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CHEMICAL TECHNOLOGY DIVISION

QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING MAY 20, 1951

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CHEMICAL TECHNOLOGY DIVISION

F. L. Steahly, Division Director
F. R. Bruce, Laboratory Chief
J. O. Davis, Unit Operations Chief
H. K. Jackson, Pilot Plant Chief
F. L. Culler, Process Design Chief

QUARTERLY PROGRESS REPORT
for Period Ending May 20, 1951

Edited by

W. K. Eister

DATE ISSUED SEP 24 1951

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LIST OF PERSONNEL

F. L. Steahly, Director — June Parrott, Secretary

- W. K. Eister, Special Assignment
- C. W. Schersten, Assistant to Director — Virginia Wells, Secretary; J. W. Clark, Technician; Aola Johnson, Janitress
- F. R. Bruce,[a] Section Chief - Laboratory — Mary Pemberton, Secretary; C. J. Shipman, Technician
  - W. B. Lanham, Problem Leader - Purex
    - J. A. Blair[b]
    - S. V. Castner[b]
    - C. W. Cline[b]
    - J. R. Flanary
    - A. T. Gresky
    - R. G. Mansfield
    - V. J. Reilly[b]
    - E. B. Sheldon[b]
    - M. D. Snyder[b]
    - B. L. Taber[b]
    - F. W. Tober[b]

    Technicians: L. A. Byrd; W. B. Howerton; E. R. Johns; R. C. Lovelace
  - F. R. Bruce,[a] Problem Leader - Homogeneous Reactor Studies
    - Chemical Processing
      - J. O. Blomeke
      - D. E. Ferguson
      - I. R. Higgins
      - D. D. Rauch[c]
      - W. E. Tomlin

      W. E. Shockley
    - Fuel Slurry Studies
      - G. A. Eaton
      - C. P. Johnston
      - L. E. Morse
      - T. C. Runion

      J. L. Bamberg; V. L. Fowler; C. F. Keck
  - R. E. Leuze, Problem Leader - Volatility
    - C. E. Schilling
    - B. L. Baker[d]

    H. B. Graham
  - R. E. Blanco, Problem Leader - RaLa
    - A. H. Kibbey

    J. E. Farmer; D. M. Helton
  - J. A. McLaren, Problem Leader - Electrochemistry
    - J. H. Goode
    - H. L. Peeler
  - D. C. Overholt - Isolation

    J. M. Delozier; R. B. Quincy

[a]Dual capacity.
[b]Du Pont personnel.
[c]Reactor School student.
[d]Research participant.

F. L. Culler,[a] Section Chief - Process Design

Lucille Kuykendall, Secretary

F. L. Culler,[a] Problem Leader - Idaho Chemical Plant

F. N. Browder (New York)
W. L. Carter[e]
P. J. Falivene[f]
H. E. Goeller, (New York)
W. J. Greter[g]
F. E. Harrington
J. H. Hinman[f]
J. M. Holmes[f]
G. W. T. Kearsley[e]
R. J. Klotzbach (New York)
A. D. Mackintosh
F. C. McCullough
R. P. Milford
E. L. Nicholson (New York)
P. L. Robertson[e] (New York)
A. M. Rom
J. B. Ruch
D. H. Stewart
W. G. Stockdale (New York)
W. Tinberger[f]
H. O. Weeren[e]
L. W. Zahnstecher[f]

Stenographic Staff

Frances Bray
Bettye Burns
Julia Gillock
Sarah Hudgens
Virginia Malone
May Pepper

Draftsmen

G. Doyle[f]
John J. Hall[f]
Lee MacAlpine[f]
E. J. Meyer[f]
J. M. O'Keefe[f]
F. L. Peishel[f]
William Richman[f]
J. Roberts[h]

N. J. Rigstad - Idaho Chemical Plant, Operations Planning

W. E. Unger, Problem Leader - RaLa

B. F. Bottenfield[e]
R. H. Vaughan

Helen Hamrick, Typist

G. B. Berry,[e] Draftsman
R. V. Foltz,[e] Draftsman

J. R. McWherter, engineer, on loan to Reactor Experimental Engineering Division

J. O. Davis, Section Chief - Unit Operations

Ruth Pennington, Secretary

A. C. Jealous[i] - Solvent Extraction

J. E. Conaway[b]
C. V. Ellison
A. N. Parkes[b]

Technicians

G. B. Dinsmore
G. Jones

T. A. Arehart[j] - Special Equipment

J. W. Foster[b]
R. W. Hinterleiter[b]
D. M. Paige[b]
G. A. West

T. D. Napier
R. O. Payne

C. D. Watson - Radioactive Waste

M. R. Bennett
R. R. Hood[b]
J. N. Hunsberger[b]
J. C. Suddath

G. R. Guinn
F. L. Rogers

E. O. Nurmi[k] - Metal Dissolution

L. G. Anderson[b]
D. L. Foster
E. M. Sampson[b]
A. E. Wible[b]

D. B. Masters
J. C. Rose
H. F. Soard

[e]On loan from Engineering Department.
[f]On loan from Foster Wheeler Corporation.
[g]On loan from Instrument Department.
[h]On loan from Research Director's Division.
[i]Responsible in this Section for Metal Recovery and Purex.
[j]Responsible in this Section for RaLa.
[k]Responsible in this Section for "25" Process.

H. K. Jackson,[a] Section Chief - Pilot Plant

Agnes Hair, Secretary
R. B. Waters, Draftsman

H. K. Jackson,[a] Problem Leader - Purex

D. O. Darby - Chemistry

J. W. Landry - Engineering

R. B. Lindauer - Engineering

T. D. Barclay[b]
W. H. Farrow[b]
R. A. Lewis[l]

J. W. Ullman - Data Analysis

H. L. Hull[b]
T. H. Spencer[b]

W. H. Lewis - Bldg. 3503 Operations

G. S. Parker
R. W. Yancey[b]

G. S. Sadowski - Bldg. 3019 Operations

M. J. Connair[b] - Shift Supervisor
C. B. Hill[b] - Shift Supervisor
C. D. Hylton - Construction & Maintenance
R. B. Keely
P. H. Porter[b] - Operations Manual
W. B. Watkins[b] - Shift Supervisor
R. H. Winget - Run Sheets
H. P. Wood[b] - Shift Supervisor

"A" Operators

T. R. McLellan
H. L. Sexton
W. E. Ledbetter
E. E. Shields

Operators

C. W. Boatman	R. J. Shannon
W. T. Bostic	W. A. Shannon
E. W. Brown	R. C. Shipwash
H. S. Caldwell	D. E. Spangler
G. D. Davis	B. J. Strader
J. H. Groover	D. H. Summers
J. E. Higgins	G. R. Thompson
D. C. Hubbard	H. C. Thompson
W. Jennings, Jr.	C. H. Tipton
C. H. Jones	C. E. Waddell
J. F. Land	J. T. Wiggins
J. F. Lockmiller	J. R. Vest
R. E. Purkey	J. H. Walker

E. C. Stewart, Problem Leader - Metal Recovery

E. M. Shank, Problem Leader - MTR RaLa

[l]California Research & Development Company personnel.

