silver bromide-lithium bromide electrolyte.

A semi-works group has been set up to scale-up those techniques which appear promising in the laboratory and to test the feasibility of adapting the process of zone melting to uranium decontamination.

V. Denitration of Uranyl Nitrate in a Fluidized Bed (pages 75 to 80)

Studies leading to the development of a technique for denitrating uranyl nitrate in a fluidized bed have continued. By introducing the liquid feed into the side of the fluidized bed, troubles previously reported with caking of the solids have largely been eliminated.

VI. Development of Analytical Techniques (pages 81 to 87)

Known methods of analysis for fluoride, bromide, and low level plutonium have been adapted to analysis of samples from the fluoride volatility program. A modified iodine fission product analysis shows more reliability than the older method.

VII. Processing and Utilization of Radioactive Wastes (pages 88 to 97)

The processing of above-tolerance radioactive liquid wastes continued routinely and without incident. Laboratory investigations into the use of iron in conjunction with ion exchange columns and into the disposal of radioactive NaK using molten nitrate baths were extended.

Pilot plant equipment for studying two processes employing permselective membranes is nearly completed.

The acid recovery equipment was used for three more tracer runs studying recovery and decontamination of nitric acid wastes from the Hallex process and was, in addition, used to concentrate some 400 liters of highly active Hallex waste to about 3 liters. This concentrate was then immobilized in concrete in the Solidification Cell and made into an experimental waste fission product source having a radiation dose rate of about 10^4 r./hr.

189 004

DECLASSIFIED

I. EXPERIMENTAL BREEDER REACTOR PROGRAM

The recovery process used in the Argonne analytical facility on the unalloyed uranium fuel has been modified to accommodate the 2 per cent zirconium in uranium fuel. Safe procedures for the pickling and dissolving of up to 20 per cent zirconium in uranium alloys have been completed.

Program plans have been formulated for the chemical determination of an alpha for a number of fissionable isotopes in the EBR.

A. EBR Flowsheet (TBP) Alterations Required by 2 Per Cent Zirconium in Uranium Fuel (S. Vogler)

The first EBR fuel elements were unalloyed rods of uranium, 94 per cent enriched. A recovery process based on this fuel for use in the Argonne analytical facility was developed and is described in ANL-4530. It has been proposed that the next EBR fuel charge be 2 per cent zirconium in enriched uranium. The results of the work described below point out that certain modifications in the present recovery process for unalloyed fuels which are necessary are compatible with satisfactory recovery and decontamination requirements.

The present recovery process for unalloyed uranium may be described as follows. Each fuel rod is composed of four sections. After removal from the pile, each section is encased in an aluminum can to prevent contact contamination. Four such sections totaling 240 grams represent a dissolver charge. These slugs are dissolved at refluxing temperatures with 900 ml. of concentrated nitric acid containing approximately 10^{-3} M mercuric ion which acts as a catalyst for aluminum dissolution. The dissolver solution, which is about 1.0 M uranium at the completion of the dissolution, is then diluted and the proper reagents added to give the following feed solution:

$\text{UO}_2(\text{NO}_3)_2$	0.1	M
$\text{Hg}(\text{NO}_3)_2$	0.0002	M
HNO_3	3.0	M
$\text{K}_2\text{C}_2\text{O}_4$	0.01	M
$\text{Al}(\text{NO}_3)_3$	0.06	M
$\text{Fe}(\text{SO}_3\text{NH}_2)_2$	0.05	M

The uranium is decontaminated by solvent extraction with tributyl phosphate-carbon tetrachloride. The potassium oxalate is added to both feed and scrub solutions to complex the fission product zirconium in the aqueous phase and so help decontamination. The ferrous sulfamate is added to reduce plutonium to the trivalent state and thus insure its removal in the waste solution.

The use of uranium fuel elements, which contain 2 per cent zirconium by weight, necessitates changes in the dissolution procedure. Explosions have been observed in the reaction of these alloys with nitric acid. The work of this Division on the problem is reported in ANL-5169, page 47, and page 9 of this report. If such a dissolution in nitric acid should proceed without incident, a uranium-bearing residue remains. The addition of fluoride ion (ANL-5103, page 13) to the nitric acid insures complete dissolution of the

alloy. However, the presence of the aluminum from the can makes the fate of the fluoride ion questionable. Thus to insure the availability of the fluoride ion for the zirconium, the aluminum can is first separately dissolved in 2 M nitric acid containing 0.001 M mercuric nitrate at reflux. Approximately 100 ml. of this acid solution is required per gram of aluminum, and the dissolution is completed in about 2 hours. This treatment is without effect upon the uranium. However, to insure against possible losses of uranium, this aluminum dissolver solution may be used to dilute the dissolver solution in preparing the fuel solution.

The zirconium-uranium alloy is then dissolved in the solution of the following composition: HNO_3 , 11 M; $\text{Al}(\text{NO}_3)_3$, 0.75 M; and HF, 0.3 M. Approximately 4 liters of solution are required per kilogram of 2 per cent zirconium alloy, and at the completion of dissolution, the solution should be 1 M in uranium. Under these conditions the fluoride ion complexes the zirconium yielding a clean dissolution, and the aluminum nitrate inhibits the fluoride corrosion of the stainless steel dissolver.

A feed solution was prepared by the type of procedure outlined above, and this was carried through a laboratory batch extraction experiment. Since no irradiated 2 per cent zirconium-uranium alloy material was available, the activity for the laboratory experiment was supplied by an irradiated pin of 10 per cent zirconium-uranium alloy weighing 0.1 gram. The irradiated pin was first dissolved in 100 ml. of the dissolving solution in a stainless steel beaker at approximately 90°C . The 24 grams of 2 per cent zirconium-uranium alloy were dissolved at approximately 100°C . in about 6 hours. At the completion of dissolution, the solution was made up to 100 ml. Analysis of the dissolver solution indicated a uranium concentration of 0.964 M and an acid concentration of 4.42 M. A 10-ml. aliquot of this solution was used to make 100 ml. of feed solution, prepared so that the requisite amount of mercury was present. This feed solution was then carried through a laboratory batch extraction procedure. The compositions of the solutions used are given in Table 1. Thirty ml. of feed was combined with 5 ml. of the scrub solution, and the resulting solution was equilibrated for 3 minutes with 25 ml. of the solvent. The phases were separated and the solvent was equilibrated five times with 1/5 volumes of fresh scrub solution. After the final scrub the organic phase was equilibrated with an equal volume of water, the strip solution. Uranium recovery was demonstrated by equilibrating the aqueous solution after the first equilibration five additional times with fresh solvent. Appropriate assays were made at each of the various steps, and the data are given in Table 1.

The decontamination obtained is summarized briefly in Table 2 and compared with previous similar experiments.

These data indicate:

- (1) After five extraction equilibrations the apparent uranium loss is very low, approximately 0.01 per cent.
- (2) At the extraction step the beta decontamination is about one-third as large as that obtained in the early work with unalloyed fuel. Scrubbing is sufficiently effective so that after five scrubs the total decontamination is about twice that obtained in experiments with unalloyed fuel.

189 006

DECLASSIFIED

8

Table 1

EFFECT OF A FLUORIDE DISSOLUTION PROCEDURE ON
DECONTAMINATION AND RECOVERY OF URANIUM

<u>Feed (IAF)</u>	<u>Scrub (IAS)</u>	<u>Solvent (IAS)</u>	<u>Strip (IBX)</u>
0.2 M UNH*	3.0 M HNO ₃	0.4 M TBP in CCl ₄ (washed	Distilled H ₂ O
3.0 M HNO ₃		2x with 1/10 vol. of H ₂ O	
0.14 M Al(NO ₃) ₃		once with 1/10 vol. 0.1 M	
0.0053 M Zr		NaOH and once with 1/10	
0.03 M F ⁻		vol. of H ₂ O)	
0.0002 M Hg ⁺⁺			

Activity supplied by irradiated 10 per cent zirconium-uranium alloy. Burn-up — 1 per cent; cooled 200 days.

Feed:Scrub:Solvent:Strip = 6:1:5:5

<u>Step</u>	<u>Phase</u>	<u>Activity,</u> <u>ct./ (min.) (ml.)</u>		<u>Uranium, M/L</u>
		<u>Beta</u>	<u>Gamma</u>	
Feed		1.68 x 10 ⁷	1.48 x 10 ⁷	0.21
Extraction 1	organic	3.65 x 10 ³	1.32 x 10 ⁴	-
	aqueous	1.44 x 10 ⁷	1.27 x 10 ⁷	-
Extraction 5	aqueous	-	-	2.31 x 10 ⁻⁵
Extraction 6	aqueous	-	-	1.68 x 10 ⁻⁶
Scrub 1	organic	280	443	-
	aqueous	1.75 x 10 ⁴	5.62 x 10 ⁴	-
Scrub 5	organic	40	40	-
	aqueous	86	135	-
Strip	organic	14	7	-
	aqueous	40	19	-

*The feed solution was made 0.2 M since this is the uranium concentration present at the feed point of a continuous extraction unit.

- 9
- (3) The gamma decontamination at the extraction step is approximately one-tenth that for the earlier experiment with unalloyed fuel. However, the scrubbing is effective, and after the fifth scrub the decontamination is approximately five times larger.
 - (4) Attempts to identify the activities limiting decontamination by means of the single channel pulse analyzer were fruitless because of the very limited residual gamma activity.
 - (5) Only at the first scrub was there sufficient activity so that it was possible to take a material balance. The beta material balance was 104 per cent, and the gamma balance was 88 per cent.

It was thus indicated that the proposed modification for dissolving zirconium-uranium alloy fuel should not be deleterious to uranium recovery or decontamination.

Table 2

EFFECT OF A FLUORIDE DISSOLUTION PROCEDURE ON DECONTAMINATION AND
RECOVERY OF URANIUM FROM URANIUM-ZIRCONIUM ALLOY

	Decontamination Factor			
	This Experiment		Previous Data*	
	Beta	Gamma	Beta	Gamma
Extraction	5.5×10^3	1.34×10^3	1.5×10^4	1×10^4
1st Scrub	7.2×10^4	4.1×10^4	-	-
5th Scrub	5.1×10^5	4.4×10^5	1.9×10^5	1×10^5

*Data obtained in a similar experiment in which Hanford dissolver solution supplied the activity (ANL-4499, page 40).

B. Safe Pickling and Dissolution of Zirconium Alloys (H. Feder, R. Larsen)

The work reported in ANL-5103, page 10, and ANL-5169, pages 47 to 49, has been continued. In previous work it had been demonstrated that uranium alloys containing 2 to 4 per cent zirconium could be safely pickled or completely dissolved in nitric acid if about 4 moles of fluoride ion were added (as HF) per mole of zirconium present. The range has now been extended up to 20 per cent zirconium alloys.

These high concentration alloys have been safely pickled using a solution which was 8 M nitric acid-0.5 M hydrofluoric acid. Adherent oxide

189 008

DECLASSIFIED

films were either dissolved or quickly undercut leaving a shiny metallic surface. Slight coatings of uranium tetrafluoride which sometimes formed on the surface were readily removed by a dip in hot 0.5 M aluminum nitrate solution. The same technique was also successfully used for the complete dissolution of these alloys. Aluminum nitrate can be added subsequent to the nitric-hydrofluoric acid treatment to dissolve the precipitated uranium tetrafluoride.

C. Chemical Determinations of Nuclear Constants (M. Levenson)

The program to determine nuclear constants by chemical analysis was originated to evaluate the conversion ratio of the Experimental Breeder Reactor. A complete breeding analysis of the first loading of the EBR consisting of fuel consumption and product production patterns is given in ANL-5095.

The results of this analysis pointed out the extreme importance of alpha (the ratio of the capture cross section to the fission cross section — σ_c/σ_f) in any breeding cycle. It has been decided to determine values of alpha for uranium-235, plutonium-239, uranium-233, and uranium-238 at twenty different locations in the EBR. The spectrum covered will be from that existing at the center of the core to that existing at the outer edge of the outer blanket. Since all four materials will be irradiated simultaneously in all twenty locations, relative fission rates will also be determined. In order to insure accurate results, the materials being irradiated will be of high isotopic purity. The plutonium being used is some of the material previously produced in the EBR (1.1 parts of Pu²⁴⁰ per 100,000 parts of Pu²³⁹).

It is planned to expand this general program into those areas where absolute amounts of materials produced or destroyed by nuclear reactions may be determined by chemical or radiochemical methods so that some reactor analysis may be done independently of cross section and spectrum data.

189 009

0371229.030

II. SOLVENT EXTRACTION

Work was continued toward the development of a flowsheet designed to eliminate the possibility of violent reactions between nitric acid and organic solvents. Pertinent distribution data between tributyl phosphate-carbon tetrachloride and hydrochloric acid systems are reported.

The fundamental program studying the coalescence of temporary emulsions in immiscible liquid systems has continued. Satisfactory methods are available for obtaining the desired physical properties, density, viscosity, and interfacial tension. Most of the effort has been expended in developing a satisfactory photographic technique for measuring interfacial area.

Work on the Stacked Stage Extractor was continued, and results on two additional runs are reported.

A. Solvent Extraction Processes Using Chloride Systems

(R. P. Larsen, H. M. Feder)

1. Extraction Studies (E. Reilly, G. Kesser)

The partition of uranyl chloride between 30 volume per cent tributyl phosphate in carbon tetrachloride and aqueous hydrochloric acid has been studied as a function of uranium concentration, acidity, and added sulfuric acid. The data are summarized in Table 3 and are shown graphically in Figures 1 and 2. The partition ratios were obtained with pre-equilibrated solutions and, hence, are free of difficulties arising from mass transfer of the components. These data will be of use in the design of extraction, scrubbing, and stripping operations of the projected flowsheet.

The extraction exhibits the usual effects of salting, self-salting, and organic saturation. However, in addition to the expected effects of added sulfuric acid at low acidities, i.e., repression of extraction due to complex formation, there occurred an unpredicted increase in the extraction at high acidities. A possible explanation might be that the added electrolyte caused a decrease in the activity of water in the system which exceeds extraction inhibition due to complexing.

The extraction of sulfate was determined for solutions 0.1 M in uranyl chloride and 1 M in sulfuric acid. In the absence of added hydrochloric acid, no sulfate was detectable by barium ion in the water strip of the organic solution. For 3, 6, and 8 M solutions of hydrochloric acid, the equilibrated organic phases were 0.024, 0.018, and 0.008 M in sulfate, respectively. This decreasing extraction with increasing acidity in the high acid range indicates a diminution of the activity of sulfuric acid, as well as that of water by hydrochloric acid. Thermodynamic data on the mixed acid system are not available for checking this interpretation.

2. Electrolytic Dissolution of Uranium (M. Beederman)

The feasibility of electrolytic dissolution as an alternative to more conventional chemical methods has been further studied. There are

189 C10
DECLASSIFIED

12

Table 3

DISTRIBUTION RATIOS (O/A) FOR URANYL CHLORIDE BETWEEN
30 PER CENT TRIBUTYL PHOSPHATE AND AQUEOUS
HYDROCHLORIC ACID AT 23°C.

<u>Molar Concentration,</u> <u>Hydrochloric Acid</u>	Distribution Ratios (O/A) for Uranyl Chloride at Equilibrium Molar Uranyl Concentrations of:			
	<u>0.01</u>	<u>0.1</u>	<u>1</u>	<u>0.1 M UO_2Cl_2, 1 M H_2SO_4</u>
0.0	0.00012	0.0010	0.043	—
0.1	0.00029	0.0021	0.055	0.0004
0.5	0.0011	0.0032	0.082	0.0028
1.0	0.0081	0.013	0.12	0.010
2.0	0.089	0.12	0.23	0.21
3.0	0.54	0.35	0.27	—
4.0	2.5	0.64	0.32	—
5.0	3.6	1.9	0.37	2.4
6.0	9.0	2.5	0.39	3.5
7.0	15	2.7	0.45	3.8
8.0	21	3.2	0.45	4.0

189 011

0371228.030

13

FIGURE 1.

PARTITION RATIO (O/A) URANYL
CHLORIDE INTO 30 Vol. %
TBP-CCl₄ vs. ACIDITY.

DECLASSIFIED

189

012

FIGURE 2.

PARTITION RATIO (O/A) URANYL CHLORIDE
INTO 30 Vol. % TBP- CCl_4 vs.
AQUEOUS URANIUM CONCENTRATION.

two principal problems which require solution if electrolytic dissolution is to become practicable.

- (1) It is necessary to provide a means of electrical contact with the mass of metallic uranium to be dissolved. Preferably this should be by simple contact requiring no mechanical parts. Moreover, the contact material must exhibit negligible anodic corrosion or gas evolution in warm dilute sulfuric acid.
- (2) It is necessary to select a cathode reaction which will add no undesirable products to the solution and be economical to use.

A number of plausible contact materials have been subjected to a simple screening test with results shown in Table 4.

Table 4

RESULTS OF SCREENING TESTS IN 3 M SULFURIC ACID, 35°C.

<u>Material</u>	<u>Contact with Uranium</u>	<u>Anodic Corrosion</u>	<u>Gas Evolution</u>
Aluminum and Aluminum Alloys	Good	Fair	None
Anodic Graphite	Poor	Disintegrated	Poor
Duriron	Poor	Moderate	Poor
Lead-Antimony (92-8)	Poor	Excellent	Poor
Molybdenum	----	Poor	None
Nickel	----	Poor	None
Platinum	Good	Excellent	Fair
Tantalum	Poor*	Excellent	None
Zirconium	Excellent	Excellent	None

*Initially good, becoming poor after a few minutes.

The results with zirconium were sufficiently encouraging to warrant further experimentation. An unclad Clinton slug lying on its side on a bent strip of sheet zirconium was made anodic in 3 M sulfuric acid. Electrical contact

DECLASSIFIED

189 014

16

was made with the zirconium. Currents up to 90 amperes were successfully sustained for considerable periods, and the dissolution proceeded rapidly with no evidence of filming on the zirconium, decreasing contact, or gassing. With currents greater than 90 amperes, sparking occurred between isolated points on the uranium surface and the zirconium strip. In view of these experiments, it would appear that zirconium sheet-clad slug baskets may make suitable containers for use in electrolytic dissolutions.

Three cathode reactions have been investigated in connection with this process. They are reduction of lead dioxide, reduction of uranyl ion, and evolution of hydrogen.

The reduction of lead dioxide in the form of storage battery plates has been shown to be useful in small scale operations. The net reaction is:
$$U + 3PbO_2 + 4H_2SO_4 = UO_2SO_4 + 3PbSO_4 + 4H_2O$$
 In a typical experiment 1 kg. of uranium in slug form was dissolved in 4 liters of 3 M sulfuric acid at 35°C. in 16 hours. The average current taken was about 40 amperes at 6 volts. Vigorous mechanical stirring was maintained throughout, and concentrated sulfuric acid was added continually to replace the sulfate consumed as lead sulfate. Although the anodic dissolution proceeded smoothly and no other anodic reactions were perceptible, it was concluded that the technique would be of probable value only on this scale. This is due to the fact that the edges of the plates nearest the anode became completely sulfated, and the efficiency dropped sharply even though the more remote areas still showed no appreciable sulfation. Because 3 grams of lead dioxide are required per gram of uranium, it does not appear possible to supply sufficient lead dioxide close to the dissolving metal in large scale dissolutions. Economically, the process is deficient because it requires the consumption of such large quantities of lead dioxide. Even with repeated regeneration of the lead dioxide by electrolysis, the costs tend to become excessive. It should be noted that the electrical cost for the primary anodic dissolution of uranium is only \$0.05/kg., assuming 6-volt power at 10 mils/kw.-hr. This may be compared with \$0.25/kg. of uranium using nitric acid as oxidant.