AMERICAN CYANAMID COMPANY REPRESENTATIVES

D. G. Reid, IDO Plant Superintendent

P. V. G. Wardle, Personnel Supervisor

Trainees in Chemical Technology Division

W. F. Allaire
J. C. Ciardelli
P. J. Drury
E. R. Edmundson
K. K. Kennedy
M. L. Nielson
G. M. Smith
G. C. Voss

T. W. Clapper, Technical Director, IDO Plant

Marian Hoppe, Secretary
Dorothy Ross, Secretary, ORNL
Betty Large, Typist

DU PONT COMPANY REPRESENTATIVES

L. C. Peery, Liaison Office Manager

A. L. Denny, Administrative Assistant

Cathleen Foster, Secretary

ABSTRACT

Progress on and status of the following problems are reported: TBP Metal Recovery Process, Purex Process, Thorex Process, RaLa Process, Idaho Chemical Rrocessing Plant Design, Volatility Study, Radiochemical Waste Treatment, Electrolytic Studies, Homogeneous Reactor Chemistry, Isolation, and Special Equipment.

INTRODUCTION

The major development problems in the Chemical Technology Division were the Purex Process, the Idaho Chemical Processing Plant, Homogeneous Reactor Chemistry Studies, and the MTR RaLa Process. Construction of the Metal Recovery Plant was continued, and a contract was let for the construction of the building for processing high-alpha-activity material.

In the laboratory the Purex process study emphasized work on metal dissolution and off-gas decontamination, an electrolytic head-end treatment for ruthenium removal, study of alternate complexing agents for improving decontamination and plutonium separation, the effect of tributyl phosphate hydrolysis products on the chemistry of the process, and the use of jacket-removal waste for the neutralization of the first-cycle nitric acid waste. In the MTR RaLa program precipitation studies and ion-exchange studies were continued. The effect of initial nitric acid concentration on the dissolution of aluminum was studied for the Idaho chemical plant. Chlorination-reaction-rate studies were initiated, and the work on the fluoride system was continued in the volatility program. Work was resumed on an electrochemical process for the separation of uranium, plutonium, and fission products from normal uranium reactor fuel.

The homogeneous reactor problems have included studies of slurry fuel and fuel-recovery processes for both the Homogeneous Reactor Experiment and the long-range homogeneous reactor program. The work on a fused-salt thorium blanket for a homogeneous reactor has been terminated. A process was developed for the recovery of plutonium from the isolation process waste resulting from the Chalk River program. This process involves a TBP solvent extraction followed by ion exchange; all the plutonium has now been processed.

In the Unit Operations Section the dissolution of uranium and uranium-aluminum alloy was continued for both Idaho and Savannah River application. An intensive study was also in progress on the separation of the radioactive gases from the dissolver off-gas. A new technique was developed for evaluating the efficiency of a gas decontamination unit, and a Cottrell electrostatic precipitator is now being evaluated with this new technique. The evaluation of solvent-extractor operability including pulse-column tests for the Thorex and the Purex processes and evaluation of a centrifugal contactor was carried out. The special equipment studies have included concrete-penetration tests, radiation-damage studies, surface evaluation for ducts and hoods, and decontamination of stainless steel by electrostripping.

In the Pilot Plant Section the Purex process evaluation in packed columns was completed. The evaluation of this process in pulse columns was initiated, and runs were completed at 100% Clinton activity level. The construction of the Metal Recovery Plant was continued, and modifications of this plant were made to enable the processing of irradiated normal uranium in the plant.

In the Design Section the design of the Idaho Chemical Processing Plant continues to be the major program. The ORNL responsibilities yet to be completed are field engineering, equipment testing for acceptance, plant start-up, off-gas system development and design, MTR RaLa process development and design, and manual preparation.

Work was initiated on the design of the MTR RaLa Pilot Plant. The greater number of the Design personnel assigned to the Idaho Chemical Processing Plant have now been transferred to New York.

SUMMARY

Slurrex Process

The scrub and strip operations of the Slurrex process were satisfactorily demonstrated in pulse columns.

Purex Process

1. The dissolution rate of uranium increased from 4 to 94 mg/sq cm/min when the nitric acid concentration was increased from 10 to 55%.

2. Control combustion of uranium metal in a pure oxygen atmosphere was demonstrated to be feasible at a temperature of 650 to 750°C.

3. During uranium dissolution in nitric acid, approximately 7000 cu ft of gas is produced per metric ton of uranium metal. Approximately 98% of this gas can be removed by oxidative scrubbing.

4. Scrubbing the dissolver off-gas with concentrated nitric acid removed all the oxides of nitrogen. It is proposed to use this procedure for the Metal Recovery Plant.

5. Preliminary tests indicate that 97% of the ruthenium may be removed by electrolytic plating from metal solution.

6. The uranium decay products UX_1 and UX_2 were separated from the uranium and plutonium only in the first extraction column; thereafter they followed the plutonium. Under the conditions of the August flowsheet a decontamination factor of only about 7 was obtained.

7. The addition of oxalic acid to the first-cycle scrub was effective in increasing the zirconium decontamination by a factor of 4. The major disadvantage to its use is the fact that it corrodes stainless steel at high temperatures.

8. Sulfurous acid was found to be a satisfactory partitioning agent for plutonium; however, it could not be used because of its corrosive attacks on stainless steel.