Two inert cathode processes have been considered. In the first, hydrogen is liberated at the cathode. The net reaction is:
$$U + H_2SO_4 + 2H_2O = UO_2SO_4 + 3H_2$$
 A process in which hydrogen is evolved has the disadvantage of requiring gas disposal by dilution or combustion. In actual trials smooth operation was achieved using a low overvoltage electrode such as bright platinum. Even without agitation, high current densities were obtained, and the high density uranyl sulfate solution formed at the bottom of the cell was drained as a concentrated (0.85 M) solution. In theory at least, this method is the least costly of all oxidations of uranium to the hexavalent state because no chemical oxidant is required.

The second cathode process involves the reduction of uranyl ion using a high hydrogen overvoltage cathode to prevent hydrogen evolution. The net reaction is:
$$U + 2UO_2SO_4 + 4H_2SO_4 = 3U(SO_4)_2 + 4H_2O$$
 The uranous solution must be subsequently oxidized chemically. At least two-thirds of the resulting uranyl sulfate solution is then recycled to the dissolver. This method has been demonstrated on a small scale. Unfortunately, it requires a large consumption of chemical oxidants which are relatively expensive.

An early choice of one of the possible dissolving procedures will be necessary in order that the fission product behavior in succeeding cycles may be studied in properly conditioned solutions.

B. Droplet Settling in Systems of Immiscible Liquids

(W. A. Rodger, V. G. Trice, W. J. Mayer)

A fundamental program on liquid extraction has been initiated (see ANL-5169, page 36) to attempt to develop correlations of the settling rates of temporary emulsions with the physical properties of the system. Such correlations would aid in the prediction of through-put capacity of liquid extraction equipment and contribute to the fundamental understanding of the unit operation of liquid extraction.

Consideration is limited at present to systems of pure components in which no mass transfer occurs. If successful, the work may be extended to more complicated systems, systems of process interest, and some involving mass transfer between phases.

Satisfactory methods are available for the measurement of the desired physical properties, viz., density, viscosity, and interfacial tension. Special attention has been given to the measurement of interfacial tension in order to investigate reported difficulties experienced in making these determinations on thoroughly mixed phases. A series of tests was made which indicated that satisfactory measurements could be made after the mixed phases had completely settled and that errors found shortly after mixing (within 1 hour) were not serious.

Photographic methods have been developed to obtain the interfacial area of the droplets and emulsion break time. In the case of the former, it is hoped that the measurement may be simplified by use of the percentage light transmission through the emulsion.

Five settling runs have been made, and size distribution measurements have been completed for one run.

1. Investigation of Reported Difficulties with Interfacial Tension Determinations

Christian and Rushton¹ reported considerable difficulty in the determination of the interfacial tension of carbon tetrachloride and toluene against water in agitated systems. Since they used the capillary height and ring methods, it appeared desirable to compare this work with results obtained using the drop-weight volume apparatus described in ANL-5169, page 38.

Interfacial tension measurements were made on these two systems as soon as possible after mixing and the readings followed with time for periods up to 7 hours. While the results appeared to be about 5 per cent lower during the first hour (phases cloudy during this period), thereafter literature values were obtained and the results were constant.

¹Master's Thesis of W. Christian at the Illinois Institute of Technology.

2. Measurement of Drop Size and Interfacial Area

In order to study settling rates, it is necessary to determine the particle size and size distribution of the dispersion. Considerable effort has been devoted to the development of satisfactory photographic techniques for obtaining this information. Drop size distribution measurements have been completed for the system 80 per cent tributyl phosphate in carbon tetrachloride dispersed in water.

Drop size is measured indirectly from enlarged photographs taken during agitation. A typical photograph is shown in Figure 3.

a. Description of Photographic Equipment and Techniques

A standard procedure has been developed which leads to a fair measure of the drop size distribution. The camera is focused on the drops immediately behind the cell window (those in the uppermost layer).

Considerable difficulty was experienced in developing techniques for taking these photographs. The equipment and techniques as finally developed are itemized below:

Camera	Deardorff 8 x 10
Lens	Goerz Dagor 6-1/2 inch
Direct Magnification by Lens	3.5X
Film	Super Panero Press
Light Source	Comet repeating flash mercury light
Intensity of Light	100 watt sec.
Duration of Peak Intensity	1/5000 sec.
Typical Exposure	f45 with G filter or f90
Background	Black non-reflecting
Angle of Incident Light	About 40° (back lighting)
Film Development Specifications	Double development in DK50
Typical Enlargement of Negative	About 5X
Over-all Magnification	15 - 25X

b. Procedure for Producing Emulsions and Obtaining Data

The settling cell described in ANL-5169, page 36, is carefully cleaned to prevent contamination, and the liquids to be investigated are placed in the cell in the proper volume ratio. It has generally been found advisable to wet the walls of the cell with the continuous phase prior to the introduction of the discontinuous phase in order to prevent drops of the discontinuous phase from collecting on the windows.

The emulsion is then created by agitation of this mixture. The minimum agitator speed selected is necessarily established as the lowest speed which will produce what appears to be uniform emulsion. This minimum speed varies with the system under observation. The maximum agitator speed is set by the limiting motion which the camera will stop. With the equipment presently in use, that speed appears to be about 1200 r.p.m.

19

Figure 3

TYPICAL PHOTOGRAPH OF EMULSION CREATED BY
AGITATION AT 800 R.P.M.

System: 1 vol. of 80 per cent by vol. TBP in CCl_4
dispersed in 4 vol. of water.

Actual area photographed — about 6.5 x 6.5 mm.

189 018

DECLASSIFIED

c. Discussion of Data

To test the precision of the method, a series of measurements of interfacial area were made from the same photograph by several observers. The results of these measurements, made from a photograph considerably inferior to that shown in Figure 3, are presented below:

<u>Observer</u>	<u>Interfacial Area/Unit Volume of Total Mixed Phase, sq.cm./cu.cm.</u>
A	102
A	98
B	101
C	97
D	107
E	100

In each case, between 100 to 200 drops were measured. The average value for these measurements is 100.8 sq.cm./cu.cm. with a standard deviation of 3.2.

Particle size measurements have been completed only for the first run — 80 per cent tributyl phosphate-20 per cent carbon tetrachloride dispersed in water. Drop size distribution curves (obtained from the measurement of over 3000 drops) for emulsions formed at 800 and 1000 r.p.m. are shown in Figure 4. The over-all distribution of sizes is rather small. The particle size ranged from about 150 to 850 microns for emulsions created at both 800 and 1000 r.p.m.; however, the median diameter was about 450 microns at 800 r.p.m. and 375 microns at 1000 r.p.m. This indicates, as expected, that smaller drops are produced at the higher agitator speeds. In the case of emulsions created at 800 r.p.m., the average ratio of surface area created per unit volume of dispersion was 113.5 with a standard deviation of 2.5; and at 1000 r.p.m., the average value was 135.3 with a standard deviation of 8.4. As might be expected, the measurements show a marked decrease in precision as the limits of the photographic equipment are approached with respect to the stopping of motion.

These measurements are tedious, and it is hoped that suitable correlations of the light absorbency of the various emulsions with interfacial area may be developed. So far, however, this line of attack has not met with success.

3. Observations on Settling Times

After the drop size photographs have been taken, the agitator is turned off and the emulsion allowed to settle. Settling of the emulsion

2/
FIGURE 4.

DROP SIZE DISTRIBUTION IN SYSTEMS
OF IMMISCIBLE LIQUIDS. Run I.

System: One volume of 80 per cent tributyl phosphate by volume
in carbon tetrachloride dispersed in four volumes of
water.

Emulsification at Agitator
Speed of 800 RPM

Emulsification at Agitator
Speed of 1000 RPM

189 020

DECLASSIFIED

is recorded on movie film. No attempt is made to measure drop size during the settling period. Although this probably would be desirable information, wall effects, not present during agitation to as great an extent, would exert considerable influence on the drops next to the windows. Therefore, photographs of these drops would not be representative of the bulk of the emulsion. Study of these movies facilitates accurate measurement of break time (time required for the emulsion to completely disappear) and comparison of settling patterns of various systems. Since the settling process is followed photographically, the entire run is permanently recorded and direct comparison with other runs made subsequently is possible.

Data concerning break time which is obtained from the movies of the settling process have not been analyzed. However, certain generalized comments may be made concerning the settling process. In the case of the first run where the interfacial tension was quite low, about 10 dynes/cm., the over-all break time appears to be controlled by the interfacial tension and not by the density difference, particle size, or the continuous phase viscosity. The drops appeared to settle rapidly into a packed band and then coalesce slowly from this band. Most of this coalescing appeared to take place at the interface with little sign of activity within the bulk of the emulsion. Measurements from the movie revealed that the original emulsion settled from a 20 per cent by volume organic in water (O/W) dispersion to about a 55 per cent (O/W) concentrated band.

In a later run, the system benzene-water was studied with a 20 per cent by volume benzene (O/W) dispersion. Despite the higher density difference and interfacial tension, about 35 dynes/cm., the tendency for the emulsion to pack in a concentrated band was still noticeable although considerably less so than in the first run. The break time was also shorter.

C. Investigation of Stacked Stage Extractor

(K. A. Varteressian, G. J. Bernstein)

During the past quarter, two additional runs similar to that reported in ANL-5169, page 31, were completed. The first of these (Run 13) was a duplicate of that reported previously. In the second (Run 14) the solvent-to-feed ratio was reduced from 9.6 to 5.9, and the scrub-to-feed ratio was reduced from 4.7 to 1.2. These changes reduced the volume of waste per volume of feed from 14.4 to 5.9. Operation during both runs was reasonably steady. Certain operating conditions, losses, and decontamination factors for the two runs and for Run 12 (previously reported) are given in Table 5.

Results of the two duplicate runs (12 and 13) indicate fair reproducibility. The lower reflux ratio in Run 14 probably accounts for the lower decontamination factors and lower plutonium loss in the aqueous waste.

An attempt was made to use this equipment to recover some very low g./t. plutonium by processing two hundred gallons of uranyl nitrate solution which had been produced during the EBR analytical program. The extractor proved incapable of handling this feed, however, due to a combination of low density difference at the feed point and gassing caused by the ferrous sulfamate in the feed and scrub solutions. This feed was therefore batch extracted with tributyl phosphate-carbon tetrachloride in the solvent washing tanks to remove

Table 5

STACKED STAGE EXTRACTOR TESTS —
OPERATING CONDITIONS, LOSSES, AND DECONTAMINATION FACTORS

Solvent	30 per cent TBP in CCl_4		
Temperature	21 to 25°C.		
Interface	At bottom of extractor		
Mixer Stroke	5/16 inch		
Mixer Speed	500 cycles/min. ⁽¹⁾		
	<u>Run 12</u>	<u>Run 13</u>	<u>Run 14</u>
Feed Rate, gal./hr.	0.52	0.50	0.65
Volume Ratios			
Solvent:Feed	9.5	9.6	5.9
Waste:Feed	13.8	14.4	5.9
Scrub:Feed	4.5	4.7	1.2
Nitric Acid in Scrub, <u>M</u>	7.9	8.0	9.9
Reflux to Product Ratio	3.0	3.0	1.25
Uranium Losses, per cent of feed			
In Aqueous Waste	0.006	0.035	0.001
In Solvent Waste	0.00015	0.00023	0.11
Plutonium Losses, per cent of feed			
In Aqueous Waste	5	0.94	0.25
In Solvent Waste	2.4	0.43	0.79
Decontamination Factors			
Beta ⁽²⁾	2860	3800	450
Gamma	2950	4200	1520

⁽¹⁾ 400 cycles/min. in Run 14.

⁽²⁾ Corrected for growth.

189 022

DECLASSIFIED

uranium. The uranium-free aqueous phase was subsequently fed to the Stacked Stage Extractor set up as a compound (exhausting-enriching-stripping) unit, and the plutonium was successfully concentrated into an aqueous stream.

165-23

03712281030

III. FLUORIDE VOLATILIZATION SEPARATION PROCESS

A major laboratory effort has been directed toward uranium dissolution studies and related problems. Several dissolutions of normal uranium slices in bromine trifluoride solution have been completed in the laboratory dissolver. Appropriate liquid and vapor samples were taken and analyzed. The results of these runs have indicated the necessity of certain equipment changes and have furnished a valuable operations test of the analytical methods. Test-tube scale dissolution studies have also been continued in order to establish more clearly those factors influencing rates. Plutonium-uranium alloy has been obtained for small scale experiments on the production of volatile plutonium hexafluoride when the metal is dissolved in halogen fluorides. A few results have been obtained on the reaction of uranium metal with halogen fluorides at high temperatures.

Interhalogen corrosion studies of proposed long duration on several materials of construction generally used in these systems were initiated. The solid-liquid phase diagram of the system bromine pentafluoride-uranium hexafluoride has been completed, and the experimental work on the vapor-liquid equilibrium of the system bromine trifluoride-bromine pentafluoride has been concluded.

Preliminary spectrophotometric studies have been made on the vapors of bromine, bromine trifluoride, and bromine pentafluoride over the range 210 to 800 mμ. Research has continued on hydrolyzing and analyzing chemically the interhalogen samples resulting from various laboratory operations.

The status of pilot plant construction is noted, and progress of leak testing and shakedown operations is described. Also noted are studies connected with uranium hexafluoride purification steps other than distillation (viz., sublimation, vacuum pumping, recrystallization, and zone melting).

Consultations were held with personnel of Oak Ridge and Brookhaven National Laboratories.

A. Laboratory Investigations (R. C. Vogel)

1. Uranium Dissolution Studies

a. Laboratory Dissolver Runs

(J. G. Schnizlein, F. R. Linzer, W. Wade)

The laboratory group is doing experiments directed toward flow-sheet development using a dissolver vessel somewhat larger than conventional laboratory scale. The vessel itself has a volume of 2.3 liters. It and its auxiliary equipment are described in ANL-4979, page 81. The current objectives of experiments in this equipment are to study plutonium behavior. Recent experiments have been made on cold uranium to test the sampling procedure for the liquid and vapor phases and then to establish procedures for various types of hot runs.

100 026
DECLASSIFIED

26

Six cold shakedown runs have been made. From 60 to 130 grams of uranium metal in about 250 ml. of bromine trifluoride is used in a typical run. These runs have provided some operational experience and have suggested certain equipment modifications. A solenoid-operated plunger stirrer has been added to improve the homogeneity of the dissolver solution so that liquid samples taken during the course of the dissolving are representative. The vapor sampling system has been modified. The previous vapor sampling system was designed to give information on plutonium behavior only; but during the runs mentioned above, it became obvious that data on components present in macro amounts in the vapor phase were desirable. In the present untested sampling system, a vapor sample is taken as a gas into a calibrated volume, and then condensed into the sample tube. This arrangement allows direct measurement of the non-condensibles present and calculation of the total number of moles of gas removed. Neither of these observations was possible when samples were condensed directly from the dissolver vapor space.

If these equipment modifications prove to be successful, they will be detailed in the next quarterly report.

b. Studies on Rate of Uranium-Bromine Trifluoride Reaction

(R. K. Steunenberg, H. D. Tyler, W. Wade)

Since the dissolving of uranium in bromine trifluoride is one of the largest scale reactions in this process, it merits considerable study. Of particular interest are the factors which influence the rate of the reaction. Pertinent variables might be purity, metallurgical history and crystal orientation of uranium, velocity of solution past the metal, the presence of components which will accelerate the reaction in the solution or metal, and, of course, the temperature.

In one type of study an attempt has been made to control all the pertinent variables. A cylinder of uranium is rotated in the reagent for a short period. The amount dissolved is found by the weight loss of the cylinder. The duration of the experiment is so selected that the area of the cylinder does not change, and the composition of the solution is not appreciably changed by the reaction products. A detailed description of the apparatus and methods used in this work was given in ANL-5103, pages 57 to 62. The problem mentioned therein of cracks developing in the samples of beta-treated high purity uranium during dissolution was found to arise from the method of preparation of the uranium, and the trouble has been remedied. Difficulty with the interhalogen solution seeping under the gaskets which hold the cylinder also appears to have been corrected through a slight modification of the sample holder.

Rate measurements on the high purity uranium in solutions of bromine trifluoride containing bromine have been continued. Bromine concentrations were measured by sampling the solution before and after each rate determination, the analysis being done either colorimetrically or by hydrolysis and chemical analysis. The loss of free bromine into the vapor space of the apparatus during a run was appreciable, but not sufficiently large to give significant rate errors when appropriate corrections are made.

189 025

017029.030

27

The number of rate measurements now available does not yet permit a quantitative statement of rate dependence, but it is clear that the rate increased somewhat with bromine concentration in a regular manner up to at least 10 mole per cent bromine. Measurements have not yet been made at higher concentrations.

These kinetic studies are primarily concerned with basic chemical information. To complement these studies, rate measurements of total dissolutions in which normal area changes are allowed to take place have been started. These data, although taken under less definitive conditions than the kinetic studies, should allow some prediction and interpretation of rates found in pilot-plant scale dissolutions.

c. Ignition Experiments (L. Stein, W. Wade)

It is desirable to set a safe upper temperature limit for dissolving procedures. It is also pertinent to characterize the conditions necessary for dangerously accelerating reactions with materials of construction and various fluorinating media. An apparatus has been set up to do this type of experiment. Five runs have been made studying the behavior of uranium with bromine trifluoride at temperatures above 150°C. The apparatus is represented schematically in Figure 5. The uranium sample is placed in the bottom of the 3/4-inch nickel reaction tube and heated to the desired temperature under vacuum. The bromine trifluoride is placed in the pre-heater tube, pressurized with helium, and heated to approximately the same temperature. When the intervening valve is opened, the hot bromine trifluoride is blown onto the hot uranium. Temperature and pressure are then observed as the reaction proceeds. The reaction is stopped after a given contact time by boiling off the bromine trifluoride and volatile products under reduced pressure. The entire apparatus is built behind a concrete block wall for the protection of the operator; valves are opened and closed by extension handles, and pressure gauges are observed with mirrors. All parts in contact with vapor are heated electrically to prevent condensation. The two free-volume vessels prevent the pressure from rising too rapidly, and a rupture disc provides protection in the event of an uncontrolled pressure increase.