9. Pulse-column studies have indicated that the total volume throughput is the function of the column height. The plutonium second cycle was demonstrated in packed columns with a 0.1% plutonium loss and a gross beta decontamination of 13. The original feed was 100-g/T uranium. Satisfactory decontamination of the used solvent has been obtained by washing for 1 hr with one-fifth volume of 10 *N* sodium carbonate solution.

RaLa Process

1. A tentative chemical flowsheet for the MTR RaLa process has been prepared, and design work has been initiated.

2. When barium sulfate was precipitated from an aluminum-uranium sulfate dissolver solution, 50 to 75% of the cerium activity was coprecipitated.

3. A Versene ion-exchange process has been selected for the purification of the barium in the MTR RaLa process.

Idaho Chemical Processing Plant Design

1. Operable conditions have been found for the dissolution of uranium-aluminum slugs. In 10 hr 93 to 100% of the slug is dissolved, with the final solution containing 1.2 *M* aluminum and 0.8 *M* nitric acid.

2. Feasibility of the reduction of nitrous oxide in a hydrogen atmosphere and over a palladium catalyst has been demonstrated.

Homogeneous Reactor Chemistry

Radiation of uranium trioxide-bentonite slurries and thorium oxide-bentonite slurries in a neutron flux of 5×10^{11} for one week at an elevated temperature has had no significant effect on the stability of the slurry.

1. METAL RECOVERY PROCESS — PLANT STATUS AND PROGRAM

The Oak Ridge National Laboratory has agreed to a proposal by the Atomic Energy Commission whereby the irradiated fuel rods from the Chalk River reactor would be processed for plutonium in the ORNL Metal Recovery Plant. This new program entails the processing of a large number of irradiated rods now in the Chalk River canal in addition to the processing of rods to be discharged during the next several years. The new program has been designated as the SCRUP Program (Separation of Chalk River Uranium and Plutonium). The Metal Recovery Program will be deferred until January, 1952 while the backlog of Chalk River material is being processed; at that time the two programs may be run concurrently. Capital additions required for the new program will cost about $91,000, and the first hot runs using Chalk River material are scheduled for August, 1951.

Equipment Alterations and Modifications. The SCRUP Program will require only minor alterations to the equipment already planned for the Waste Metal Recovery Program. Major equipment additions will be required, including three carriers, storage basin, dissolver with off-gas facilities, and additional plutonium handling equipment.

Shipping Schedule. The fuel rods are to be sheared in 12-in. lengths, and 100 lengths will be shipped in each carrier. A railroad freight car will be leased full time for the shipments, which are planned to begin about July 1, 1951 and which will continue at the rate of one per month for the duration of the program.

Process Flowsheet. It is currently planned to employ the Purex Flowsheet No. 1 for the SCRUP Program. The plutonium will be processed through one cycle of solvent extraction followed by an ion-exchange concentration step and a second solvent cycle, and will be removed from the system to isolation in an ion-exchange cartridge bed. The uranium will be partially recycled to provide column equilibrium conditions prior to the starting of the feed to the columns and subsequent to feed runout time. However, the bulk of the uranium will be stored in the waste tank farm for further processing during the Metal Recovery Program at a later date.

The detailed process conditions will be governed largely by the conditions of criticality and batching. Storage of process raffinates is contemplated.

Program Status. The original Metal Recovery Plant is estimated to be 70% complete. Close coordination of the construction may incorporate many of the direct alterations required by the SCRUP Program, thus reducing the expenditures required for this program. The additions and alterations are expected to extend the construction approximately five weeks. Initial hot runs using Chalk River fuel are scheduled for August, 1951.

2. SLURREX PROCESS STUDY — PULSE COLUMN EVALUATION OF SCRUB AND STRIP OPERATION

The scrub and strip operations of the Slurrex process for the recovery of uranium from ores were briefly investigated in a 2-in.-diameter glass pulse column 8 ft high. A feed solution received from the Mallinckrodt pilot plant was used for this study under conditions agreed upon with the Catalytic Construction Company, architect-engineers for the new ore refinery. The objective was to check the flooding rates and the process operability using specified flowsheet conditions.

The scrub test indicated that the combined effect of increasing the temperature from 20 to about 60°C and increasing the flow ratios (organic to aqueous) from 10 to 20, decreased the flooding rate from 2500 to less than 1800 gal/sq ft/hr. These changes in conditions had little effect on the percent uranium extracted from the organic phase. However, the molybdenum concentration in the aqueous scrub effluent was increased from 10 to 26 ppm of uranium. The flooding results, particularly in the second run, are somewhat in doubt. In the second run the column operated smoothly for 3 hr, then flooded. By increasing the pulse amplitude the flooding condition was eliminated, and it was felt that the run would have been generally more satisfactory if it had been run at an amplitude higher than 0.5 in. (Table 2.1).

Strip studies indicated that changing from a continuous aqueous to a continuous organic phase increased the flooding rates from 2400 to 3000 gal/sq ft/hr at 20°C. With the organic phase continuous, the flooding rate was not affected by elevating the temperature to 50°C and simultaneously increasing the organic-to-aqueous flow ratio from 1 to 1.67. However, under roughly similar conditions, with the aqueous phase continuous, the flooding rate was decreased from 2400 to 1200 gal/sq ft/hr. The uranium strip loss was decreased by elevating the temperature, with either phase continuous in spite of using a higher organic-to-aqueous flow ratio at the higher temperature. It also appeared that the continuous organic phase reduced the uranium loss slightly. However, it is not known how much the loss was affected by the considerably higher throughput rate used in the run with the continuous organic phase.

Perforated Teflon plates, used in one run with the organic phase continuous and a column temperature of about 50°C, did not give significantly different stripping or flooding results as compared to the use of stainless steel plates (Table 2.2).

TABLE 2.1

Scrub Tests in Pulse-Column Slurrex Process

Pulse column: plate section, 8 ft by 1.916-in.-i.d. true-bore glass pipe

Plates: 18-gage stainless steel, 0.125-in. holes, 23% free area

Plate spacing: 2 in.

Pulse amplitude: 0.5 in.

Pulse frequency: 70 strokes/min

Organic phase: continuous

Feed solution: organic sample from St. Louis pilot plant diluted with additional Gulf BT to 13.5% TBP (dielectric constant method), 37 g of uranium per liter, and 0.20 *N* HNO_3

RUN	TEMPERATURE (°C)	FLOW RATIO, O/A	TOTAL FLOW RATE (gal/sq ft/hr)	RUN DURATION (hr)	AQUEOUS SCRUB EFFLUENT		FLOODING RATE (gal/sq ft/hr)
					U AS % OF FEED	Mo CONC. AS ppm OF U	
MF-1	20	10	1750	4.6	10	10	2500*
MF-2	60	20	1350	3.5**	7	26	1800

*Limiting rate of pumps.

**Flooded after 3.5 hr, perhaps because of large temperature change in building since run started at 4 P.M. and finished (flooded) 1.5 hr after sundown. A short test in which the amplitude was increased to 0.9 in. eradicated the flooding condition.

TABLE 2.2

Strip Tests in Pulse-Column Slurrex Process

Pulse column: plate section, 8 ft by 1.916-in.-i.d. true-bore glass pipe

Plates: 18-gage stainless steel except as noted, 0.125-in. holes, 23% free area

Plate spacing: 2 in.

Pulse amplitude: 0.5 in.

Pulse frequency: 70 strokes/min

Feed solution: organic product solution from scrub column tests (about 33 g of uranium per liter) and 0.1 to 0.14 *N* HNO_3

RUN	CONTINUOUS PHASE	TEMPERATURE (°C)	FLOW RATIO, O/A	TOTAL FLOW RATE (gal/sq ft/hr)	RUN DURATION (hr)	URANIUM LOSS (%)	FLOODING RATE (gal/sq ft/hr)
CC-1	Aqueous	20	1	640	1	25	2400
CC-2	Aqueous	60	2	950	1	12	1200
CC-3	Organic	20	1	2200	0.5	19	3000
CC-6	Organic	50	1.67	2150	0.7	12	3000
CC-5*	Organic	50	1.67	2150	0.7	16	2900

*Teflon plates 1/16 in. thick (other dimensions same as those of the stainless steel plates) were substituted for stainless steel plates.

3. PUREX PROCESS

Dissolution Rate of Uranium Metal. In qualitative tests it was demonstrated that, as the nitric acid concentration was increased from 10 to 55%, the dissolution rate of the uranium metal increased also. The rates obtained were 4 mg/sq cm/min with 10% nitric acid, and 94 mg/sq cm/min with 55% nitric acid. In a second test, starting with the fresh metal slug section, successive dissolving of the same slug section demonstrated that the rate of dissolution increased as the surface area of the slug was increased by a pitting action of the previous dissolving step. Here the rates of dissolution for the first 50% of the run varied from 49 to 84 mg/sq cm/min. In these tests the apparent areas and densities were determined by superficial dimensions and slug weights in order to indicate the degree of pitting (Table 3.1).

TABLE 3.1

Rate of Uranium Dissolution in 55% HNO_3 as a Function of Metal Heel

Experimental Conditions: Fresh metal slug section dissolved in consecutive runs; apparent area determined by superficial dimensions and slug weight to indicate degree of pitting; average rates calculated with the assumption of constant gas rate per gram dissolved

RUN	HEEL (%)	APPARENT AREA (sq cm)	APPARENT DENSITY* (g/cc)	RATE (mg/sq cm/min)	
				FIRST HALF	SECOND HALF
1	400	6.0	18	49	22
2	300	5.5	17	78	25
3	200	5.2	15	70	26
4	80	4.9	13	84	31

Controlled Combustion of Uranium Metal. An alternate method for the dissolution of uranium metal was studied which involves first the combustion of uranium metal in an oxygen atmosphere with oxygen to form U_3O_8, followed by the dissolution of uranium oxide in nitric acid. By this procedure, the radioactive gases (iodine, krypton, and xenon) would be released during the combustion of uranium metal, and the subsequent dissolution of the uranium

oxide in nitric acid was demonstrated to require only 2.25 moles of nitric acid per mole of uranium as opposed to 4.25 required in the present metal dissolving procedure.

Preliminary laboratory demonstration indicated that the uranium metal burned with a steady rate at a temperature of 650 to 750°C in a pure oxygen atmosphere. The temperature was easily controlled by controlling the rate of oxygen addition to the system. These experiments were carried out in an airtight stainless steel vessel.

No further work is planned on this procedure at the present time.

Gas Evolution During Uranium Dissolution. Approximately 7000 cu ft of gas (STP) is produced when 1000 kg of uranium metal is dissolved in 55% nitric acid (200 ml per gram of uranium). The gas evolution rate is relatively slow at the start of the dissolution but surges to a maximum rate when 10 to 15% of the dissolution is complete, then rapidly falls off from a maximum of about 155 ml/min per gram of uranium to a rate of approximately 90 ml/min per gram of uranium when 25% of the dissolution is complete, and holds fairly steady until 50% of the dissolution is complete. From this point on the gas evolution rate drops at a uniform rate to zero at the end of the run.

The average composition of the off-gas of 15 runs was as follows: 59% NO, 39% NO_2, and 1.94% nonoxidizable gas (Table 3.2). After oxidative scrubbing of the off-gas, the nonoxidizable gases remaining have the average composition of 90.3% N_2, 6% CO_2, 1.5% CO, 1.3% N_2O, and 0.5% H_2.

TABLE 3.2

Off-Gas Composition from Uranium Dissolution in 55% HNO_3

GAS	PERCENT OF TOTAL	MILLILITERS PER GRAM OF URANIUM	CUBIC FEET PER 1000 kg OF URANIUM
NO	59.0	115.0	4050
NO_2	39.0	80.0	2950
N_2	1.75	3.40	120
N_2O	0.02	0.04	1.5
CO_2	0.12	0.18	6.0
CO	0.04	0.08	2.0
H_2	0.01	0.02	0.5
TOTAL	99.94	198.72	7130.0

It was found that the ratio of NO_2 to NO gas evolved during the dissolution of uranium in 55% nitric acid varied from 3, at the start of the dissolution, to about 0.25 at the end of the run (Fig. 3.1). The volume of nonoxidizable gases also varied from about 2% of the total off-gas at the start of dissolution to a minimum of about 0.7% at the mid-point of the dissolution and then increased to about 1.5% at the end of dissolution. These data were obtained by the collection of the dissolver off-gas over mineral oil because of the negligible solubility of the off-gas in the mineral oil. During the study of the effect of nitric acid concentration on the uranium dissolution rate, the gas phases from this reaction were collected over water. Under these conditions the NO_2 dissolved in the water, forming HNO_3 and HNO_2 with the NO in the dissolver off-gas remaining in the gaseous phase. About 2.5 moles of nitrous acid was formed per mole of nitric acid. Total amount of nitrogen oxides dissolved varied from about 50% when the initial nitric acid concentration was 55% to about 5% when the initial nitric acid concentration was 25%. This again reflects the effect of nitric acid concentration on the ratio of NO to NO_2 that is formed during the dissolution reaction.