The experiments thus far indicate that the reaction mechanism may be different under these conditions from low temperature reactions since intermediate products such as uranium tetrafluoride and uranium pentafluoride can be isolated if the dissolution is not carried to completion. In the usual dissolution procedure, in which uranium is placed in bromine trifluoride at room temperature and then heated to the desired temperature, the metal surface remains shiny throughout the dissolution, and uranium hexafluoride appears to be the only uranium product. However, in several of the ignition runs, in which hot bromine trifluoride was flashed onto hot uranium and then boiled off after a short contact time, undissolved residues were obtained which appeared to be uranium tetrafluoride and uranium pentafluoride.

It has been suggested that the reaction occurring under these conditions may be a vapor phase fluorination since the hot metal may be

105 626

DECLASSIFIED

FIGURE 5.

IGNITION APPARATUS.

29

surrounded by a sheath of bubbles even though it is immersed in liquid. If a reaction vessel with windows proves to be feasible, this point will be investigated further.

In several of the runs, the temperature of the reaction vessel rose in sharp jumps, indicating that "ignition" of the uranium may have occurred. Rapid temperature fluctuations could not be followed easily with the portable potentiometer which was used in these early runs, so a fast pen-type recording potentiometer will be used in future runs.

A summary of the five runs is given below. The uranium samples were in the form of cylinders, approximately 1/4 inch in diameter and 3/16 inch long. Metallurgical examination indicates that these were cut from reactor-grade material which was alpha rolled and unrecrystallized. Chemical analysis of the material indicates the following amounts of impurities in parts per million: carbon, 255; nitrogen, 220; oxygen, 200. In all runs, between 2.2 and 2.5 grams of uranium and from 22 to 24 ml. of bromine trifluoride (except 15 ml. in Run 1) were used.

In Run 1 bromine trifluoride at 167°C. was blown over onto the uranium which was at 175°C. The temperature jumped immediately and appeared to climb above 250°C. within 1 minute, although this is somewhat uncertain. The temperature then fell rapidly, reaching 175°C. in 15 minutes. The bromine trifluoride was pumped off 20 minutes after the start of the run; all of the metallic uranium had disappeared, but a granular green residue was found caked on the bottom of the reaction tube.

In Run 2 the uranium was added to the bromine trifluoride at room temperature, and both were heated gradually to 193°C. The bromine trifluoride was pumped off after 43 minutes contact time. A small amount of uranium remained undissolved; the center of the cylinder had been completely penetrated along the axis, leaving a thin cylindrical shell, black and granular in appearance. No other residue remained.

In Run 3 the bromine trifluoride at 151°C. was blown onto the uranium which was at 145°C. The temperature rose slowly to 166°C. in 10 minutes. The bromine trifluoride was pumped off after 12 minutes contact time, leaving a caked green residue with a black center.

In Run 4 the bromine trifluoride at 160°C. was blown onto the uranium which was at 157°C. The temperature rose smoothly to 174°C. in 13 minutes. The bromine trifluoride was pumped off after 15 minutes contact time, leaving a caked green residue with a black center.

In Run 5 the bromine trifluoride at 180°C. was blown onto the uranium which was at 189°C. The temperature rose smoothly to 212°C. in 7 minutes, then jumped abruptly to 226°C. (in 30 seconds), and fell steadily thereafter. The bromine trifluoride was pumped off after a contact time of 37 minutes; no residue remained in the reaction tube.

Additional runs will be made with uranium and bromine trifluoride, and the effect of bromine addition to the bromine trifluoride will also

189 028

RECEIVED

be studied. Upon completion of that work, the behavior of Fluorothene and Teflon in bromine trifluoride above 150°C. will be studied.

2. Plutonium Volatilization Studies (L. Stein)

It is desirable in small scale laboratory experiments to study the behavior of plutonium. Such experiments should be done in a manner closely duplicating the expected large scale conditions. Thus, it is appropriate to use plutonium admixed with uranium in a manner approximating its existence in an irradiated slug. An unirradiated uranium-plutonium alloy of about 400 g./t. level has been obtained from Los Alamos. This furnishes ideal starting material since the experiments can be carried out without shielding.

Equipment has been constructed for these experiments and runs have been carried out in which the alloy was dissolved in bromine trifluoride and the volatile fractions examined for plutonium hexafluoride. No complete analytical data are yet available. It is planned to do runs at controlled bromine concentrations so that the effect of bromine on the formation of plutonium hexafluoride can be quantitatively evaluated.

3. Physical-Chemical Measurements

a. Liquid-Vapor Equilibria for the System Bromine Trifluoride-Bromine Pentafluoride (R. D. Long*)

Since the fluoride volatility process depends upon distillation or sublimation for most of the separations, liquid-vapor equilibrium data are needed for a number of systems. If the dissolving of uranium is carried out in a fluorine atmosphere, one of the binary systems which requires study is bromine trifluoride-bromine pentafluoride. The experimental work on this system has been completed.

A schematic diagram of the Othmer equilibrium still used in collecting the bromine trifluoride-pentafluoride data and a diagram and table of isobaric data at 1 atmosphere have been presented previously in ANL-5103, pages 66 to 71. Some additional data points at 1 atmosphere were reported in ANL-5169, page 54. Also reported in ANL-5169, pages 55 to 56, were isothermal data at 75°C. and 100°C. in diagrammatic and tabular form, and vapor pressure data for bromine pentafluoride, which were fitted with a modified Antoine equation.

More recently, isothermal measurements were made at 50°C., 125°C., and 150°C., and few more data points were determined on the 75°C. and 100°C. isotherms. The data for the 50°C., 125°C., and 150°C. isotherms are presented in Tables 6 and 7.

In order to check the data given in the literature,² vapor pressure measurements were made on bromine trifluoride. These data are listed

* On loan from the University of Michigan, Participating Institution Program

² J. W. Grisard and G. D. Oliver, The Vapor Pressure and Heat of Vaporization of Bromine Trifluoride, K-766, Carbide and Carbon Chemicals Company, K-25 Plant, June 8, 1951.

31

Table 6

LIQUID-VAPOR EQUILIBRIA FOR THE SYSTEMBROMINE TRIFLUORIDE-BROMINE PENTAFLUORIDE

Data obtained using Othmer still described in ANL-5103, pages 66 to 71.

<u>Temperature,</u> <u>°C.</u>	<u>Pressure,</u> <u>mm. Hg</u>	<u>Mole Per Cent</u> <u>BrF₅ in Liquid</u> <u>(x)</u>	<u>Mole Per Cent</u> <u>BrF₅ in Vapor</u> <u>(y)</u>
<u>At ~ 50°C.</u>			
49.67	330.6	20.56	92.42
53.04	385.1	22.54	91.04
49.82	445.5	29.72	96.11
49.98	546.5	39.34	95.96
49.50	597.8	44.92	96.27
49.87	711.1	55.96	97.65
49.96	769.1	62.28	98.32
50.02	927.0	85.92	98.95
50.00	961.9	91.29	99.50
<u>At ~ 125°C.</u>			
125.02	994.2	1.94	26.80
123.89	1548.9	7.16	55.09
125.32	1970.8	9.37	63.86
123.88	2417.8	13.62	73.11
123.55	2715.3	17.70	76.70
125.24	2997.4	18.11	77.20
123.60	3942.8	25.89	87.39
123.34	4252.4	34.22	90.33
124.89	4495.2	35.87	88.86
125.00	5289.2	47.21	90.99
125.27	5600.7	54.13	94.04
124.93	5628.7	50.01	94.70
124.69	5746.9	55.12	94.24
123.25	6191.8	-	95.49
125.08	6704.4	73.60	96.63
125.08	6970.6	80.91	96.94
124.98	7058.3	81.57	98.56
124.91	7358.0	91.64	99.29
124.97	7393.7	92.55	99.23

189 C30

DECLASSIFIED

32

Table 7

LIQUID-VAPOR EQUILIBRIA FOR THE SYSTEMBROMINE TRIFLUORIDE-BROMINE PENTAFLUORIDE

Data at approximately 150°C. obtained from Othmer still described in ANL-5103, pages 66 to 71.

<u>Temperature, °C.</u>	<u>Pressure, mm. Hg</u>	<u>Mole Per Cent BrF₅ in Liquid (x)</u>	<u>Mole Per Cent BrF₅ in Vapor (y)</u>
150.03	2563.6	3.54	38.42
149.92	2603.4	3.62	42.55
150.40	3249.8	6.98	54.88
149.97	4429.3	13.24	68.93
149.92	5903.8	21.07	78.48
149.95	6037.8	23.17	81.04
149.84	6078.6	24.72	79.70
149.87	7309.2	33.69	71.42
149.82	7459.6	34.50	84.46
150.70	9084.2	45.85	85.23
149.81	9500.5	52.33	91.01
150.21	10228	58.95	94.48
149.60	11312	76.36	96.93
150.01	12522	97.04	100.00

189 021

0371228.1030

in Table 8 and are fitted by the Antoine equation

$$\log_{10} p = 7.65757 - \frac{1627.5}{(t + 215)}$$

where p is pressure in millimeters and t is temperature in degrees centigrade. The accuracy of this equation is $0.1^\circ\text{C}.$, or 0.25 per cent in pressure, and it also agrees with the data of Grisard and Oliver³ within these limits.

Temperature measurements were made with a platinum resistance thermometer with a Bureau of Standards certificate in conjunction with a Leeds and Northrup G-2 Mueller bridge. Pressure measurements were made by a comparative method with a metal steam ebulliometer described in ANL-5169, page 57. The condensation temperatures of bromine trifluoride were measured in an ebulliometer of the same design and construction. The pressures over the boiling bromine trifluoride were measured with the same manifold as was used with the equilibrium still.

The behavior of bromine trifluoride during the vapor pressure measurements showed certain ambiguities which have no clear explanation. The condensation temperature varied somewhat with the heat input to the ebulliometer, especially at higher temperatures, the condensation temperature being lower at the higher heat inputs. For temperatures up to $180^\circ\text{C}.$, it was possible to vary heat input from 20 to 50 watts without changing the condensation temperature. In the case of the three highest temperature points in Table 8, this was not possible, and they were not used in fitting the equation to the data. Their inclusion in Table 8 serves only to indicate that a steady state was reached. A tentative suggestion concerning this observation might be an equilibrium decomposition of bromine trifluoride. If this is the case, it could be stated further that (1) the decomposition reaches equilibrium very rapidly, (2) the decomposition products are more volatile than bromine trifluoride, and (3) the equilibrium shifts in the direction of decomposition as the temperature is raised. The behavior of the ebulliometer could then be explained as being due to decomposition of the bromine trifluoride in the heated zone and recombination in the cooler zone. A lowering of the condensation temperature with increased heat input would then result from the rate of decomposition increasing relative to the rate of recombination. If bromine trifluoride does exist in equilibrium with its decomposition products, it appears that accurate pressure-temperature measurements would require the use of a static method with a large liquid-to-vapor ratio.

b. Solid-Liquid Equilibrium for the System Bromine Pentafluoride-Uranium Hexafluoride

(J. Fischer, J. D. Bingle)

Since it will be necessary to have the solid-liquid equilibria for the ternary system which will be used in the dissolver, the laboratory group has been collecting data for the necessary binary systems. The condensed phase diagram of solid-liquid equilibria for the system uranium hexa-

³J. W. Grisard, ibid.

DECLASSIFIED

34

Table 8

VAPOR PRESSURE OF BROMINE TRIFLUORIDE AT VARIOUS TEMPERATURES

Data fitted to the equation:

$$\log_{10} p = 7.65757 - 1627.5/(t + 215)$$

where p = pressure (mm. Hg)
t = temperature (°C.)

Data collected from four different fillings of the ebulliometer.

Temperature, °C.	Obs. Pres., mm. Hg	$\frac{100(\text{obs. } P - \text{calc. } P)}{\text{Calc. } P}$
63.475	65.010	-0.06
64.342	67.831	0.01
64.809	69.472	0.16
74.252	107.15	-0.23
75.049	111.26	-0.03
84.875	169.70	-0.14
85.020	171.33	0.21
94.428	250.28	0.13
94.693	252.28	-0.11
104.410	365.34	0.11
104.663	268.26	-0.03
104.690	268.78	0.02
114.026	514.57	0.07
114.264	518.96	0.09
114.354	520.14	0.01
124.965	741.74	-0.01
125.013	743.15	0.02
134.141	991.31	0.02
134.421	999.86	0.02
144.732	1359.9	0.03
144.916	1364.5	-0.16
154.429	1787.4	0.02
155.589	1844.7	0.01
164.580	2343.1	-0.03
165.223	2384.5	0.03
173.699	2954.9	0.00
180.730	3508.9	0.06
201.4	5839	4.1
215.0	7786	4.4
225.4	9660	5.4

183 033

0370291030

35

fluoride-bromine pentafluoride has been determined by the use of time-temperature cooling and thaw curves. The system, shown in Figure 6, is a simple eutectic type. The solid phases in equilibrium with the saturated solutions are the pure components. The procedural details and data may be found in a topic report on this subject.⁴

c. Spectrophotometric Measurements (R. K. Steunenbergh)

Measurements of the visible and ultraviolet absorption spectra of various interhalogen gases have been started. The initial studies are concerned with the bromine-fluorine system in the hope that the spectrophotometric method may prove applicable to investigation of chemical problems occurring in the volatilization process. The method may also be a useful analytical tool in both fundamental and process work.

Both 10-cm. and 1-cm. nickel cells with replaceable quartz windows have been designed and built. The measurements are made in the range 210 to 800 mμ on a Cary double-beam recording spectrophotometer. A manifold has been constructed for filling the cells, the gas pressure being measured on a mercury manometer, using a Series 206 RF Taylor Pneumatic Pressure Transmitter as a null-point instrument.

Preliminary measurements have given the following results:

(1) Bromine exhibited a well-defined peak at 415 mμ and showed slight absorption below 280 mμ.

(2) Bromine trifluoride showed rather strong absorption below 280 mμ, but if this is due to a peak, it appears to be below 210 mμ, the practical limit of the instrument. Pure bromine trifluoride vapor showed only a very slight absorption at 415 mμ, the characteristic bromine peak; but if the liquid bromine trifluoride was not thoroughly pumped down before the vapor sample was taken, the bromine peak became quite insignificant.

(3) Bromine pentafluoride gave a strong absorption peak at 217 mμ. No other absorption was found over the range 210 to 800 mμ.

4. Corrosion Studies (J. G. Schnizlein, F. R. Linzer)

Long-term corrosion studies are being conducted on several materials of construction commonly used for interhalogen systems. The tests are carried out in nickel boilers constructed of 3-inch nickel pipe 12 inches long with attached condenser (see Figure 7). Air is used for cooling the condenser. Temperature regulators are installed to prevent an unexpected increase in temperature. A gauge and manifold system permit pressure measurement and control. Approximately 450 ml. of interhalogen is refluxed continuously. The metal coupons, 1-3/8 inches square and 1/16 inch thick are supported in the liquid, at the liquid-vapor interface, and in the vapor space. The coupons are held in a nickel rack (see Figure 8) by Teflon insulation to prevent electrical couples. Coupons of nickel, Monel, K Monel,

⁴J. Fischer, R. C. Vogel, Phase Equilibria in the Condensed System Bromine Pentafluoride-Uranium Hexafluoride, ANL-5167, Nov. 27, 1953

FIGURE 6.

SOLID-LIQUID EQUILIBRIA OF THE SYSTEM
URANIUM HEXAFLUORIDE-BROMINE PENTAFLUORIDE.

57

Figure 7

CORROSION BOILER FOR INTERHALOGEN SYSTEM

129 636

DECLASSIFIED

38

Figure 8

COUPON ARRANGEMENT IN CORROSION BOILERS

169

31

03712291030

59

Inconel, welded nickel, and welded Monel are being tested under the following conditions:

<u>Interhalogen</u>	<u>Temp., °C.</u>
100 per cent BrF_3	125
10 mole per cent Br_2 , 90 mole per cent BrF_3	125
10 mole per cent BrF_5 , 90 mole per cent BrF_3	125

The coupons are removed and weighed over periods of about a month. In the few months over which the tests have been made, no significant change has been observed in the weights of the coupons.

5. Analytical Development

a. Chemical Analysis of Interhalogen Samples

(J. G. Schnizlein, F. R. Linzer)

An effort has been made in recent months to set up analytical procedures which can conveniently handle the many samples which will originate from the pilot plant and the laboratory-scale dissolver. The analysis of dissolver solutions depends upon hydrolysis of the interhalogen sample followed by chemical analysis for uranium, fluoride, bromide, plutonium, and appropriate fission products. The development of suitable chemical procedures for these hydrolyzed solutions is discussed on pages 81 to 85 of this report. In order to check the over-all procedure, pure components and standard interhalogen solutions similar in composition to liquid and vapor samples from the laboratory dissolver were prepared from bromine trifluoride, uranium hexafluoride, and bromine. Standard solutions were also prepared by dissolving a known amount of uranium in bromine trifluoride. The interhalogen samples were then hydrolyzed according to the procedure described in ANL-5169, page 71, and submitted to the analytical laboratory for analysis. The nitric acid concentration was left at 0.6 M in the vapor samples and adjusted to 3.0 M in the liquid samples.

One of the problems shown by the data in Table 9 is a low uranium analysis. To test, qualitatively, the possibility of absorption of uranium hexafluoride in the Fluorothene sample tubes, a series of tests was made. Tubes containing uranium hexafluoride and uranium hexafluoride interhalogen mixtures were allowed to stand overnight in dry ice, at room temperature, and at 85°C. Only a tube containing pure uranium hexafluoride maintained at 85°C. showed any weight gain. In actual practice, the standard samples were generally not pure uranium hexafluoride and were stored for only short periods of time at room temperature or below. Therefore, under conditions of sampling dissolver runs, there should be no serious uranium hexafluoride absorption by Fluorothene sample tubes.

The results indicated in Table 9, although usable, are not yet considered satisfactory. Attempts are being made to find the reasons for the low uranium and bromide analysis.

189 038

DECLASSIFIED

40

Table 9

ANALYTICAL RESULTS FOR HYDROLYZED INTERHALOGEN STANDARDS

Sample Designation*	Sample Composition, grams				Per Cent of Error			Material Balance, per cent
	UF ₆	BrF ₃	Br ₂	BrF ₅	U	Br	F	
C	7.8487	0.2746	0.5982	-	-3.5	-3.0	-1.5	97.13
D	2.9921	0.4447	0.9166	-	-2.2	-2.3	0	98.38
G	0.8743	-	2.5273	-	-3.1	-1.1	+0.8	98.69
H	3.5410	-	-	-	-1.2	-	-0.1	99.19
K	5.8107	-	-	-	-0.3	-	-0.2	99.71
L	-	-	4.1181	-	-	+0.6	-	100.62
M	-	2.5204	-	-	-	-4.8	-0.5	96.96
O	U metal 0.2235	2.8315	-	-	-2.3	-2.0	-1.8	98.06
P	U metal 0.2337	2.7835	-	-	-0.8	-1.8	+0.2	99.03
N	-	-	-	1.6135	-	-0.5	-0.1	99.71

*Samples C through L hydrolyzed in 0.6 M HNO₃, 0.5 M N₂H₄·H₂O, 0.5 M H₃BO₃ solution.
 Samples M through N hydrolyzed in 0.6 M HNO₃, 0.5 M N₂H₄·H₂O, 1.0 M H₃BO₃ solution,
 then HNO₃ concentration adjusted to 3 M.