During the dissolution of irradiated uranium metal, iodine, krypton, and xenon will be evolved, and the expected volumes have been calculated, on the basis of liters of gas per tons of 300-g/T metal, cooled 100 days, to be 1 liter of krypton and 6 liters of xenon (Table 3.3).

TABLE 3.3

Summary of Krypton and Xenon Fission Products Evolved in Rare Gas Recovery

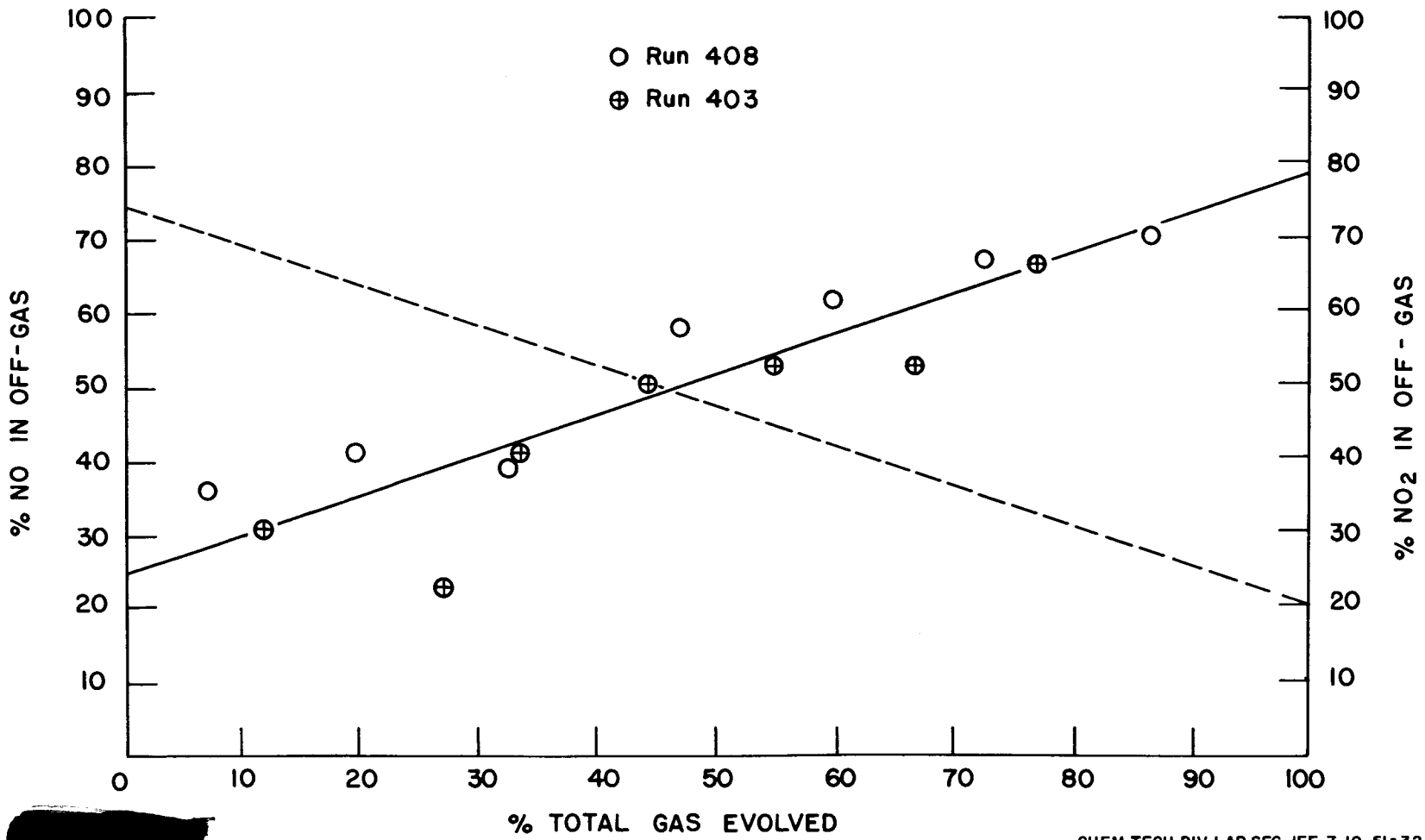
ISOTOPE	YIELD (%)	HALF-LIFE	RADIATION	VOLUME OF GAS EVOLVED (liters per ton of 300-g/T uranium)
Kr^{83}	0.4	Stable	Stable	1.0
Kr^{84}	0.65	Stable	Stable	
Kr^{85}	0.24	10 years	0.74-Mev β, no γ	
Xe^{129}	0.19	Stable	Stable	6.0
Xe^{131}	2.8	Stable	Stable	
Xe^{132}	3.6	Stable	Stable	
Xe^{133}	4.5	5.3 days	0.34-Mev β, 0.1-Mev γ	
Xe^{134}	3.6	Stable	Stable	
Xe^{135}	5.9	9.4 hr	0.9-Mev β, 0.25-Mev γ	

FIGURE 3.1

RATE OF NO AND NO_2 EVOLUTION IN DISSOLVER OFF-GAS

URANIUM DISSOLUTION IN 55 % HNO_3

[redacted] DWG No 11693



[redacted]

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Treatment of Dissolver Off-Gas. The treatment of the dissolver off-gas involves the following steps: (1) removal of iodine by reaction with silver nitrate, (2) removal of NO and NO_2 by oxidative scrubbing, (3) removal of the nonoxidizable nitrous oxide, and (4) adsorption of xenon and krypton. A program for the installation of the required equipment for a pilot plant dissolver is now in progress. The iodine removal unit will be similar to the one now in use at Hanford. The oxidative scrubbing system, which involves the addition of oxygen to the dissolver off-gas, to oxidize the NO to NO_2, and then scrubbing the gas with water to remove the NO_2, has been demonstrated in the laboratory to bring about almost complete removal of the NO and NO_2.

During this quarter work was initiated on the removal of nonoxidizable nitrous oxide (N_2O) in the dissolver off-gas stream. Three methods of removing the N_2O were studied:

1. Reduction of the oxide on a hot metal bed.
2. Reduction of the oxide on a palladium catalyst.
3. Removal of the oxide by an acid caustic scrub.

All three methods have been demonstrated to be effective, but each has a major drawback. These are: (1) the high temperature required by the hot metal bed, (2) the explosive hazard of hydrogen required from the catalytic unit, and (3) the radioactive liquid waste created by the solution scrubber.

If the oxidative scrubber was operated in such a manner that no excess oxygen remained in the nonoxidizable gas, the gas feed for the reduction unit contained nitrogen, nitrogen oxides, and carbon oxides. Passing the feed through a copper bed at a temperature of 800°C reduced the nitrous oxide from 7.3 to 0.3%. The hot copper bed was not expected to reduce the carbon oxides, but their concentration was reduced from 8.5 to 4.7%.

Two solution scrub systems were investigated in a preliminary study. The first used three scrubs, 70% nitric acid, 92% sulfuric acid, and 10 *M* sodium hydroxide; the second used two scrubs, 70% nitric acid and 10 *M* sodium hydroxide. Scrubbing the off-gas with 70% nitric acid was effective in removing the NO and NO_2 and some of the N_2O. The 10 *M* sodium hydroxide scrub removed the carbon oxides. The sulfuric acid scrub was expected to remove residual nitrogen oxides that might not be removed by the nitric acid, but it was not effective. Further study of the scrubbing system will be required to determine the total amount of solution required for this step (Table 3.4).

TABLE 3.4

HNO_3 Dissolution of Uranium — Clean-up of Inert Reaction Components by Solution Scrubbing and Hot Copper Reduction

Experimental Conditions: 400 to 500 ml of nonoxidizable gases was passed through a series of five or six solution contactors, each containing 5 ml of the reagent in the order indicated; initial vs. off-gas compositions were determined; rate was 20 ml/min

	COMPOSITION (%)					
	N_2	N_2O	CO_2	CO	NO	NO_2
Feed, nonoxidizable gas from U-HNO_3 dissolution	83.4	2.7	4.6	3.9	2.1	2.5
Cu reduction at 800°C	93.2	0.3	4.4	0.3	0.0	0.0
70% HNO_3 (2-stage), 92% H_2SO_4 (1-stage), 10 *M* NaOH (2-stage)	94.2	1.9	0.2	0.7	0.0	0.0
70% HNO_3 (4-stage), 10 *M* NaOH (2-stage)	97.2	0.7	0.1	0.1	0.0	0.0

The use of a nitric acid scrub to remove all the nitric oxide from the total off-gas from the dissolver was also considered. It was found that, by scrubbing with 70% nitric acid, with a mole ratio of nitric acid to uranium equal to 1, 90% of these oxides were removed from the gas. Such a mechanism could be considered as a procedure for plant application provided that the nitrogen oxides dissolved in the nitric acid could be removed by a low-temperature crystallization of N_2O_4 or by reaction with sodium hydroxide. An alternate method that was considered used a 1 to 2 mixture of 70% nitric acid and 92% sulfuric acid, with 1 mole of nitric acid present for each mole of uranium. With this system 100% removal of the nitric oxide and nitrogen dioxide was obtained as nitrososulfuric acid, and the effluent gas had a composition of 95% N_2, 0.9% CO_2, 0.6% CO, and 0.7% N_2O.

Uranium Dissolution — Unit Operations Study. Based on laboratory-scale studies, a study of uranium dissolution in nitric acid is now being made on a 7-kg scale. The object of this study is to determine the effect of increasing the scale of operation on the dissolution rate and the gas evolution.

The procedure used in dissolving is similar to the Hanford procedure in which a 300% excess of metal is charged to the dissolvers, the jackets are removed by caustic dissolution, and two dissolvings are carried out, at the end of which a 100% heel of metal remains. Metal is again charged to bring the total up to 300% excess, the jackets are removed, two dissolvings are made, and the cycle is repeated. By this method the number of jacket-removal operations is reduced by a factor of 2, and a satisfactory rate of uranium dissolution is obtained.

When starting with 4 moles of nitric acid per mole of uranium metal at a 55% nitric acid concentration, a final solution of 1.6 to 2.9 *M* uranium and 0.0 to 0.13 *M* nitric acid was obtained in approximately 10 hr. The uranium metal used for this test was extruded rods 1.25 in. in diameter and 8 in. long and was not jacketed with aluminum. The nitric acid per mole of uranium varied from 4.1 to 4.6 moles. In one run in which care was taken not to lose the gases remaining in the dissolver at the end, it was found that the nitrate ion material balance was on the order of 98% (Table 3.5). The analytical data indicated that for the first half of the dissolving only 3.8 moles of nitric acid per mole of uranium was consumed. However, for the last part of the dissolving, 5.5 moles of nitric acid per mole of uranium was consumed. This was significantly different from the laboratory results, which indicated higher acid consumption at the start of the run.

Specific measurement of the rate of dissolution and gas evolution was not made. However, it was observed that in the second dissolving the maximum gas evolution rate was obtained. This was, apparently at least, twice the maximum gas evolution rate of the first run. Equipment for the determination of the gas flow rate is now being installed, and data on flow rates will be obtained during the coming period.

This work was done with a downdraft condenser and a gas holder for the oxidation of the NO to NO_2 and its removal by scrubbing with water. The residual gas from each of the runs was analyzed (Table 3.6), and it was found that the average volume of the nonoxidizable gas per kilogram of uranium was approximately 4.3 liters, with values ranging from 3 to 6 liters. During the build-up of acid concentration in the aqueous scrub solution, it was found that the ratio of nitric to nitrous acid was about 10 to 1.

The work on this problem is being continued.