4/

b. Spectrophotometric Method for Bromine in Bromine Trifluoride
(R. K. Steunenberg, H. D. Tyler)

Since one of the products of the reaction between uranium and bromine trifluoride is bromine, and since bromine affects the rate of the uranium reaction, it is important to have a bromine analytical method. A convenient method frequently used in the laboratory for the estimation of bromine in bromine trifluoride consists of simple visual comparison of the color with standards. This principle has been applied in a rough spectrophotometric procedure. A Coleman Model 11A spectrophotometer was used with a cuvette adaptor which accommodated a standard type 5-ml. Kel-F sample tube. The measurements were made at 650 mμ so as to avoid the intense absorption of bromine in the region of 415 mμ. An empirical calibration curve was prepared for a given sample tube which was held in a fixed position. It was found that rotating or interchanging the sample tubes increased the error of the determination by a factor of 2 to 3. A typical calibration curve is given in Figure 9. This method has a practical range of approximately 0 to 3.5 mole per cent bromine in bromine trifluoride with a precision of ± 0.1 mole per cent. Higher concentrations can be determined by dilution with some loss in accuracy. Although this method is not recommended for precise work, it appears to be superior to visual comparison both in accuracy and objectivity.

6. Laboratory Equipment Development

Many of the laboratory operations with interhalogen systems have involved the use of semi-transparent plastic test tubes about 6 inches in length, 3/4 inch O.D., and provided with a flare at the top which will fit a 3/4 inch SAE male refrigerator fitting. In the past such tubes have been compression molded from Kel-F powder at the Argonne Instrument Shop. These tubes were used with good results until a crack in the mold halted their production. Similar tubes have also been machined from solid Kel-F stock, but this practice is wasteful of both labor and material.

Satisfactory tubes of this type are now being produced by an injection molding process under the direction of G. Lobell of the Central Shops at Argonne. Grade 300 Kel-F molding powder is used, Grade 270 having been found unsuitable. This material is of the high density type, i.e., it is in the form of small pellets rather than a powder. The liquid material is injected into the mold at 30,000 p.s.i. and 290°C., then quenched. The no-strength temperature of the finished tubes is 260 to 280°C.; 250°C. is considered a satisfactory minimum. The bursting strength is about 800 p.s.i. Temperature cycling tests from room temperature to 120°C., and from room temperature to -195°C., produce no observable defects. The transparency is adequate, and the tubes have given good service as test tubes, cold traps, etc., for the few weeks they have been in use.

109 040

DECLASSIFIED

42

FIGURE 9.

TYPICAL CALIBRATION CURVE FOR
SPECTROPHOTOMETRIC DETERMINATION
OF BROMINE IN BROMINE TRIFLUORIDE.

Cell: 3-ml. Kel-F Test Tube

Wave Length: 650 m μ

Instrument: Coleman Model IIA Spectrophotometer

189 141

03712281030

43

B. Engineering and Process Development

(W. J. Mecham, M. Levenson, W. A. Rodger)

1. Pilot-Plant Scale Equipment

(N. Levitz, R. C. Liimatainen, I. O. Winsch)

a. Status of Pilot Plant Construction

The construction of the fluoride volatility pilot plant has advanced to the point where leak testing and shakedown operations are under way. The panel board is entirely complete as far as control functions are concerned. Labelling of the panel board and enclosure of the back are in progress. The electrical wiring is complete except for mounting of the thermocouple junctions and of the process line heating wire. Piping and welding is complete for all service and process lines, and that for the sampler manifolds is under way. Air ducts to the exhaust air scrubber (6000 c.f.m. capacity) are being installed.

Packing of the 2-inch diameter fractionating columns has been started. Two columns will have 9 feet of 1/4-inch nickel Cannon Protruded packing, and a third column will have 16 feet of 1/4-inch nickel Podbielniak Helipak (3019). The packing is poured singly into a water-filled column.

b. Valve Testing Program

It has been found necessary to have a complete program of inspection, cleaning, leak testing, seat refinishing, and reassembly of valves for the pilot plant.

Vacuum leak testing has been done with the aid of the Stokes Vacorder, a strip chart recorder connected to a McCleod gauge. With this instrument the leakage rate of a fraction of a mm. of mercury per day can be detected in a test of only a few minutes duration. Pressure testing was done with freon and a G.E. Halogen Leak Detector. Pressures of 100 and 150 p.s.i. were attained by adding nitrogen from a high pressure cylinder to the freon. The 1/2 and 1-inch Monel bellows process valves (Fulton-Sylphon) have not all passed the above test, but a sufficient number of usable valves have been obtained to permit complete installation in process lines.

The 1/4-inch Monel bellows valve (Hoke) for the sampler manifolds have been received and freon leak tested. No leakage was found either across the seat, or through the bellows or body, at 100 p.s.i.

c. Equipment Leak Testing and Shakedown Operations

Freon leak testing of process vessels, lines, and valves in their final installation is well under way. Both welds and Flexitallic gasket connections have proved very satisfactory at this point.

One complete sampler installation has been completed and tested using a methanol-water mixture. Samples are forced through a sample cup and

189 042

DECLASSIFIED

into a small cooled reservoir by heating the process vessel being sampled. The reservoir is then heated, and the excess solution drained back into the process tank. Repeated operations showed that the sample taken was between 1.0 and 1.5 ml., and the time required for the transfer operation was not more than 4 minutes.

The fractionation of a sample taken by this method was determined by using the composition of the vessel contents and of the sample by density determination. The fractionation for a 50-50 methanol-water mixture was less than 1 per cent, which is about the order of accuracy of sample analysis expected on process solutions. Further tests of this kind will be made. The present tests show, however, that this method of transfer and sampling is fast and generally satisfactory.

Complete tests of transfer operations, heating and cooling performance, and hold-up determinations will be made shortly with water as a test material. The fractionating columns will be tested for H.E.T.P. and flooding capacity with n-heptane-methylcyclohexane and/or iso-octane-methylcyclohexane mixtures. After these tests, the equipment will be completely dried and the tests repeated with inactive halogen fluorides. The dissolver will be operated with inactive uranium before active runs are begun.

Several tests are planned of the gas scrubbing tower installed to treat cell exhaust air. Flow and pressure drop characteristics of this unit have been reported previously in ANL-5169, page 75.

- (1) The gas absorption efficiency of the scrubber on carbon dioxide air mixtures will be measured in order to compare performance of this unit with other types of commercial scrubbing equipment and to evaluate its feasibility for application to this widely used system.
- (2) The scrubbing performance on solid ammonium chloride aerosol (of the order of 0.3 micron particles) will be measured to observe the efficiency of this equipment for the removal of solids from air streams.
- (3) Removal of iodine from air will be measured both because of general interest in this system and to supplement halogen absorption data in caustic spray towers reported for the other halogens in a similar but smaller tower (ANL-5015, page 20).
- (4) Performance check points will also be obtained for the interhalogens of interest on the large scrubber to compare its operation with that of the smaller unit described in the above report.

2. Consideration of Separation Processes Other Than Distillation (R. C. Liimatainen)

Some exploratory laboratory work on halogen fluoride separations processes other than distillation is being carried out. This has included

45

study of sublimation, low temperature distillation (vacuum pumping), recrystallization, and zone melting.

The pilot plant has been designed around the basic flowsheet reported in ANL-4720, page 56, in which the separation of uranium hexafluoride from bromine trifluoride and bromine pentafluoride is to be accomplished by fractionation in a packed distillation column. This separation method is most promising for separations in a broad middle range of compositions (5 to 95 per cent) for all components where the relative volatility is high. However, for the extremes of composition, and for separations under conditions where the relative volatility is low, fractionating column separations are not always so successful. An example is the removal of traces of bromine from uranium hexafluoride. Furthermore, it may develop that a rough separation of the bulk of a component is desirable (for example, uranium hexafluoride from the dissolver solution during dissolution). If use can be made of the fact that uranium hexafluoride forms a solid at temperatures at which all other components are liquid or vapor, then a much simpler piece of equipment than a fractionating column might be used. The following exploratory experiments were made with the above considerations in mind.

a. Sublimation

Attention has been directed mainly toward sublimation, i.e., separation of uranium hexafluoride from a vapor mixture by forming solid uranium hexafluoride in a condenser under such conditions that the other components form a liquid which may drain away. Small-scale, all-metal equipment (100 to 300 grams uranium hexafluoride per charge) was enclosed in a lucite box maintained at 65°C. The equipment consisted of a still pot, a water-cooled condenser, and a liquid condensate receiver connected beneath the condenser through a seal which permitted only liquid to pass. A diagram of the equipment is shown in Figure 10.

The charge composition for each batch was predetermined by mixing weighed amounts of pure materials. The still pot charges were completely vaporized. The weights of uranium hexafluoride condensed and liquid condensate were determined from the fractions in the condenser and receiver, respectively. Samples of each were taken, hydrolyzed, and analyzed for uranium and bromine. At low concentrations the bromine analysis was performed nephelometrically by precipitating silver bromide. At high concentrations the bromine was determined by a Volhard titration. The uranium determination was performed colorimetrically by the thiocyanate method. The results are shown in Table 10.

Since the solid product formed in the condenser is pure uranium hexafluoride, the halogen material remaining with the product is occluded liquid. No compounds or solid solution are formed according to the phase diagram. The extent of this impurity is about 10 per cent (as low as 5.7 per cent in SU-4 and as high as 21.6 per cent in SU-5). This is not surprising since the solid is quite porous and thoroughly wetted in appearance.

It would be expected that the separated liquid would carry with it at least sufficient uranium hexafluoride to saturate it at the condensation temperature. While the amount carried with the bromine pentafluoride

100

044

DECLASSIFIED

46

FIGURE 10.

SUBLIMATION EQUIPMENT.

189 645

0372281030

47

Table 10

RESULTS OF URANIUM HEXAFLUORIDE SUBLIMATION TESTS

Run No.	System	Weight Per Cent UF ₆ in Charge	Condenser Product (1) Fraction		Condensate Receiver (2) Liquid Fraction		Material (3) Balance, per cent
			Per Cent of Charge	Weight Per Cent UF ₆	Per Cent of Charge	Weight Per Cent UF ₆	
SU-2	UF ₆ -BrF ₅	65.5	36.0	85.0	30.2	42.2	66.2
SU-3	UF ₆ -BrF ₅	78.3	52.7	88.3	22.9	46.0	75.6
SU-4	UF ₆ -BrF ₃	94.4	65.5	94.3	0.8	30.8	66.3
SU-5	UF ₆ -Br ₂	43.1	45.8	78.4	43.2	26.8	89.0
SU-6	UF ₆ -BrF ₃	79.8	71.5	89.4	9.7	37.5	81.2
SU-7	UF ₆ -Br ₂	52.8	62.0	89.7	21.1	22.6	83.1

Notes:

- (1) The condenser temperatures were about 20°C. for all runs, measured on the outside of the condenser wall.
- (2) The solubility in weight per cent at 20°C. of UF₆ in BrF₃ is 15; in BrF₅, 52; and in Br₂, 6.
- (3) The failure of the product and liquid condensate weights to add up to 100 per cent of charge weight is due to material collected in the cold trap of the vacuum system during transfer operations at the end of the run. The over-all material accounted for was better than 90 per cent of the total.

48

is about equal to the solubility, that carried with the bromine is about twice the solubility; and that carried with the bromine trifluoride, which has a relatively low solubility for uranium hexafluoride, is more than four times the solubility. Erosion of the solid or condensation of uranium hexafluoride on cold liquid surfaces may be responsible for the high carry-over of uranium hexafluoride into the condensate receiver.

A similar experimental separation of uranium hexafluoride from bromine and bromine trifluoride in a cold condenser was reported in K-1012.⁵ The uranium hexafluoride purities reported in this work were higher than those herein reported in Table 10. However, the operations described in K-1012 included both fluorination and vacuum pumping as part of the process, and it is difficult to determine how much of the separation was due to simple solid-liquid separation in the condenser.

The present data (Table 10) show relatively low purity and low fraction recoverable of uranium hexafluoride as solid in a condenser, and this makes its application less attractive, although the purity might be further improved by combination with vacuum pumping.

b. Low Temperature Distillation

In general, relative volatility, α , increases considerably with decreasing temperature, and this situation is often exploited in sublimation processes. While the presence of a solid makes multi-stage operation difficult, in many cases the α is so high that a single stage equilibrium sublimation is quite effective. That this is so for the systems bromine-uranium hexafluoride and bromine pentafluoride-uranium hexafluoride is shown in Table 11.

Table 11

RELATIVE VOLATILITY OF BROMINE-URANIUM HEXAFLUORIDE AND BROMINE PENTAFLUORIDE-URANIUM HEXAFLUORIDE

<u>System</u>	<u>50°C.</u>	<u>0°C.</u>	<u>-30°C.</u>
<u>Vapor Pressure Br₂</u>	1.06	3.9	7.4
<u>Vapor Pressure UF₆</u>			
<u>Vapor Pressure BrF₅</u>	1.96	7.8	23
<u>Vapor Pressure UF₆</u>			

189-
E. B. Olszewski, Preparation of Uranium Hexafluoride from Uranium Tetrafluoride Using Bromine Trifluoride Prepared in Situ, K-1012, May, 1953.

0370281030

49

The wet solid products from the sublimation runs (see Table 10, page 47) were partially volatilized at less than 50 mm. pressure and a temperature of 0°C. The apparatus consisted simply of a vessel containing the charge; the vessel was immersed in an ice bath while pumping through a valve and line at the top. The results are shown in Table 12. This process (sometimes known as vacuum pumping) gives a considerable increase in uranium hexafluoride purity at the cost of increased recycle requirements.

Table 12

VACUUM VOLATILIZATION OF IMPURE URANIUM HEXAFLUORIDE AT 0°C.

<u>System</u>	<u>Charge from Sublimation Run</u>	<u>Weight Per Cent UF₆ in Charge</u>	<u>Weight Per Cent UF₆ in Residue</u>	<u>Weight of Residue, per cent of charge</u>
UF ₆ -BrF ₅	SU-2	85.0	98.9	84.8
UF ₆ -BrF ₅	SU-3	88.3	99.5	67.7
UF ₆ -Br ₂	SU-5	78.4	97.3	58.3
UF ₆ -Br ₂	SU-7	89.7	99.7	66.6

c. Batch Recrystallization

The wet solid product from one sublimation run (SU-4 — UF₆-BrF₃) was remelted and recrystallized, decanting the remaining liquid. This initial composition was 94.3 per cent (weight) uranium hexafluoride; the final — 95.5 per cent. The final material was 88.8 per cent (weight) of the charge.

A second recrystallization yielded a final purity of 97.3 per cent. After the two operations, the final product was 60.8 per cent of the original charge. The data show the batch crystallization gives less purification for a given recovery than does low temperature pumping.

d. Zone Melting

Purification of some solid materials has been achieved by zone melting, a process in which a small section of a bar of material is melted under confinement. This molten zone is then slowly moved in one direction through the bar many times, the effect being (in cases where the method is successful) that impurities are "swept" to one end or the other, or both. The ends may then be cropped, leaving a bar of purer material.

In an effort to estimate the feasibility of this method on the uranium hexafluoride-bromine trifluoride and uranium hexafluoride-bromine systems, three runs were made in a 3/8-inch diameter Fluorothene tube with charge compositions of respectively 48.5, 78.8, and 96.8 per cent (weight) uranium hexafluoride. The former two were done at 0°C. with bromine trifluoride, and the latter at -30°C. with bromine. The molten zone was maintained at 80°C. for all three, the heat being provided by an infrared lamp. After one pass, the tube was sampled at three points. No definite results of directional enrichment appeared; in fact, the results showed large random variation of composition.

The poor results obtained were not due to indecisive results of only a single pass, but rather to operational problems inherent in the characteristics of the mixture. First, the solid was porous, and the melted material penetrated the solid regions on both sides. Second, the vaporization-separation effects were of a higher order than the solubility effects, vapor transfer taking place even when no visible liquid appeared.

This method does not appear promising with the present materials, but it may be applicable for some contaminants in uranium hexafluoride not yet encountered, or to produce a very high purity uranium hexafluoride from relatively pure product.

IV. ELEVATED TEMPERATURE SEPARATIONS

Further studies on the high temperature redistribution of fission products between uranium metal and metalloid phases were carried out. The metalloid phases were formed as a result of reaction between metal and metal impurities, crucible materials, and atmospheric impurities. Thoria, urania, alumina, and magnesia crucibles were used. The metalloid phases were found to be a dense, thin layer of urania at the surface in contact with the crucible and a liquation layer of uranium nitride, oxide, and monocarbide dispersed in the metal matrix. The redistribution of fission products appears to be independent of these crucible materials. Under the experimental conditions employed, the redistribution reaction was nearly complete after 4 hours.

Experiments directed toward the electrorefining of uranium using a molten bath consisting of uranium tetrafluoride in lithium chloride-potassium chloride eutectic were terminated after it was concluded that the system was not easily adaptable for continuous, remote operation. Attention has been directed toward electrorefining operations employing liquid alloy electrodes and stable electrolytes.

Exploratory investigations of the possible production of uranium hexafluoride by electrolysis were continued. Fundamental research directed toward the use of crystalline quartz diaphragms in molten salt electrochemical cells began to give encouraging results. Stable potentials were obtained for a concentration cell operated at 500°C. with silver electrodes and a silver bromide-lithium bromide electrolyte. The transference was shown to be due to the lithium ion.

During the past quarter, a semi-works group was organized to work on engineering aspects of the high temperature processing program. This is a program for developing fast, economical processing methods of a metallurgical type for processing discharged reactor fuel. It is a portion of the over-all ANL program of developing an economically feasible Fast Power Breeder Reactor for central station power application.

The functions of the semi-works group will be:

- (1) scale-up of techniques which have been tested in the laboratory and appear promising;
- (2) independent testing of possible processing methods; and
- (3) study of unit operations at high temperatures (such as heat transfer, mixing, and fluid flow).

It is expected that from this work will come recommendations for the process to be employed and design criteria for full plant scale facilities.

Conferences have been held with personnel of the Ames Laboratory, Knolls Atomic Power Laboratory, Brookhaven National Laboratory, and Bell Telephone Laboratories.

108 050

DECLASSIFIED

52

A. Laboratory Studies of Elevated Temperature Separations (H. M. Feder)

1. Decontamination of Molten Uranium

(N. Chellew, M. Ader, C. Cushing, B. Blumenthal*)

a. Residual Activities After Slagging

A series of active runs made in the manner described in ANL-5169, page 82, has been made principally to determine the effect of various refractory oxide crucible materials and the kinetics of the process whereby fission products are removed by slagging and volatilization. Table 13 lists the residual activities remaining in the recovered metal from each run. The results have been given in terms of the per cent of activity present in an untreated specimen having the same cooling time. In order to improve the accuracy of these comparisons, the activities present in the untreated metal at various cooling times were analyzed seven times, and the results plotted semi-logarithmically versus cooling time. Smooth curves through the points of these plots were then used as a basis of comparison. The estimated (fractional) probable errors of the tabulated values are: plutonium, ± 3 per cent; gross beta and gamma, ± 10 per cent; and individual fission products, ± 20 per cent. Taking into account the fact that the technique of slag removal varied somewhat from run to run, the results given in Table 13 justify the conclusion that variation in the refractory oxide crucible material alone does not cause significant variation in the removal of activities. Thus, the average values for the runs of 4 hours' duration may be considered to be representative for these crucibles.