TABLE 3.5

Uranium Dissolution — Unit Operations Study

Dissolver: Temperature, 108°C
Pressure, 0 to 1 in. Hg
Ratio of HNO_3 to U, 4/1
Concentration of HNO_3 = 11.7 *M* (55%)
Uranium slugs, 1.25 in. in diameter, 8 in. in length

Condenser: Reflux rate, 80 to 100 ml/min

RUN	TIME (hr)	URANIUM CHARGE (kg)	URANIUM DISSOLVED		PRODUCT SOLUTION		HNO_3/U RATIO	HOLDER HNO_3/U RATIO
			(kg)	(%)	U (*M*)	HNO_3 (*M*)		
SR-11	9.7	24.55	8.04	33	2.9	0.13	4.3/1	1.4/1
SR-12	10	16.51	8.20	50	2.5	0.25	4.1/1	1.5/1
SR-13	10	23.60	7.81	33	2.4	0.13	4.2/1	1.7/1
SR-16	10	24.34	7.08	29	1.6	0.25	4.4/1	1.8/1
SR-17*	10	17.26	7.08	41	1.6	0.13	4.5/1	2.4/1
SR-19	10	24.70	8.52	35	1.8	0.0	4.6/1	1.9/1

*Run SR-17 was made without discharging the slugs and purging the system after Run SR-16. Discrepancies between the HNO_3 consumed in the dissolver and that recovered in the spray chamber were shown to be due to NO-NO_2 holdup in the dissolver and associated lines.

TABLE 3.6

Nonoxidizable Gas Composition

RUN	COMPOSITION (%)							
	NO	NO_2	CO_2	O_2	N_2O	CO	H_2	N_2
SR-11	10.8	5.4	4.1	0.5	5.3	0	0	74.0
SR-13	0.9	1.8	4.0	0	0.7	0.8	0.1	91.7
SR-14	7.4	6.8	6.8	0.3	0.2	0.2	0.9	77.4

Electrolytic Removal of Ruthenium. A preliminary study has indicated that 97% of the ruthenium may be removed from the metal solution by an electrolytic plating process. It is therefore possible that this procedure could be used as a head-end treatment in the Purex process.

The effectiveness of ruthenium removal was studied as a function of electrolyte temperature and type of anode. Platinum, silver-platinum, and copper-platinum anodes were investigated, with both the silver-platinum and copper-platinum anode operated at 70 to 80°C; efficient removal of the ruthenium was obtained (Table 3.7). Dissolving copper or silver anodes were employed which plated out on the cathode and were thus probably responsible for the observed increased ruthenium removal by acting as a carrier for the ruthenium and/or by providing a fresh cathode surface during the deposition. This study is being continued.

Effect of Dissolver Operation on Ruthenium Decontamination. Ruthennium chemistry studies by other investigators suggested the possibility that, by dissolving to a high-acid final product, the ruthenium decontamination factor might be significantly affected. The factors studied were the variation of initial nitric acid concentration from 7 to 16 *M*, final nitric acid

TABLE 3.7

Removal of Ruthenium from Uranyl Nitrate Solution

ANODE MATERIAL	TEMPERATURE (°C)	CURRENT (amp-hr)	VOLUME (ml)	RUTHENIUM REMOVED (%)	REMARKS
Platinum	25	5	50	Trace	
Platinum	70 to 80	26	100	41	
Silver-platinum	70 to 80	4	100	97	Silver for 0.25 amp-hr
Copper-platinum	25	8	100	8	Copper for 0.25 amp-hr
Copper-platinum	70 to 80	8	100	90	Copper for 0.25 amp-hr

concentration from 1.2 to 5.8 *M*, final uranium concentration from 1.5 to 3.8 *M*, addition of hydrogen peroxide, addition of urea, and sparging with oxygen or nitrogen. These variables had no significant effect on ruthenium decontamination or on the gross-beta decontamination.

The data discussed above were obtained by dissolving irradiated uranium wafers to the final conditions indicated and then adjusting the solution to 1.35 *M* uranium and 2 *M* nitric acid, and carrying out three extractions and four scrub operations on the solution using the standard August flowsheet (ORNL-846).

Effect of Decreasing Acid Concentration in Scrub Solution. It was demonstrated in laboratory-batch countercurrent studies that the nitric acid concentration in the scrub solution of the I-A column could be reduced from 3 *M*, now recommended in the August flowsheet, to 2 *M* without significantly affecting the plutonium loss or the gross-beta decontamination factor. In this study, the nitric acid concentration was varied from 0 to 3 *M*, and, at the same time, the relative volume of the scrub stream was also varied in order to maintain the same acid concentration in the extraction section (Table 3.8). At lower nitric acid concentrations, 0 to 1 *M*, the gross decontamination factor was significantly reduced.

TABLE 3.8

Effect of Varied Acid Concentration in Scrub Solution on Decontamination and Recovery

AF composition: 1.35 *M* $UO_2(NO_3)_2$, 2.12 *M* HNO_3, 1.08 x 10^7 gross β c/min/ml, and 1.48 x 10^5 Pu α c/min/ml

AX composition: 30 vol % tributyl phosphate plus 70 vol % washed Amsco 123-15

Volume ratio: AF/AX = 18 ml/60 ml

Stages: Five extraction and six scrub

RUN	SCRUB		LOSS (%)		GROSS β DECONTAMINATION FACTOR
	ACID CONCENTRATION (*M*)	VOLUME (ml)	URANIUM	PLUTONIUM*	
M-63	0	4	<0.001	0.75	1470
M-64	1	6	<0.001	1.23	2750
M-65	2	9	<0.001	0.65	3960
M-66	3	12	<0.001	0.55	3560

*The plutonium losses as reported are probably not significant inasmuch as nearly all the "extractable plutonium" was extracted by the third extraction stage. The "nonextractable plutonium" may actually be higher transuranic elements.