Accepting, then, the observation that crucible material does not appear to be the determining factor, the effects of run duration may be examined for significance. The retention of specific activities in the bulk metal 1/2 hour at temperature was significantly greater than after 4 hours. From two to ten times greater retention was observed for rare earths, cerium, strontium, cesium, and tellurium. No significant difference in retention was observed for niobium and zirconium. Only a few results are available for runs longer than 4 hours; these results, however, appear to indicate that there is no further significant removal of major activities. It is therefore tentatively concluded that a fairly stable equilibrium situation is attained after about 4 hours at 1200°C.

b. Loss of Fission Elements by Volatilization

The volatilization of fission products has been studied by examination of the volatilized material. During Run 6-A a water-cooled copper disc covered with aluminum foil was suspended about 10 inches above the melt surface. A gamma-ray spectrometer scan of this foil exhibited a strong peak at the cesium gamma energy and another peak (partly obscured by Compton electrons) at the energy characteristic of the rare earths. No alpha activity was observed. The activities were then removed from the foil with nitric acid and analyzed for beta activity. The results obtained are shown in Table 14. About 20 per cent of the gross activity was unaccounted for, but this is probably to be ascribed to differences of mounting

*Consultant, Metallurgy Division, ANL

Table 13

RESIDUAL ACTIVITIES AFTER SLAG REMOVAL AND VOLATILIZATION

Test Material: Sliced ORNL slugs, 50 to 70 grams, 260 to 320 days cooling,
7.1 p.p.m. plutonium

Run Conditions: Temperature 1200°C. Flowing helium atmosphere, 110 cc./min.
Degassed crucibles.

Run No.	Crucible	Time at Temp., hours	Uranium Recovered, per cent	Residual Activities, per cent of starting material										
				Pu	Gross Beta	Gross Gamma	Rare Earths	Ce	Sr	Ru	Cs	Te	Nb	Zr
5-A	ThO ₂	4	95.4	92	10	60	1.2	1.4	0.05**	105	3.6	20	80	29
6-A	MgO	4	95.2	92	11	67	1.8	1.9	1.7	101	2.8	4.2	78	26
8-A	Al ₂ O ₃	4	93.8	92	9.4	60	2.0	-	0.34	119	1.4	10	65	14
2-A*	UO ₂	4	92.6	91	13	74	1.0	0.34	1.2	80	2.9	8.8	95	40
Average		4	94.4	92	11	65	1.5	1.2	1.1	101	2.7	11	80	27
9-A	MgO	1/2	95.2	87	26	50	22	-	-	-	20	24	67	46
7-A	UO ₂	1/2	97.2	100	19	68	11	12	11	96	13	17	80	36
10-A	ThO ₂	11	95.5	87	8.8	52	1.4	-	-	-	-	13	70	19

*Previously reported in ANL-5169, pages 85, 86.

**This result has not been included in the average.

54
Table 14

ANALYSIS OF BETA ACTIVITIES DEPOSITED ON FOIL

Run 6-A

(Magnesia crucible, 4 hours at 1200°C.)

	<u>Per Cent of Gross Beta</u>	
	<u>Deposit</u>	<u>Starting Material</u>
Rare Earths	55	70
Cesium	23	2.7
Strontium	~0.25	6.2
Tellurium	1.7	0.14
Ruthenium	~0.25	4.6

and counting efficiencies. It was therefore established that the most volatile activities were cesium, tellurium, and rare earths. Because the counting rates were in some cases too low for accurate determinations, the furnace tube was disassembled after Run 7-A and subjected to leaching with refluxing nitric acid for several hours. This treatment removed the deposit completely. The leach solution was evaporated to a small volume, silica was removed by a hydrofluoric-sulfuric acid fuming, and the resultant solution analyzed as shown in Table 15. Some 30 milligrams of uranium were found to have been deposited. This fraction of the approximately 550 grams of which had been kept at 1200°C. for varying periods of time may not have been entirely deposited by volatilization; it is possible that part of it was spattered or dusted to the walls.

The observed enrichments generally confirm the previous observations concerning volatilities; they are not as large, however, as might be expected if deposition took place entirely by volatilization. The ultimate enrichment for a given element is a function of its partial pressure. The fraction actually removed by volatilization will also depend on the rate of oxidation of the fission element, the surface area of the melt, its cleanliness and depth, and the time allowed.

c. Loss of Fission Elements by Diffusion

In Table 16 are given the material balances obtained by analyses of the slag and recovered metal. Aside from the analytical errors, the dif-

55

Table 15

SPECIFIC ACTIVITIES DEPOSITED ON FURNACE WALLSRuns 1-A to 7-A

(Temperature 1200°C.)

	<u>Deposit*</u>	<u>Starting Material*</u>	<u>Enrichment of Deposit</u>
Plutonium	0.046	0.013	3.5
Gross Beta	150	3.6	42
Gross Gamma	70	3.65	19
Rare Earths	100	2.5	40
Cerium	97	1.88	52
Strontium	1.05	0.223	4.7
Ruthenium	0.02	0.166	0.12
Cesium	28.6	0.0985	29
Tellurium	0.079	0.0050	15
Niobium	4.1	2.00	2.0
Zirconium	3.3	0.96	3.4

*Units: 10^7 cpm/millimole uranium

189

54

DECLASSIFIED

Table 16

ACTIVITIES RECOVERED FROM SLAG AND METAL

Test Material: Sliced ORNL slugs, 50 to 70 grams, 260 to 320 days cooling, 7.1 p.p.m. plutonium

Run Conditions: Temperature, 1200°C. Flowing helium atmosphere, 110 cc./min. Degassed crucibles.

Run No.	Crucible	Time at Temp., hours	Recovered, per cent of starting material										
			Pu	Gross Beta	Gross Gamma	Rare Earths	Ce	Sr	Ru	Cs	Te	Nb	Zr
5-A	ThO ₂	4	93	87	89	89	87	96	104	47	71	89	96
6-A	MgO	4	95	87	95	82	87	102	96	45	103	87	93
8-A	Al ₂ O ₃	4	93	54**	97	38**	--	106	128	44	113	97	73
2-A*	UO ₂	4	94	94	103	92	81	98	79	52	106	109	114
Average		4	94	89	96	88	85	101	101	47	98	95	94
9-A	MgO	1/2	88	--	76	--	--	--	--	--	118	85	98
7-A	UO ₂	1/2	104	94	96	92	98	103	96	73	101	94	96
10-A	ThO ₂	11	89	82	84	79	--	--	--	--	37	85	105

*Previously reported in ANL-5169, pages 85 to 86.

**Not included in the average

57

ferences from 100 per cent represent the activities lost by both vaporization and diffusion into the crucible. Examination of the results reveals that only for the known volatiles — rare earths, plutonium, cesium, and tellurium — are the recoveries significantly less than 100 per cent. For tellurium, the loss by evaporation does not become perceptible until the melt is held at temperature some time longer than 4 hours. The remaining relatively non-volatile elements, strontium, ruthenium, niobium, and zirconium, show no significant losses in 4-hour runs. On the other hand, hard radiation scans of the crucibles show some fraction of the activities to be present in them. How much of this is due to diffusion, and how much is due to slight adherence of the slag, is not presently known. This fraction adhering to the crucible is presently estimated to be less than 10 per cent.

d. Examination of Slags

Several ingots of unirradiated uranium have been made under conditions closely similar to conditions for the irradiated uranium runs, i.e., 4 hours at 1200°C. in alundum and magnesia crucibles. These ingots were sectioned and examined metallographically and spectrographically. Figures 11 and 12 are typical photomicrographs. The sections were not electropolished, and the uranium had the usual smeared appearance. It may be seen (Figure 11) that the surface in contact with the crucible walls is a dense layer which has a thickness of 30 microns. There were no important differences between the results with different crucibles. Some of this material was subsequently scraped off and examined by X-ray diffraction by D. S. Flikkema. Lines characteristic of uranium dioxide were most prominently present. The liquation layer present at the top of the ingot (Figure 12) had a thickness of 300 microns. Comparison with the results of Blumenthal⁶ shows that the characteristic angular inclusions of uranium nitride, oxide, and monocarbide are present in the uranium matrix. The photomicrographs are not sufficiently clear to permit an estimation of the fraction of volume occupied by these inclusions.

e. Distribution of Fission Elements in Slags

As information has accumulated regarding the nature and distribution of slags, various techniques have been evolved for obtaining maximum information concerning the concentration of fission products occurring in them. To illustrate the type of information being obtained by the etching or fractional dissolving technique, the results for two runs have been compiled in Tables 17 and 18.

Table 17 shows the marked gross concentration in the outermost surface of those fission elements which tend to migrate. The results do not imply, however, that the actual surface layers are inhomogeneous with respect to fission product concentration. The variation may arise because of the existence of the two distinctly different surface structures of different thicknesses. This is illustrated in Table 18 in which the two structures were etched separately by the expedient of covering each in turn with a layer of wax. It is then readily seen that the specific activity of the liquation layer is less than that of the dioxide layer. The specific

⁶B. Blumenthal, The Melting of High Purity Uranium, ANL-5019, Nov. 14, 1952.

58

Figure 11

PHOTOMICROGRAPH OF URANIUM INGOT:

VERTICAL SECTION AT CRUCIBLE (MgO) WALL

Test Conditions: 4 hours at 1200°C.; helium atmosphere
Photographic Scale: 1 cm. = 10 μ

Surface
Layer

METAL

189 657

03712281030

59

Figure 12

PHOTOMICROGRAPH OF URANIUM INGOT:

VERTICAL SECTION AT TOP OF INGOT

Test Conditions: 4 hours at 1200°C.; helium atmosphere
Photographic Scale: 1 cm. = 50 μ

Liquation
Layer

METAL

109 058

DECLASSIFIED

Table 17

60

89

DISTRIBUTION OF ACTIVITIES IN SLAG AT VARIOUS DEPTHS OF PENETRATION, RUN 6-A

Magnesia crucible; 4 hours at 1200°C.; helium atmosphere

Slag	Uranium Content, per cent of total	Penetration,* microns	Pu	Concentrations relative to starting material							
				Gross Beta	Gross Gamma	Ce	Sr	Cs	Te	Nb	Zr
Outer	1.19	0-50	3.1	36	16	39	62	21	36	4.5	36
Middle	1.11	50-100	1.6	18	6.7	23	16	11	8.3	2.2	14
Inner	1.93	100-190	0.88	5.1	2.4	6.5	3.3	2.9	1.7	1.3	4.7

*Based on density of uranium dioxide.

Table 18

DISTRIBUTION OF ACTIVITIES IN SLAG AT VARIOUS DEPTHS OF PENETRATION, RUN 10-A

Thoria crucible; 11 hours at 1200°C.; helium atmosphere

Slag	Uranium Content, per cent of total	Penetrations, microns	Concentrations relative to starting material					
			Gross Beta	Gross Gamma	Rare Earths	Tellurium	Niobium	Zirconium
Liquation Layer	3.31	260*	13	5.2	13	2.9	2.5	10
Sides and Bottom	0.91	30**	33	19	35	13	11	61

*Based on density of uranium.

**Based on density of uranium dioxide.

61

activity of the inclusion particles alone is not known because of the unknown extent of dilution by the uranium matrix. The data of Table 18 also indicate that the inclusion layer is neither more nor less selective than the dioxide layer so far as specific fission elements is concerned.

2. Decontamination of Uranium by Electrorefining (K. Rohde)

Experimental work on the electrorefining process⁷ employing solid uranium electrodes and an electrolyte of fused lithium chloride-potassium chloride eutectic containing 17 per cent uranium tetrafluoride has been completed. Instability of electrolyte, low uranium yield, and dendrite formation on the cathode discouraged consideration of this system for use in recovering and decontaminating uranium on a large scale. A detailed consideration of the pertinent problems is given in the following paragraphs.

a. Uranium Yields

The over-all uranium yields obtained in short-term electrorefining operations are summarized in Table 19. These values, which average about 60 to 65 per cent, were determined by weighing the metal deposit after it had been washed free of salts, rinsed in acetone, and dried in vacuum. The crude product consisted of gray to black dendrites and heavy dust. Before this material could be recast it would have to be washed with dilute acid to remove the oxide film. This operation, as well as the discarding of the dust, which is essentially oxide, would further reduce the yield stated above. This is also a maximum yield value since the uranium depletion of the bath has not been taken into consideration. This problem is considered on page 63.

It is believed that the successful application of a process of this type would require a marked improvement of the recoveries.

b. Cathode Drag Out

In any electroplating process a quantity of the plating bath adheres to the cathode when it is withdrawn from the bath after plating. This adherent bath material is called the "drag out". The uranium metal cathode plated in fused salts is of such a spongy nature that the "drag out" of salt is considerable. This salt is occluded on the macro scale by the uranium dendrites and on the micro scale within the crystals. It may be partially removed by leaching of the water soluble salts and flotation of the water insoluble materials. Completeness of washing was determined by tests for chloride ion and turbidity.

In a typical early experiment, Run 13 of Table 19, a "drag out" loss of uranium of 12 per cent was experienced. In a later series of experiments (Runs 129-1 thru 129-3) the "drag out" losses were investigated further. In these runs the cathode was withdrawn from the melt but held in the hot zone of the furnace tube for about 30 minutes. This allowed some opportunity for drainage of the molten salt from the deposit. The "drag out" losses for the three cathodes averaged 5 per cent. Although these losses were not the major losses in the process, efficient operation would require that they be decreased or the material recovered as a side stream.

⁷R. A. Noland and C. Marzano, The Electrolytic Refining of Uranium, ANL-5102, August 2, 1953.

100 (60)

DECLASSIFIED

62

Table 19

URANIUM YIELDS AND CURRENT EFFICIENCIES FOR URANIUM
ELECTROREFINING IN FUSED LiCl-KCl-UF₄ AT 425°C.

Equipment and experimental procedure
described in ANL-4872, page 147.

Run No.	Dissolved from Anode	Plated on Cathode	Yield, per cent	Current Efficiencies ⁽¹⁾ per cent		Accumulated Time, minutes
				Anode	Cathode	
13	24.7	14.3	58	110	60	143
25	13.5	7.8	58	140	80	68
29 ⁽²⁾	14.3	6.4	45	120	50	111
75-1	16.9	2.8	16	110	20	48
75-2	15.3	15.0	98	100	100	137
75-3	16.2	13.7	85	70	60	193
75-4	10.8	9.0	83	80	70	467
129-1	13.9	8.9	64	110	70	92
129-2	16.1	10.5	65	110	70	218
129-3	13.7	10.3	75	70	50	479

(1) Based on an assumed three electron process at the electrode.

(2) Run 29 was made at 725°C.

189 - 061

037029.030

c. Uranium Material Balances

A complete uranium material balance was obtained for one run. During this extended run ten separate cathode deposits were withdrawn. The first three of these (previously listed in Table 19, Runs 129-1, -2, -3) were obtained under short-term conditions. They accounted for 60 per cent of the metal eventually deposited. The cumulative deterioration of the electrolyte was reflected in decreasing deposition on subsequent cathodes. The material balance data are presented in Table 20. The anode drag out and sample losses were experimental artifacts rather than losses inherent in the process; the distribution of uranium in product streams has been normalized to allow for this. It is evident that the major loss of uranium is due to formation of an insoluble sludge.

d. Deterioration of Electrolyte Composition

During electrolysis, progressive chemical changes take place in the electrolyte. This is illustrated by the following facts:

- (1) The initial electrolyte (13 per cent uranium) remains homogeneous on freezing and is colored dark green. Its only water insoluble component is uranium tetrafluoride. After a run of short duration (e.g., Run 13 of Table 19) the water insoluble fraction after drying still contained 77 per cent uranium (calcd. UF_4 , 75.8 per cent).
- (2) After a run of longer duration (e.g., Run 75 of Table 19) the electrolyte on freezing separated into a pale green upper layer and a red lower layer. Analyses for uranium and fluoride of these layers indicated that the upper layer had been depleted to 12 per cent by weight uranium and the lower layer enriched to 21 per cent uranium. The mole ratios of fluorine to uranium in these layers had dropped to 1.8 ± 0.2 and 2.0 ± 0.2 , respectively, from their initial value of 4.
- (3) After a run of still longer duration (e.g., Run 129 of Table 19) a dark colored crystalline precipitate ("sludge") was detected in the molten electrolyte bath. The supernatant had become still more depleted in uranium, to 4 per cent by weight. The precipitate, incompletely freed of mother liquor, contained 53 per cent uranium by weight. This material was leached with hot water to remove soluble salts. The mole ratio of fluorine to uranium in the gray-green residue was determined to be 1.8 ± 0.2 . Leaching the original sludge with hot ammonium oxalate removed only 2 per cent of the total uranium content, indicating that uranium tetrafluoride was only a minor constituent, presumably occluded with the mother liquor. Complete analyses of the residue have not been made. The available evidence requires that it be either a chance mechanical mixture of uranium trifluoride with uranium metal or dioxide in the proper ratio, or an as yet unknown mixed halide, UF_3Cl . The existence of other mixed halides of trivalent uranium⁸ makes the latter hypothesis not unattractive.

⁸J. J. Katz and E. Rabinowitch, The Chemistry of Uranium, McGraw-Hill Book Co., New York, 1951, page 352.

64

Table 20

ELECTROLYTIC REFINING EXPERIMENTSURANIUM MATERIAL BALANCE, RUN 129

Accumulated Time: 45 hours

Equipment and experimental procedure described in ANL-4872, page 147.

<u>Feed Streams</u>	<u>Weight, grams</u>	<u>Per Cent</u>	<u>Per Cent*</u>
Anode, metal	82.0	63	
Electrolyte, as UF_4	<u>48.0</u>	<u>37</u>	
TOTAL	130.0	100	
<u>Product Streams</u>			
Cathode Deposits	48.7	38.0	45.0
Cathode Drag Out	8.4	6.5	7.7
Sludge	47.7	37.2	44.0
Electrolyte	3.6	2.8	3.3
Anode Drag Out	19.1	{ 15.5	{ —
Samples	<u>0.7</u>		
TOTAL	128.2	100	100

*Normalized to eliminate experimental losses.

189 063

0370291030

65

Observations of the reduction of uranium tetrafluoride in sodium fluoride melts have been made previously (ANL-5103, page 78). This reduction was in part electrolytic and in part non-electrolytic, as evidenced by occasional runs in which weight was lost by both anode and cathode. The high anode current efficiencies experienced in the current series of runs with fresh electrolyte (Runs 13, 25, 29, 75-1, 129-1 of Table 19) also indicate non-electrolytic dissolution of uranium. From these and similar facts it has become evident that progressive deterioration takes place in the bath compositions during the electrorefining operation. The exact sequence of reactions has not been elucidated; presumably, however, its main feature is the gradual reduction of uranium tetrafluoride to less soluble trivalent species which eventually precipitate when their solubility is exceeded.

3. Decontamination of Uranium by Electrolytic Fluorination

(M. Steindler, K. Schoenemann)

If an electrolytic cell could be devised in which uranium could be fluorinated to the hexafluoride, it might have wide application in the production of uranium hexafluoride for gaseous diffusion plants or in separations processes. Two exploratory attempts to produce uranium hexafluoride by electrolysis of solutions of uranium tetrafluoride in molten potassium acid fluoride have been made without success. These failures may be ascribed to one or more of the following possibilities: (1) the anode process is incapable of producing uranium hexafluoride from uranium tetrafluoride; (2) the fluorine generated is incapable of producing uranium hexafluoride from uranium tetrafluoride; or (3) the hexafluoride produced formed stable non-volatile compounds with the components of the electrolyte. The latter two possibilities are being subjected to experimental investigation.

The fluorination of uranium fluoride in a potassium acid fluoride melt has been studied. The apparatus was constructed of nickel lines and Hoke diaphragm valves having a Monel body. It is shown in Figure 13. The joints were silver-soldered and tanks attached to the system by flare couplings. Monel Bourdon gauges (oxygen service) were used throughout. In a typical experiment the nickel reaction vessel was charged with 5 per cent uranium tetrafluoride in potassium acid fluoride, and was heated to $250^{\circ}\text{C} \pm 10^{\circ}\text{C}$. The storage system was filled to a pressure of about 3000 mm. with fluorine, hydrogen fluoride, and argon. The amount of hydrogen fluoride needed was established by the vapor pressure of hydrogen fluoride over molten potassium acid fluoride at the operating temperature and the total pressure of gases in the storage system. The amount of fluorine needed was established by the amount of uranium tetrafluoride introduced and the desired excess above the stoichiometry of the reaction. Argon was added as a diluent. The rate of flow was regulated by the valve between the storage system and the reaction vessel. The gases were bubbled through the melt, which was subsequently cooled and analyzed. This analysis showed that the uranium was present in the hexavalent state. However, no hexafluoride was distilled from the melt. These results will be verified in the near future. Utilizing the same apparatus, the interaction of the hexafluoride with potassium acid fluoride will be studied as a function of temperature. In addition, the system uranium tetrafluoride-potassium acid fluoride is being investigated further.

129

064

DECLASSIFIED

66

FIGURE 13.

APPARATUS FOR THE FLUORINATION
OF UF_4 IN KHF_2 AT 250 °C.

Legend

- A. Fluorine Tank in Protective Steel Box
- B. Hoke Diaphragm Valves
- C. Bourdon Gauge, 0-4000 mm. Hg. Abs.
- D. Storage Tank
- E. Anhydrous HF Tank
- F. Bourdon Gauge, 0-6000 mm. Hg. Abs.
- G. Storage Tank
- H. Argon Tank
- I. Nickel Reaction Vessel, 250 ml. Capacity
- J. Furnace

- K. Aluminum Block Containing Thermocouples
- L. Laboratory Jack
- M. Trap at Room Temperature
- N. Bubbler Trap
- O. Exit Line
- P. Heated Section of Line
- TC₁ Thermocouple to Controller
- TC₂ Thermocouple to Recorder
- TC₃ Thermocouple to Indicator

189 665

037209.030

4. Electrochemical Measurements with Quartz Membrane Cells

(M. Steindler, D. Fredrickson)

An investigation of binary systems of fused salts has been undertaken with the hope of obtaining thermodynamic data of value to other high temperature investigations.

It has long been known that ions of lithium and sodium can be transported through quartz "membranes" under the influence of an electric field. The passage of such ions is not isotropic, but is in the direction of the principal axis of the crystal.⁹ The examination of the crystal structure of crystalline quartz shows "pores", approximately 1Å in radius, running through the crystal. These channels are formed by a helical arrangement of oxide ions. It has been found experimentally that lithium and sodium ions (ionic radii of 0.75Å and 1.00Å, respectively) may be transported but that potassium ions (radius 1.33Å) and other larger ions or ions of greater charge cannot.^{10,11} In view of this property of crystalline quartz, attention has been directed toward possible application of thin quartz membranes to high temperature electrolytic cells.^{12,13} In such cells, the quartz serves as a semi-permeable membrane with a known or readily measured transference number. These membranes should facilitate potential measurements of cells at elevated temperature with elimination of such disturbing effects as junction potentials and diffusion. The references to be found in the literature dealing with the application of these membranes involve for the most part studies of the nature of the transport processes.

The availability of data on some systems containing lithium salts determined the choice of the initial experiments. Salstrom and Hildebrand¹⁴ have investigated the system silver bromide-lithium bromide using electrochemical cells and have obtained thermodynamic data which will be useful for establishing the merit of the quartz membrane system.

Considerable effort has been expended in attempts to overcome the many mechanical problems associated with this system. A thin quartz plate, cut correctly, oriented, and held between two ground tubes of pyrex or quartz by spring tension, was unsatisfactory due to the leakage of the electrolyte and cracking of the fragile membrane. Attempts to attach crystalline quartz to various glasses failed due to the differences in coefficient of expansion. The use of sauerisen proved structurally unsatisfactory at elevated temperatures. Cracking of the diaphragm may also occur as a result of temperature changes in excess of 2°/min. or of wetting by the electrolyte. The latter phenomenon occurs unless the cell is evacuated.

⁹A. F. Joffe, Physics of Crystal, Chap. 9, McGraw-Hill Book Co., New York, 1928.

¹⁰E. Warburg and F. Tegetmeier, Am. Physics, 35, 455 (1888).

¹¹G. Gibson and R. C. Vogel, J. Chem. Physics, 18, 1094 (1950).

¹²P. M. Harris and C. E. Waring, J. Physical Chem., 41, 1077 (1937).

¹³R. C. Vogel and G. Gibson, J. Chem. Physics, 18, 490 (1950).

¹⁴E. J. Salstrom and J. Hildebrand, J. Am. Chem. Soc., 52, 4650 (1930).

189 066

DECLASSIFIED

68

The present cell design consists of a crystalline quartz block $1/2 \times 1/2$ inch drilled out so that a 1 to 2-mm. plate, oriented correctly, remains on the bottom. This block is placed into a fused quartz test tube containing stops which position it correctly, as shown in Figure 14. The inside of the quartz block and the bottom of the test tube are filled with appropriate electrolyte. Heavy silver wires serve as the electrodes in each compartment. The cell and its evacuated container is set into a furnace of high heat capacity capable of maintaining a temperature of $500^{\circ}\text{C}.$ to $\pm 1^{\circ}$. Temperatures and other data are recorded on a Leeds and Northrup Speedomax recorder which also serves as the controlling unit for the furnace. The e.m.f. of the cell is continuously recorded and may also be checked by a conventional potentiometer.

Exploratory experiments using this assembly indicate that concentration cells containing silver bromide-lithium bromide electrolyte yield approximately the predicted e.m.f. A cell of this type,

*
mole fraction

operating at $500^{\circ}\text{C}.$ developed a potential which after a period of time became relatively constant at 20 to 23 mv. The calculated e.m.f. for such a cell, from the data of Salstrom and Hildebrand (ref. 12, page 67), is 29.5 mv. A number of factors, the effects of which are not known, must be considered before a comparison of these data can be made. The volatilization of electrolyte at these temperatures makes knowledge of the exact composition difficult. It has been observed that quartz membranes used for this purpose need to be "conditioned" before reliable, reproducible data can be obtained. Silver foil was spot-welded to the silver wire; this may have produced strains with accompanying thermoelectric effects. Finally, the purity of the reagents used was subject to question. These points are being investigated.

Evidence from other measurements of cells containing silver bromide alone and silver bromide-lithium bromide mixtures indicated that the lithium ion was the major species contributing to ionic transport in this system. The resistance of the cell with both compartments filled with silver bromide at $500^{\circ}\text{C}.$ was 200,000 ohms. An identical cell filled with the silver bromide-lithium bromide mixtures had a resistance of 6,200 ohms. With the latter cell appreciable rates of electrolysis, presumably by lithium ion transport, were obtained by the application of reasonable voltages.

It is planned to extend the study of the silver bromide-lithium bromide system and obtain sufficient data to permit understanding of the conditions under which a quartz membrane may be used to obtain thermodynamic data. Extension of the system to other nonaqueous electrolytes is also planned.

B. Semi-Works Studies of High Temperature Processes

(L. Burris, D. C. Hampson, C. Stockman,** W. A. Rodger)

67¹. Purification of Fuel by Zone Melting

In addition to other possible processing techniques previously described in ANL-4820, page 105, (vacuum melting, liquation and slagging, liquid

**Loaned employee from R. F. Goodrich Co.

.....

69

FIGURE 14.

APPARATUS FOR ELECTROCHEMICAL MEASUREMENTS WITH QUARTZ MEMBRANE CELLS.

Legend

- A. Outer 45mm. Quartz Tube, Surrounded by Furnace
- B. Inner Quartz Tube
- C. Molten Electrolyte
- D. Silver Wire Electrode
- E. Quartz Sleeve Attached to B with Crimped Bottom
- F. Hollow Crystalline Quartz Block
- G. Thermocouple
- H. Molten Electrolyte
- I. 12/30 $\frac{3}{8}$ Containing Tungsten Thermocouple Leads
- J. Serum Bottle Stoppers Holding Cell Electrodes
- K. Electrode Lead Wire
- L. 50/50 $\frac{3}{8}$, Quartz Female, Pyrex Male
- M. To Vacuum System and Inert Gas Train

109 068

DECLASSIFIED

metal or fused salt extraction), the technique of zone melting has been proposed as a promising purification technique. This method, the basic theory of which has been described by Pfann of Bell Laboratories,¹⁵ is one in which a small molten zone is made to traverse a relatively long bar of metal either by moving a bar of metal through a heater or moving a heater along the bar. Constituents or impurities in the metal which lower the freezing point will tend to remain in the melt and move in the direction of zone travel, while those which raise the freezing point will tend to freeze out and move in a direction opposite to the zone travel. The zone travel is in one direction only. After repeated passes of a molten zone have been made, impurities will be concentrated in either or both ends of the bar. Such a procedure is thought to have application in the separation of at least some of the fission products from desired fuel constituents. The speed of the refining operation can be increased by causing a number of molten zones to traverse the bar in a single operation as shown below:

a. Theory of Zone Melting

The distribution coefficient "k" for any constituent is defined as the ratio of concentration of that constituent in the solid to that in the liquid at equilibrium ($k = c_s/c_L$). This, together with the ratio of molten zone length to total bar length, is the important factor which determines the rate of change in solute concentration along the bar and the ultimate degree of separation attainable. The distribution coefficient "k" may be obtained from constitutional diagrams as illustrated in Figure 15. The greater the departure of "k" from unity, the greater the purification obtained in a pass. No separation is possible when "k" equals 1.

Theoretical equations developed to describe zone melting are based on the following assumptions: (1) constant "k", (2) negligible diffusion in the solid, and (3) complete diffusion or uniform composition in a molten zone. The assumption of a constant "k" is probably valid when dealing with fission products whose concentrations in fuel will be low. The rate of zone travel will influence greatly how closely assumption (3) is approached. Zone movements are generally in the neighborhood of 1/8 or 1/4 in./min.

¹⁵W. G. Pfann, Transactions of American Institute of Mining and Metal Engineers, 194, 747-752 (1952).

7/

FIGURE 15.

ILLUSTRATION OF CALCULATION OF "k"
IN ZONE MELTING.

$$k = \frac{C_s}{C_L}$$

189 070

DECLASSIFIED

Theoretical equations included in the article by Pfann have been extended by D. W. Flanders of the ANL Physics Division. For a bar of metal having a cross-sectional area of A and dimensioned as shown below:

the concentrations at point "x" after the n^{th} pass of a molten zone of length "L" is given by:

$$C_n(x) = \frac{k}{LA} \left[\int_0^{x+L} C_{n-1}(x) A dx - \int_0^x C_n(x) A dx \right] \text{ for } 0 < x < B-L$$

and

$$C_n(x) = \frac{k}{LA} \left[\int_0^B C_{n-1}(x) A dx - \int_0^x C_n(x) A dx \right] \text{ for } B-L < x < B$$

where "C" is the concentration in weight per unit volume and "n" is the number of the pass.

These equations are being solved by the trapezoidal rule using the ANL-IBM computer.

Concentration values as a function of distance along the bar are being obtained for each of ten consecutive passes for k 's of 0.01, 0.1, 0.2, 0.5, 2, 5, and 10 and for molten zone lengths 5, 10, and 20 per cent of the bar length. With these curves, and from the movement of fission products observed experimentally in zone-refined bars of active uranium metal, it should be possible to determine the "effective k " for the fission products.

In addition to determining the above concentration curves, the ultimate distribution of solute along the bar (distribution after an infinite number of passes) is also being determined using the IBM computer. When the ultimate distribution of solute is achieved, solute concentrations along the bar are not changed by succeeding passes and $C_n = C_{n-1}$.

169 CT1

03:17:28.1030

23

$$C(x) \text{ ultimate} = \frac{k}{LA} \int_x^{x+L} C(x) A dx \text{ for } 0 < x < B-L$$

and

$$C(x) \text{ ultimate} = \frac{k}{(B-x)A} \int_x^B C(x) A dx \text{ for } B-L < x < B$$

b. Experimental Zone Melting Program

Because of the high reactivity of uranium, experiments in which uranium is melted must be carried out under vacuum or in an inert atmosphere such as argon or helium. This is particularly important in zone melting work where the presence of a slag layer complicates the interpretation of experimental data since laboratory work has shown (see page 52) many fission products are preferentially distributed into a slag layer. Therefore, equipment which is being built to test zone melting will contain provisions for operation under either high vacuum or inert atmosphere. In either case, the charge and equipment will previously be degassed under high vacuum and at a relatively high temperature (about 600°C.).

A schematic diagram of this equipment is shown in Figure 16. Heating will be done inductively using a one- or two-turn coil to keep the molten zone length small. With the presently available 10-kw., 375 kilocycle induction heater, it is tentatively planned to contain the uranium in an aluminum crucible which is itself contained in an outer graphite crucible. The graphite serves as the interceptor of the flux and is heated, heating of the uranium occurring by radiation and conduction from the graphite. The crucible unit is supported by and enclosed in a Vycor tube which will be located in a hood. As protective measures, an inert atmosphere will be maintained in the hood, and a layer of sand will be placed on the bottom of the hood. The uranium bar will be moved mechanically at a rate variable from 1/32 to 1/4 in./min. It is expected that this equipment will be installed and in operation by February 15, 1954.

Attempts were made to zone melt active uranium bars contained in graphite crucibles under an inert atmosphere of argon by manual movement at a rate of 1/8 in./min. These attempts proved inconclusive because of the large slag layer formed and because the starting material was not uniform in composition. These difficulties should be rectified by the use of uniform starting material and the improved equipment now being set up.

Work will also begin in the near future on the design and installation of furnace facilities for conducting melting, slagging, and extraction operations.

189 072

REF ID: A53750

74
FIGURE 16.

SCHEMATIC DIAGRAM OF ZONE-MELTING EQUIPMENT.

V. DENITRATION OF URANYL NITRATE IN A FLUIDIZED BED (1.75-84)

(R. G. Taecker, ^{and} A. A. Jonke, W. A. Rodger)^{1/2}

As described in the previous quarterly report (ANL-5169), a program has been set up to study the possibility of applying the unit operation, fluidization, to the processes required in converting uranyl nitrate hexahydrate to uranium tetrafluoride. The process as presently visualized may ultimately employ several fluidized beds, one or more for each of the three chemical operations required, i.e., denitration, reduction, and hydrofluorination. An important feature of the fluidized solids technique is that the individual units may be interconnected so that solids will flow from one vessel to the next without the use of pumps or conveyors.

Thus far exploratory experiments have been carried out on only the first step, i.e., the conversion of uranyl nitrate solution to uranium trioxide by thermal decomposition. Previous work (ANL-5169, page 92) indicated that the denitration operation could be performed by introducing the uranyl nitrate solution in an atomized form into a heated, fluidized bed of uranium trioxide. The thermal decomposition is accomplished by the rapid transfer of heat from the solid particles in the bed to the finely divided droplets of feed.

In the first experiments considerable difficulty was encountered because of caking of the uranium trioxide at the point of introduction of the feed into the bed. During the past quarter various techniques for introducing the uranyl nitrate solution were tested in an effort to prevent caking. A method was finally adopted which makes use of a spray nozzle mounted horizontally in the side of the reaction chamber in such a way as to feed the atomized liquid directly into the rapidly moving, fluidized uranium trioxide particles.

A. Experimental Equipment

The equipment used in these experiments is illustrated schematically in Figure 17. The fluidized bed was contained in a 3-inch IPS by 15-inch-long stainless steel reaction chamber. The disengaging section consisted of a 6-inch diameter, 4-foot long pyrex glass pipe. The fluidizing air, preheated to 450°C., entered the bed through a sintered, stainless steel, gas dispersion disk. Entrained uranium-trioxide dust was removed from the off-gas by a cyclone separator and a packed bed containing dilute nitric acid.

A pneumatic spray nozzle was mounted through a hole in the side of the reaction chamber about 8 inches above the bottom. Feed solution and atomizing air were metered to the spray nozzle. The fluidized bed level was maintained about 6 inches above the spray nozzle.

Heat was supplied by an electric heater (1.7 kw. maximum) mounted on the outside of the reaction chamber. The bed temperature was controlled manually by means of a variable transformer in the heater circuit.

*On loan from Kansas State College, Department of Chemical Engineering, under the Participating Institution Program.

DECLASSIFIED

189

074

FIGURE 17.
FLUIDIZED BED DENITRATION ASSEMBLY

B. Run Procedure

Two preliminary runs were made using sea sand as the starting material in the fluidized bed. All subsequent runs were made with uranium trioxide as the starting bed material. The original oxide used was prepared by heating Mallinckrodt uranium trioxide to about 300°C. to remove moisture, then screening this material between 40 and 200 mesh. For succeeding runs, the bed material was prepared by screening the product from the previous run through a 40-mesh sieve to remove any oversize particles which were formed.

The feed material for all runs was 2 M uranyl nitrate solution. The conditions used in a typical run are summarized in Table 21.

Table 21

TYPICAL CONDITIONS FOR DENITRATION RUNS

Original Weight of UO_3 in Bed	2500 grams
Particle Size of Original UO_3	-40, +200 mesh
Depth of Bed before Fluidization	5.5 inches
Depth of Bed after Fluidization	14 inches
Bed Temperature	400°C.
Flow Rate of Fluidizing Air*	3.3 c.f.m.
Flow Rate of Atomizing Air*	0.6 c.f.m.
Feed Flow Rate	(See Table 22)

*At 25°C., 14.7 p.s.i.a.

Five runs of varying duration and feed rate were completed. The first run in this series was made at a feed flow rate of 4.5 ml./min. In subsequent runs the flow rate was successively increased up to a maximum of 15 ml./min. as shown in Table 22. The heat input obtainable with the electric heater and the insulation used was insufficient to permit feed rates above 15 ml./min. The total volume of 2 M uranyl nitrate fed varied from 450 ml. in the first run to 5000 ml. in the last.

In the first four runs the uranium trioxide product was allowed to accumulate in the bed since no provision had been made for the removal of product from the reaction chamber during a run. Following these runs the equipment was altered, and a product receiver added as shown in Figure 18. During the last run, product was removed at intervals so as to maintain an approximately constant amount of uranium trioxide in the bed at all times.

100 1076

DECLASSIFIED

FIGURE 18.

REACTION CHAMBER AND PRODUCT REMOVAL
ASSEMBLY FOR DENITRATION RUNS.

79
Table 22

FEED CONDITIONS FOR DENITRATION RUNS

Composition of Feed: 2 M uranyl nitrate

Run No.	Feed Flow Rate, ml./min.	Total Volume Fed, ml.	UO ₃ Equivalent of Uranyl Nitrate Fed, grams	Run Duration, hours
27	4.5	450	257	1.7
28	9	450	257	0.8
29	14	1100	630	1.3
30	15	2000	1140	2.2
31	15	5000	2860	5.5

C. Run Results

In every case the uranium trioxide product was a uniform, free-flowing powder except for a small amount (less than 1 per cent) which caked on the wall opposite the spray nozzle. This cake resulted from penetration of the spray through the expanded bed, and would undoubtedly be eliminated in a larger-diameter unit.

The runs thus far completed have not been of sufficient duration to establish definitely the effect of the process on the particle size of the uranium trioxide in the bed. However, a trend in the direction of particle growth was noted in Run 31. The original bed material for this run all passed through 40-mesh (420 microns). Of the uranium trioxide product which was collected in the product receiver during the run, approximately 10 per cent was in the size range -20, +40 mesh (840 to 420 microns).

An appreciable amount of very fine uranium trioxide particles was formed during the runs and was collected in the cyclone separator. The amount collected in the cyclone ranged from 15 to 20 per cent of the total uranium trioxide equivalent of the uranyl nitrate fed. These fines were probably produced both by attrition of the uranium trioxide in the fluidized bed and by calcination of very fine spray droplets. Disposal of the fines might be accomplished either by blending with the main product stream or by recycling to the fluidized bed. In the latter case, the growth of the particles in the bed as a result of contact with feed spray droplets may be sufficient to prevent an accumulation of fines.

129 C78

DECLASSIFIED

80

D. Observations

The technique of mounting the spray nozzle in the side of the reaction chamber is believed to be important for satisfactory operation without caking. This arrangement permits the uranium trioxide particles to move rapidly through the spray zone. Very high fluidizing air velocities were used (about 2.5 ft./sec.) in order to promote agitation and rapid particle movement.

Because of the relatively large particle size and the high gas velocities used, some tendency toward slugging and the formation of large gas bubbles in the bed was noted.

Future plans include an investigation of the following:

- (1) The use of smaller-diameter particles for the starting bed material.
- (2) The use of increased feed flow rates.
- (3) The recycling of fines to the bed.
- (4) The use of molten uranyl nitrate as feed.
- (5) The effect of the process on particle size of product.
- (6) The optimization of variables.

Plans for a 6-inch diameter pilot-scale unit are well under way. This equipment will provide means for continuous removal of product during running.

During the period, consultations were held with personnel at Mallinckrodt Chemical Works and Standard Oil Development Co.

189 079

0371229.030

81

VI. DEVELOPMENT OF ANALYTICAL TECHNIQUES

(R. C. Vogel)

Known methods of analysis for fluoride, bromide, and low level plutonium have been adapted to fluoride volatility samples. A modified iodine fission product analysis whose separation procedure uses distillation seems to show more reliability than the older method.

An X-ray fluorescence unit is being set up for general analytical work.

A. Determination of Fluoride, Bromide, and Low Level Plutonium in Fluoride Volatility Samples

(L. E. Ross, D. P. Krause)

Experiments on the laboratory and on the semi-works scale in the fluoride volatility program will produce large numbers of interhalogen samples containing uranium hexafluoride, plutonium, and certain fission products. A hydrolysis procedure is described in ANL-5169, page 74, which converts the nonaqueous system to one which can be easily handled in the service analytical laboratory. Hydrazine is used in the aqueous solution to convert the bromine formed during the hydrolysis to bromide, and boric acid is present to complex the fluorides in an attempt to prevent the formation of colloidal fission product fluorides. It is necessary to analyze these solutions for bromide, fluoride, uranium, plutonium, and certain fission products. Methods are given below for fluoride, bromide, and plutonium at a low level. Uranium is determined by the spectrophotometric thiocyanate procedure described in ANL-4750. Fission product analyses have not been tested, but it is believed that the conventional methods will be satisfactory.

The tests described in the paragraphs below have not been carried out on solutions originating from the hydrolysis of actual samples but have been prepared by dissolving appropriate solutes in water. However, in this report on page 40 are described additional experiments in which known amounts of various nonaqueous components are hydrolyzed and determined by these methods.

1. Determination of Low Level Plutonium

The fluoride volatility program will study the behavior of plutonium in interhalogen systems on the laboratory scale and in the semi-works. These experiments will consist of some type of dissolving in which the major portion of the plutonium remains suspended in the dissolver solution. A small fraction of the plutonium will be converted to volatile plutonium hexafluoride. This volatile plutonium will often be divided among many samples. Further, in the hydrolysis of interhalogen samples it seems inevitable that a dilution of at least fifty occurs. Therefore, the plutonium analysis of distilled interhalogen samples is likely to be at a low level. Another difficulty arises since there is a large amount of uranium present. Thus the uranium-plutonium separation must be very good.

189 080

DECLASSIFIED

The plutonium analysis of undistilled liquid phase samples can be done satisfactorily by the usual lanthanum fluoride procedure. A method for the determination of low level plutonium in distilled interhalogen samples has been established from a combination of previously used techniques and is reported below.

The aqueous solution prepared for testing the method has the following composition:

HNO ₃	1.0 M
N ₂ H ₄ ·H ₂ O	0.3 M
H ₃ BO ₃	0.45 M
HBr	0.3 M
UO ₂ (NO ₃) ₂ ·6H ₂ O	0.12 M
HF	0.7 M
Pu	~ 200 or more ct./(min.)(ml.)
Te*	Traces

The procedure makes use of a TTA extraction of the plutonium followed by a 10 M nitric acid strip of the plutonium from the TTA phase. The nitric acid strip is evaporated to dryness, and a lanthanum fluoride precipitation of the plutonium then performed. Eight analyses on the synthetic solution containing 200 ct./(min.)(ml.) of plutonium showed an average recovery of 95 per cent with an average deviation from the mean of 2 per cent. To determine the separation of uranium from plutonium, a lanthanum fluoride precipitate was dissolved in concentrated nitric acid and analyzed fluorophotometrically. The separation factor of uranium from plutonium was found to be 3×10^6 .

It was felt that these results were satisfactory for establishing the presence of plutonium in volatile interhalogen fractions. The detailed procedure can be found in Appendix A.

2. Determination of Bromide

The standard Volhard method with a potentiometric determination of the end point has been shown to be satisfactory for the determination of bromide. The procedure has been set up on the Beckman Automatic Titrator. Pure bromide standards and synthetically prepared fluoride volatility process standards have been low by about 0.3 per cent while the standard deviation from the mean is 0.3 per cent.

The data are given in Table 23, and the procedure used is given in the table heading. It is believed that the accuracy of these results is satisfactory.

3. Determination of Fluoride

The presence of boric acid, a complexing agent for fluoride, in the hydrolysis solution presents a problem in fluoride analysis. The most feasible approach appeared to be the separation of the fluoride from the boric acid. The problem therefore had to be resolved into two parts (1) separation of the fluoride from the interfering substances and (2) determination of the fluoride after separation.

83

Table 23

CHECK OF BROMIDE ANALYTICAL PROCEDURE ON
FLUORIDE VOLATILITY STANDARDS

Solution A - recrystallized KBr dissolved in distilled water

Solution B - synthetic standard typical of volatility hydrolysis procedure 0.24 M HBr,
 0.7 M HF, 0.45 M H_3BO_3 , 0.1 M $\overline{UNH}$,
 1 M $\overline{HNO_3}$, 0.7 M $\overline{N_2H_4 \cdot H_2O}$

Procedure: (1) Sample diluted to 50 ml.
 (2) Made 1 M in nitric acid
 (3) Excess of 0.1 N $\overline{AgNO_3}$ added
 (4) Back-titrated with 0.1 N $\overline{KCNS}$

End Point

Determination: Beckman Automatic Titrator used with the cell $\overline{Ag-AgCNS(s)} || \overline{Hg_2Cl_2(s)}, Hg$ using an Agar- $\overline{KNO_3}$ bridge. The end point was at 200 mv and the break from 100 to 300 mv.

<u>Type of Sample</u>	<u>mg. Br^-</u>	<u>Number of Samples</u>	<u>Average Error, per cent</u>
A	47.52	5	-0.4
B	33.26	10	-0.3
B	39.80	4	-0.3

100 082

DECLASSIFIED

In order to prove the separation method, it was first necessary to find a method suitable for the analysis of "pure" fluoride solutions in the range from 20 to 50 mg. of fluoride. The method described by P. Ehrlich and G. Pietzka¹⁶ and G. Pietzka and P. Ehrlich,¹⁷ making use of the quantitative precipitation of lead bromofluoride and subsequent determination of the bromide by a Volhard titration after dissolution of the lead bromofluoride in dilute nitric acid, was chosen as the most promising. Table 24 gives the results of precipitation of lead bromofluoride from a standard hydrofluoric acid solution. Three satisfactory methods are illustrated for determining the fluoride. These are weighing of the precipitate, titration of the bromide to a visual end point, and titration on the automatic titrator. From these results it was concluded that the precipitation of lead bromofluoride was sufficiently accurate and precise for analysis of the separated fluoride.

Table 24

DETERMINATION OF FLUORIDE ON KNOWN SAMPLESBY THE LEAD BROMOFLUORIDE PROCEDURE

- Procedure A - Precipitation of $PbBrF$ from a standard HF solution, following by weighing of precipitate.
- Procedure B - Precipitation of $PbBrF$ from a standard HF solution, followed by dissolving in HNO_3 and titration using visual end point.
- Procedure C - Same as B except that titration was carried out on a Beckman Automatic Titrator.

<u>Procedure</u>	<u>Known mg. F^-</u>	<u>Number of Samples</u>	<u>Average Error, per cent</u>	<u>Standard Deviation, per cent</u>
A	34.18	6	-0.5	± 0.4
A	68.11	7	-0.2	± 0.3
B	68.11	3	0.1	—
B	34.18	2	0	—
C	68.11	6	-0.2	± 0.3
C	34.18	4	-0.7	± 0.3

¹⁶P. Ehrlich and G. Pietzka, A. Analyt. Chem. 133, 84 (1951).

¹⁷G. Pietzka and P. Ehrlich, Angew. Chem. 65, 131 (1953).

A Willard and Winters-type distillation was deemed to be the best means of separation of the fluoride from the mixture. Figure 19 shows the type of still which was decided upon for the distillation. It is intended to further modify the distillation apparatus to provide a constant temperature bath for heating rather than the heating mantle now used. The distillation is carried out from phosphoric acid at a temperature of 180 to 200°C. Since bromide is present in the samples and would also distill at these temperatures, silver nitrate is added to the still pot to precipitate the bromide and prevent its volatilization. The presence of an unknown amount of bromide in the distillate could possibly cause difficulty in the subsequent precipitation of lead bromofluoride. Table 25 shows results obtained on distillation of various pure fluoride standards.

It is believed that it has been established that this procedure will give results of very satisfactory accuracy and precision. The procedure is given in detail in Appendix B.

B. Revised Radiochemical Iodine Analytical Procedure
(E. Turk, R. Fischer)

Radiochemical iodine samples prepared by the analytical procedure described in CN-2815 were observed to decay with a 60 to 70-day half life. The gamma ray spectrometer demonstrated a 0.7 m.e.v. gamma-emitting impurity. These two facts suggested zirconium-95 contamination in the iodine samples. The presence of zirconium-95 in the iodine samples prepared by this procedure is not unlikely as the iodine is separated by a solvent extraction procedure, and if the zirconium is colloidal, it would distribute itself between the two phases. A fraction of it would carry through and be isolated with the iodine carrier.

Since radiochemical iodine analyses may be important to future programs in the Division, it was desired to develop an improved procedure. A procedure based on the separation of iodine by distillation has been developed and tested; the procedure is to be described in detail in a forthcoming topical report.

It was demonstrated that the method could isolate iodine quantitatively from a mixed fission product activity. A series of experiments was run using tracer iodine activity alone to establish the precision of the revised procedure. Based on ten samples, it was found to be ± 2.5 per cent.

The main radioactive contaminant which may appear in samples of iodine prepared by this revised procedure is ruthenium. Its presence is easily detected by taking two counts on the activity, one with no absorber and the other through 130 mg./sq.cm. of aluminum. If the ratio of these two counts is less than 40, the sample can be considered to be contaminated with ruthenium and the data discarded.

189 084

DECLASSIFIED

86

FIGURE 19.

STILL FOR DISTILLATION OF FLUORIDE.

Distillation carried out at 180-200 °C. from H_3PO_4 .
Bromide precipitated as AgBr to prevent its distillation.

169 085

0371220.030

87

Table 25

DETERMINATION OF FLUORIDE FOLLOWING DISTILLATION

Distillation

Procedure: 180 to 200°C. from H_3PO_4

Procedure A: Distillation of HF standard followed by precipitation of PbBrF , dissolving of precipitate in HNO_3 and determination of bromide by titration.

Procedure B: Distillation of fluoride from synthetic hydrolysis standards and determination as outlined above.

<u>Procedure</u>	<u>Method of End Point Determination</u>	<u>Known mg. F^-</u>	<u>Number of Samples</u>	<u>Average Error, per cent</u>	<u>Standard Deviation from Mean</u>
A	Visual	136.52	6	-0.2	± 0.9
A	Automatic	136.52	4	-1.3	± 0.3
B*	Automatic	68.26	19	-1.3	± 1.0
B**	Automatic	121.70	12	-0.3	± 1.3

*Composition of synthetic hydrolysis standard was 13.65 mg. $\text{F}^-/\text{ml.}$, 19.96 mg. $\text{Br}^-/\text{ml.}$, 0.45 M H_3BO_3 , 0.33 M N_2H_4 , 0.10 M $\text{UO}_2(\text{NO}_3)_2$, 1.0 M HNO_3 .

**Composition of synthetic hydrolysis standard was 24.34 mg. $\text{F}^-/\text{ml.}$, 35.5 mg. $\text{Br}^-/\text{ml.}$, 0.8 M H_3BO_3 , 0.4 M N_2H_4 , 0.015 M $\text{UO}_2(\text{NO}_3)_2$, 3.0 M HNO_3 .

100 086

DECLASSIFIED

VII. PROCESSING AND UTILIZATION OF RADIOACTIVE WASTES

(W. A. Rodger)

The processing of above-tolerance radioactive liquid wastes continued routinely and without incident. Laboratory investigations into the use of iron in conjunction with ion exchange columns and into the disposal of radioactive NaK using molten nitrate baths were extended.

Pilot plant equipment for studying two processes employing permselective membranes is nearly completed.

The acid recovery equipment was used for three more tracer runs studying recovery and decontamination of nitric acid wastes from the Halex process and was, in addition, used to concentrate some 400 liters of highly active Halex waste to about 3 liters. This concentrate was then immobilized in concrete in the Solidification Cell (ANL-4922, page 190) and made into an experimental waste fission product source having a radiation dose rate of about 10^4 r./hr.

A. Routine Processing of Radioactive Wastes

(H. G. Swope, J. Harast, A. Rashinskas, K. Bremer, L. Hays)

The processing of Laboratory liquid wastes which were determined to be above tolerance continued routinely and without incident. About 52,000 gallons of miscellaneous active wastes were processed during this period.

These wastes, their volume, and treatment employed are tabulated as follows:

<u>Type of Waste</u>	<u>Gallons of Waste Treated by:</u>		
	<u>Evaporation</u>	<u>Filtration</u>	<u>Cation Exchange</u>
Retention Tank	16,000 ⁽¹⁾	23,300	4,500
Miscellaneous	5,900 ⁽¹⁾	1,100	-
	370 ⁽²⁾	-	-
Nitric Acid	360 ⁽³⁾	-	-

(1) Struthers-Wells evaporator, 125 gal./hr. capacity

(2) Batch still, 60 gal./hr. capacity

(3) 30-gallon concentrator, 8 gal./hr. capacity

189 087

037229.030

B. Ion Exchange Studies

(H. G. Swope, W. Kline, S. Jackson)

It was previously shown (ANL-5169, page 119) that, while the use of metallic iron in conjunction with a cation resin column gave decontamination factors greater than those obtained from resin alone by factors of 3 to 25, the through-put capacity was reduced by the large amount of dissolved iron. It was thought that the calcium form of the resin might prove more effective than the sodium form for the high iron content effluent.

A run was therefore made in which tap water containing mixed fission products from dissolver solution adjusted to a pH of 2.5 was passed in parallel through the following:

- (1) Column containing 3 cu.in. of Nalcite HCR-Ca⁺⁺.
- (2) Column containing 50 grams, 20-40 mesh iron followed by a column containing 3 cu.in. of HCR-Ca⁺⁺ resin.
- (3) Column containing 50 grams, 20-40 mesh iron and an equal volume (22 ml.) of activated alumina followed by a 3-cu.in. column of HCR-Na⁺ resin.

As in previous experiments, the iron column alone showed fairly constant decontamination factors of about 8. The calcium form of the resin gave much lower decontamination factors than the sodium form, 8 versus 24, respectively, after a passage of 1550 gal./cu.ft. The iron column together with the HCR-Ca⁺⁺ gave an over-all integrated decontamination factor of 30 for the same through-put as above.

The results with the iron plus activated alumina followed by the HCR-Na⁺ were excellent. An Alsop filter was used following the column containing the iron and alumina. An over-all integrated decontamination factor for the 1550 gal./cu.ft. was 740. At hardness breakthrough, 2640 gal./cu.ft., the over-all integrated decontamination factor was 640. The integrated decontamination factor for the iron plus alumina column was 10.

Since the iron and alumina column clogged just past hardness breakthrough for the ion exchange column, the run had to be discontinued.

This work is being repeated in an effort to see how long the excellent decontamination factors will be continued past hardness breakthrough.

C. Disposal of Sodium-Potassium Alloy

(H. G. Swope, E. Schap,* W. Kline)

It has been demonstrated that the disposal of NaK could be effected in an easy and efficient manner by dropping NaK slowly into a molten mixture of equimolar quantities of sodium and potassium nitrates, under a blanket of nitrogen. (ANL-5169, page 121)

*From North Central College, Department of Chemistry, Participating Institution Program.

90

In order to adapt this process to the disposal of radioactive NaK, an apparatus was devised such that the off-gases could be filtered. This apparatus has been tested using inactive NaK and has operated satisfactorily.

Before using radioactive NaK, it was pointed out that the molten mixture of sodium and potassium nitrates might form a hazardous mixture, particularly if organic matter were present.^{18,19}

Accordingly, small pieces of rubber were put into the hot molten nitrate mixture, first without adding NaK and later with the addition of NaK. Temperatures were noted with a thermocouple. Highest temperature recorded without NaK was 277°C.; with NaK, 330°C. A similar experiment was conducted in which mineral oil was added to the molten mixture. In no case did a violent reaction occur.

D. Electrodeionization of Aqueous Wastes

(W. R. Walters, L. J. Marek)

Experimental cells for the semi-works investigation of two processes utilizing the principle of permselective membranes, bulk deionization of wastes, and electroregeneration of spent, mixed cationic-anionic resins, were described in ANL-5169, page 118. Shop work on both cells has been completed.

It has been necessary to make some modifications in the resin regeneration cell. This caused some delay in the assembly of the unit, a picture of which is shown in Figure 20. The cell is assembled much like a plate and frame filter press from a series of individual units, one of which is shown in Figure 21.

The second cell, to be used for deionization of wastes, will be put into operation as soon as the regeneration cell is completed.

A topical report covering the laboratory phases of these projects will be issued in the near future.

E. Distillation of Acid Wastes

(G. Yasui, L. Burris, P. Fineman)

The acid recovery and volume reduction equipment (ANL-5103, page 45) was used for three additional tracer runs studying recovery of acid from Hallex wastes and for concentrating the waste fission products which went into the experimental source prepared for Massachusetts Institute of Technology.

1. Experimental Decontamination Studies

Three additional runs (VR-2, 3, and 4) have been completed testing the effect upon decontamination factor of varying reflux ratio (L/D) from 0 to 0.5 and the boil-up rate from 15 to 28 lb./(hr.)(sq.ft.). The over-all

¹⁸N. Irving Sax, Handbook of Dangerous Materials, Reinhold Publishing Corporation, 1951, page 351.

¹⁹Bulletin of E. I. du Pont de Nemours and Company, "Molten Salt Baths", page 45.

0372091030

189-089

91

Figure 20

UNIT FOR RESIN REGENERATION CELL

(Gasket Shown)

108

090

DECLASSIFIED

92

Figure 21

ASSEMBLED MULTI-COMPARTMENT CELL FOR ELECTROLYTIC REGENERATION
OF MIXED-BED ION EXCHANGE RESIN EMPLOYING PERMSELECTIVE MEMBRANES

189 091

0377228.030

73

decontamination factors (feed to product) for the recovered acid are of the same order of magnitude (about 10^4) for all of the runs. The results of these runs and of one reported previously (ANL-5169, page 21) are shown in Table 26. While the beta activity material balance is good, about 100 per cent, the gamma activity (principally zirconium and niobium) balance is poor, 18 to 47 per cent. Experimental evidence has shown that about 50 per cent of the gamma activity seems to be lost before it enters the evaporator. An additional 25 per cent seems to plate out in the evaporator during boil-down operation.

In Figure 22 there is shown the effect of still bottom acid molarity on total beta decontamination at constant boil-up rate, 25 lb./hr.(sq.ft.). It will be noted that as previously experienced, the decontamination factor decreases as the still bottoms nitric acid concentration increases.

2. Preparation of Feed for Experimental Source

The Volume Reduction Unit was used to concentrate 413 liters of Hallex program aqueous acid wastes for the preparation of the experimental gross fission product source described below. This volume was boiled down to about 3 liters, approximately 2.5 liters of which were transferred to the Solidification Cell. A 10-liter decontamination wash solution (0.25 M nitric acid, 0.02 M hydrofluoric acid, 0.02 M aluminum nitrate) was then added to the evaporator and boiled down to 2.5 liters, of which 2.4 liters were transferred to the Solidification Cell. The decontamination wash solution was added to enhance the removal of any zirconium and niobium that may have plated out on the stainless steel surfaces of the equipment. The concentration was limited by excessive plugging troubles. It was possible to make a qualitative observation of the concentrate after transfer to the Solidification Cell. Copious quantities of crystalline salts were observed. They did not appear to be corrosion products. A spectrographic analysis of a sample of the concentrate taken at a total volume of 10 liters indicated high sodium content. The source of a high sodium content has not been traced down.

F. Preparation of an Experimental Irradiation Source from Waste Fission Products

(P. Fineman, L. Burris, J. W. Loeding, J. V. Natale,
E. C. Petkus, I. G. Dillon, A. Chilenskas)

The program set up to prepare an experimental irradiation source from waste fission products (ANL-5169, page 122) has been completed. Nitric acid wastes (from the completed Hallex program) containing about 2000 curies of year-old fission product activity were used to prepare the source. The wastes were concentrated from 400 liters to about 3 liters in the Volume Reduction equipment (above) and were immobilized in concrete in the Solidification Cell.

A schematic diagram of the source and carrier is shown in Figure 23. The shield is designed to act both as a shipping and a use container.

The radiation intensity of the source, determined by standard ferrous-ferric dosimetry techniques,* is about 10^4 r./hr. A plot of measured intensity over the height of the source is shown in Figure 24.

*Dosimetry was done by E. J. Hart of ANL Chemistry Division.

DECLASSIFIED

74

Table 26

DATA SUMMARY FOR TRACER LEVEL RUNS

Mixed Fission Product

Activity Tracer Source: Run VR-1 - Stacked Plate Extractor aqueous acid waste from Experimental Breeder Reactor blanket material (Runs SPX-12, 13)

Runs VR-2, 3, 4 - Mixer-Settler aqueous acid waste from Halex Program (Run IBEX-35)

Inactive Aqueous Acid Wastes: Runs VR-1, 2, 3, 4 - 2.2 M HNO_3 saturated with 30 per cent TBP in CCl_4

Run No.	Feed Composition			Boil-Up Rate, lb./ (hr.) (sq.ft.)	Reflux Ratio, L/D	Recovered Acid			Per Cent of Material Balance		
	Nitric Acid, M	Activity,				Nitric Acid M	Over-All Decontam. Factors*		Nitric Acid	Activity	
		ct./ (min.)	(ml.)				Beta	Gamma		Beta	Gamma
VR-1	2.67	5.2 x 10 ⁴	2.6 x 10 ⁴	28	0-0.25	1.9	1.3 x 10 ⁴	-	103	93	47
VR-2	1.35	4.7 x 10 ⁸	5.2 x 10 ⁸	25	0-0.5	1.56	3.6 x 10 ⁴	-	103	84	18
VR-3	1.97	3.6 x 10 ⁸	2.8 x 10 ⁸	15-25	0-0.5	1.50	1.2 x 10 ⁴	6.3 x 10 ³	97	100	26
VR-4	2.19	3.1 x 10 ⁸	1.9 x 10 ⁸	19	0	1.56	3.5 x 10 ⁴	2.0 x 10 ⁴	99	116	40

* Over-All Decontamination Factor = $\frac{\text{Total Activity in Feed}}{\text{Total Activity in Recovered Acid}}$; calculated for entire run.

95

FIGURE 22.

TOTAL BETA DECONTAMINATION FACTOR
vs. STILL BOTTOMS ACID MOLARITY.

109 094

DECLASSIFIED

96

FIGURE 23.

SOURCE CONTAINER IN 30-gal. DRUM
POSITIONED IN LEAD FILLED SHIPPING CONTAINER.

189 1095

0371229.030

97

FIGURE 24.

INTENSITY vs. DISTANCE FROM
BOTTOM OF SAMPLE CAVITY.

960-687

APPENDIX A

PROCEDURE FOR DETERMINATION OF LOW LEVEL PLUTONIUM
IN FLUORIDE VOLATILITY SAMPLESEquipment:

The determination of low level plutonium in fluoride volatility samples has been discussed in general terms on page 81. A detailed description of the analysis is given below. The solution for analysis is presumed to have the approximate composition indicated on page 82. All stirring operations are carried out using a motor-driven, pump-type stirrer.

Reagents:

0.5 M TTA in xylene, 0.25 M $\text{Fe}(\text{NO}_3)_3$, 5.0 M $\text{NH}_2\text{OH}\cdot\text{HCl}$, 5.0 M NaNO_2 , 1.5 M HNO_3 , 1.0 M HNO_3 -1.0 M HF wash solution, $\text{La}(\text{NO}_3)_3$ 10 mg./ml., 10 M HNO_3 .

Procedure:

1. Pipet 25-ml. sample into extraction vessel.
2. Add 150 lambda of 0.25 M Fe^{+++} solution and 0.4 ml. of 5 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution. Stir for 10 minutes.
3. Adjust acidity by the addition of H_2O or dilute HNO_3 to 0.6 M. Use hydrion paper of 0 to 1.4 range for this adjustment.
4. Slowly add 6 ml. of 5 M NaNO_2 . Stir 20 minutes.
5. Add 10 ml. of 0.5 M TTA in xylene. Stir 30 minutes.
6. Separate phases and wash organic phase with 5 ml. of 0.5 M HNO_3 . Stir 5 minutes. Discard the aqueous phase.
7. Separate phases and add 5 ml. of 10 M HNO_3 to the organic phase. Stir for 30 minutes.
8. Drain aqueous phase into a 50-ml. centrifuge cone.
9. Repeat such extraction with another 5-ml. portion of 10 M HNO_3 . Stir 10 minutes.
10. Drain aqueous phase into the 50-ml. centrifuge cone. Discard the organic phase.
11. Evaporate combined backwash phases to dryness on sand bath.
12. Re-evaporate to dryness with concentrated HNO_3 .
13. Take residue up in minimum amount of concentrated HNO_3 . Transfer to 5-ml. centrifuge cone.
14. Run conventional LaF_3 procedure. Wash precipitate three times with HNO_3 -HF wash solution.

189-097

0370281030

99

APPENDIX B

PROCEDURE FOR DETERMINATION OF FLUORIDE
IN FLUORIDE VOLATILITY SAMPLES1. Distillation of Fluoride

The determination of fluoride in fluoride volatility samples has been discussed in general terms on page 82. The procedure given below describes the determination in detail.

- (1) Place 10-15 quartz chips in the distillation flask and pipet an aliquot of the sample containing 60-120 mg. of fluoride into the flask. Add an excess of AgNO_3 to precipitate the bromide ion present. Add 15 ml. of 85 per cent H_3PO_4 to the flask.
- (2) Assemble the apparatus. Place a 100-ml. volumetric flask containing 5-10 ml. of 6 N NaOH and 2-3 drops 1/2 per cent p-nitrophenol indicator under delivery arm of the condenser. The distillate should remain basic during the entire distillation, and the use of the nitrophenol indicator is a convenient method of visual control. The tip of the delivery tube of the condenser should be held just under the surface of the liquid at all times.
- (3) Heat contents of distillation flask to 190°C . Maintain temperature of distilling head at $140-150^\circ\text{C}$. by means of heating tape.
- (4) When temperatures reach proper level, begin flow of steam through the distillation flask. Flow of steam into flask should be regulated to give a distillation rate of about 1 ml./min.
- (5) Continue distillation until liquid in receiving flask reaches the 100-ml. mark.
- (6) Remove receiving flask and adjust volume exactly to mark with water. Turn off heat and steam, and after allowing equipment to cool, clean out flask and distilling column by copious rinsing with water. Periodically it is necessary to remove a formation of scale which appears in the distilling flask. This is best accomplished by a quick treatment with concentrated HF.

2. Procedure for Precipitation of PbBrF and Determination of Br^- in Precipitate

- (1) Pipet 50-ml. aliquot from 100-ml. volumetric flask containing the distillate from the prior distillation into a 150-ml. beaker.
- (2) Add to solution in beaker 4 drops of 0.1 per cent aerosol and 2 drops of 0.1 per cent Bromphenol Blue indicator. Stir. The mixture

189-098

DECLASSIFIED

100

of the yellow p-nitrophenol and Bromphenol Blue gives a greenish-colored solution, but at pH values below 7, the p-nitrophenol is colorless and the solution takes on the characteristic color of only the Bromphenol Blue. Add concentrated HNO_3 dropwise with stirring until the color changes from green to deep purple. Then add 1 M HNO_3 dropwise until the color of the solution changes to a light yellow-green. The pH is then 3.5-3.7.

- (3) Stirring constantly, add reagents dropwise according to the following schedule:

(a) 0.65 ml. of 0.8 M KBr for each 10 mg. F^- present.

(b) 0.65 ml. of 0.8 M $\text{Pb}(\text{NO}_3)_2$ for each 10 mg. F^- present.

Precipitation takes place at this point. Stir for 1 minute.

(c) 0.25 ml. of 0.8 M $\text{Pb}(\text{NO}_3)_2$ for each 10 ml. of solution.

(d) 0.50 ml. of 0.8 M KBr for each 10 ml. of solution.

Example: for 50 mg. F^- in 50-ml. volume,

(a) $0.65 \times 5.0 = 3.2$ ml. KBr

(b) $0.65 \times 5.0 = 3.2$ ml. $\text{Pb}(\text{NO}_3)_2$

(c) $0.25 \times 5.64 = 1.4$ ml. $\text{Pb}(\text{NO}_3)_2$

(d) $0.50 \times 5.78 = 2.9$ ml. KBr

- (4) After the addition of the last portion of KBr, the solution is stirred for 1 minute. Notice that the supernate is a definite yellow color. Add 15 per cent sodium acetate dropwise until the supernate is reddish-green. Stir for 3 minutes. Additional drops of sodium acetate may be necessary to keep the indicator at the proper color.
- (5) Filter the precipitate through a fine-grade, scintered glass filter. Use a saturated PbBrF solution for transfer and wash of the precipitate. Finally, wash the precipitate once with approximately 2 ml. of ice cold distilled water.
- (6) Discard the filtrate. Place a clean 250-ml. beaker in the filter apparatus. Dissolve the PbBrF on the scintered glass filter with approximately 70 ml. of warm 1 M HNO_3 . Using suction, draw this liquid into the 250-ml. beaker. Rinse the filter with 1 M HNO_3 and transfer rinsings to beaker.
- (7) Add 50.0 ml. of standard 0.1 N AgNO_3 to the solution of dissolved PbBrF and back-titrate the excess silver with standard 0.1 N KCNS . The titration is done potentiometrically on a Beckman Automatic Titrator using a Ag-AgCNS indicating electrode and an external saturated calomel reference electrode bridged into the solution by means of an Agar- KNO_3 salt bridge.
- (8) Calculate the F^- present from the milliequivalents of Br^- found since there is a 1-to-1 relationship between the Br^- and F^- in the PbBrF precipitate.

189-099

0000000000000000

101

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Effect of a Fluoride Dissolution Procedure on Decontamination and Recovery of Uranium	8
2	Effect of a Fluoride Dissolution Procedure on Decontamination and Recovery of Uranium from Uranium-Zirconium Alloy	9
3	Distribution Ratios (O/A) for Uranyl Chloride Between 30 Per Cent Tributyl Phosphate and Aqueous Hydrochloric Acid at 23°C.	12
4	Results of Screening Tests in 3 M Sulfuric Acid, 35°C.	15
5	Stacked Stage Extractor Tests — Operating Conditions, Losses, and Decontamination Factors	23
6	Liquid-Vapor Equilibria for the System Bromine Trifluoride-Bromine Pentafluoride at 50°C. and 125°C.	31
7	Liquid-Vapor Equilibria for the System Bromine Trifluoride-Bromine Pentafluoride at 150°C.	32
8	Vapor Pressure of Bromine Trifluoride at Various Temperatures	34
9	Analytical Results for Hydrolyzed Interhalogen Standards	40
10	Results of Uranium Hexafluoride Sublimation Tests	47
11	Relative Volatility of Bromine-Uranium Hexafluoride and Bromine Pentafluoride-Uranium Hexafluoride	48
12	Vacuum Volatilization of Impure Uranium Hexafluoride at 0°C.	49
13	Residual Activities after Slag Removal and Volatilization	53
14	Analysis of Beta Activities Deposited on Foil	54
15	Specific Activities Deposited on Furnace Walls	55
16	Activities Recovered from Slag and Metal	56
17	Distribution of Activities in Slag at Various Depths of Penetration, Run 6-A	60
18	Distribution of Activities in Slag at Various Depths of Penetration, Run 10-A	60
19	Uranium Yields and Current Efficiencies for Uranium Electrorefining in Fused LiCl-KCl-UF ₄ at 425°C.	62
20	Electrolytic Refining Experiments, Uranium Material Balance, Run 129	64
21	Typical Conditions for Denitration Runs	77
22	Feed Conditions for Denitration Runs	79
23	Check of Bromide Analytical Procedure on Fluoride Volatility Standards	83
24	Determination of Fluoride on Known Samples by the Lead Bromofluoride Procedure	84
25	Determination of Fluoride Following Distillation	87
26	Data Summary for Tracer Level Runs	94

189 - 100

DECLASSIFIED

102

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Partition Ratio (O/A) Uranyl Chloride into 30 Vol. Per Cent TBP-CCl ₄ vs. Acidity	13
2	Partition Ratio (O/A) Uranyl Chloride into 30 Vol. Per Cent TBP-CCl ₄ vs. Aqueous Uranium Concentration	14
3	Typical Photograph of Emulsion Created by Agitation at 800 r.p.m.	19
4	Drop Size Distribution in Systems of Immiscible Liquids	21
5	Ignition Apparatus	28
6	Solid-Liquid Equilibria of the System Uranium Hexafluoride- Bromine Pentafluoride	36
7	Corrosion Boiler for Interhalogen System	37
8	Coupon Arrangement in Corrosion Boilers	38
9	Typical Calibration Curve for Spectrophotometric Determination of Bromine in Bromine Trifluoride	42
10	Sublimation Equipment	46
11	Photomicrograph of Uranium Ingot: Vertical Section at Crucible (MgO) Wall	58
12	Photomicrograph of Uranium Ingot: Vertical Section at Top of Ingot	59
13	Apparatus for the Fluorination of UF ₄ in KHF ₂ at 250°C.	66
14	Apparatus for Electrochemical Measurements with Quartz Membrane Cells	69
15	Illustration of Calculation of "k" in Zone Melting	71
16	Schematic Diagram of Zone-Melting Equipment	74
17	Fluidized Bed Denitration Assembly	76
18	Reaction Chamber and Product Removal Assembly for Denitration Runs	78
19	Still for Distillation of Fluoride	86
20	Unit for Resin Regeneration Cell	91
21	Assembled Multi-Compartment Cell for Electrolytic Regeneration of Mixed-Bed Ion Exchange Resin Employing Permselective Membranes	92
22	Decontamination Factor vs. Still Bottoms Acid Molarity	95
23	Source Container in 30-Gal. Drum Positioned in Lead Filled Shipping Container	96
24	Intensity vs. Distance from Bottom of Sample	97

189-101

037229.1030