Effect of Increasing Uranium Concentration in the I-A Extraction Column. The effect of increasing the uranium concentration in the first-cycle extraction column was studied to determine its effect on uranium and plutonium losses and decontamination factors. Laboratory studies in batch countercurrent equipment have indicated that an increase in the uranium concentration from 1.35 *M*, as recommended in the August flowsheet, to 2.27 to 2.53 *M* will still give satisfactory uranium and plutonium recovery and gross beta decontamination factors (Table 3.9). To obtain a satisfactorily stable feed solution at the high uranium concentration, it was necessary to reduce the

TABLE 3.9

Effect of Scrub Variation on Extraction Process with Increased Uranium Concentration in Feed

AF composition: 2.27 *M* uranium, 0.2 *M* acid deficient, 7.76×10^6 gross β c/min/ml, 6.5×10^4 Pu α c/min/ml

Volume ratio: AF/AX = 10 ml/50 ml

Batch countercurrent stages: Five extraction and six scrub

RUN	SCRUB		ORGANIC SATURATION		LOSS (%)		DECONTAMINATION FACTORS		
	HNO_3 CONCENTRATION (*M*)	VOLUME (ml)	FEED STAGE (%)	PRODUCT (%)	URANIUM	PLUTONIUM	GROSS β	RUTHENIUM	ZIRCONIUM
August flowsheet conditions	3	6.7	80	75			4700	196	13800
M-79	5	7	91	78	0.001	0.53	1860	130	2230
M-78	7	5	90	80	0.001	0.56	735	69	69
M-77	7*	5	98	86	0.001	0.75	1220	69	2060
M-76	7*	5	99	85		0.73	2580	440	540
M-80	7	8	92	75	0.001	0.51	3850	370	660
M-89	7*,**	10	102	78	0.048	0.089	22700	1330	7800

*The scrub contained 0.01 *M* oxalic acid.

**AF composition; 2.53 *M* uranium, 0.75 *M* acid deficient; flow ratio AF to extractant = 10 ml/60 ml

nitric acid concentration in the feed solution. Then, in order to maintain the nitric acid concentration high enough in the extraction section for satisfactory recovery of the uranium and plutonium, it was necessary to increase the nitric acid concentration in the scrub stream. When using a feed 2.2 *M* in uranium and 0.2 *M* acid deficient with a 5 *M* nitric acid scrub, the gross beta decontamination and the ruthenium decontamination factors were decreased by a factor of approximately 2 under August flowsheet conditions and the zirconium decontamination was decreased by a factor of about 6. With a 7 *M* nitric acid scrub the gross beta decontamination factor was reduced again by a factor of approximately 2. However, the ruthenium decontamination factor was increased by a factor of 2 and the zirconium decontamination factor was decreased by a factor of about 200. The addition of 0.01 *M* oxalic acid increased the zirconium decontamination; however it still did not approach that obtained under August flowsheet conditions.

Better decontamination results were obtained when an extraction feed solution containing 2.5 *M* uranium and 0.7 *M* acid deficiency was processed with a scrub solution containing 7 *M* nitric acid and 0.01 *M* oxalic acid. Under these conditions the gross beta decontamination was increased by a factor of approximately 5 and the ruthenium by a factor of 6, and the zirconium was decreased by a factor of approximately 2.

On the basis of this work it appears possible to increase the uranium concentration in the extraction feed significantly, and, therefore, the laboratory studies will be continued with work initiated in the Unit Operations Section to evaluate the operability of this system in pulse columns.

Oxalic Acid and Mandelic Acid as Zirconium Scrubbing Agents. In the first-cycle extraction column of the Purex process the scrubbing is particularly effective for the removal of zirconium from the organic phase. However, a relatively long scrub section is required for the zirconium extraction. It was thought that, by the addition of the zirconium complexing agents, such as oxalic acid and mandelic acid, the zirconium extraction could be accelerated. In laboratory countercurrent batch equipment oxalic acid was demonstrated effective in increasing the gross beta decontamination by a factor of 4; however, the improvement was not sufficient to decrease the number of scrub stages required. The mandelic acid had no significant effect.

These tests were carried out in an 11-stage batch-countercurrent equipment, five extraction and six scrub stages, with a feed solution containing 320 g of uranium per liter, 1 to 10 mg of plutonium per liter, 0.2 *M* nitric acid, and 10^7 c/min/ml of Zr^{95}-Nb^{95} tracer. The best results were obtained with a scrub solution containing 0.001 *M* oxalic acid in a 3 *M* nitric acid solution.

It was anticipated that, during the nitric acid recovery from the solvent extraction wastes, the presence of oxalic acid would cause corrosion of the stainless steel evaporator. Decomposition of the oxalic acid by sparging with ozone and nitric oxide was studied. Decomposition of the oxalic acid was effected by sparging the solution containing 0.008 *M* oxalic acid, 2.2 *M* nitric acid, and 1×10^{-5} *M* manganous ion with ozone with an excess of oxygen. The manganous ion catalyzed the reduction of the oxalic acid; the reaction was carried out at room temperature. In this test, 42% of the oxalic acid was decomposed after sparging for 5 min, and about 8% of the ozone was utilized in oxidizing the oxalic acid. The tests with nitrogen dioxide as the oxidizing reagent were not successful in oxidizing oxalic acid.

Uranyl Oxalate Solubility Studies. It was found that the solubility of uranyl oxalate was sufficient to allow the use of oxalate ion as a complexing agent in the I-A column to improve zirconium decontamination. The solubility of uranyl oxalate was determined as a function of uranyl nitrate and nitric acid concentration. With no uranyl nitrate present, the solubility of the oxalate increased from 0.034 to 0.059 *M* at 24°C when the nitric acid concentration was increased from 1 to 3 *M*. At uranyl nitrate concentration of 0.25 *M* the oxalate solubility was between 0.018 and 0.021 *M*, with the solubility increasing, as the nitric acid concentration increased, from 1 to 4 *M*. Increasing the uranyl nitrate concentration to 1 *M* has little effect on the solubility of the uranyl oxalate.

Sulfurous Acid as a Plutonium Partitioning Agent. The use of sulfurous acid as a partitioning agent for plutonium was satisfactorily demonstrated in glass equipment. However, since in subsequent tests in stainless steel equipment excessive corrosion was caused by the sulfurous acid, its use is not recommended as a partitioning agent in the Purex process.

Batch countercurrent tests in glass equipment using a scrub solution containing 0.6 *M* nitric acid and 0.05 *M* sulfurous acid reduced the plutonium losses to 0.2% in six stages. In stainless steel equipment the maximum sulfurous acid concentration that could be obtained was 0.027 *M* owing to the fact that the sulfurous acid was reacting with the stainless steel equipment. A 16-hr packed-column run resulted in a maximum plutonium loss of 1.6%, and it was evident, from the color of the plutonium product stream, that considerable corrosion had occurred in the column.

Water or Uranyl Nitrate Solution as Plutonium Partitioning Agent. The use of water or uranyl nitrate solution as a partitioning agent for plutonium in the Purex I-B column was suggested because it would eliminate the use of ferrous sulfamate which increases the solid content of the waste, and, to a certain extent, complicates the second plutonium cycle. Also, the nitric acid would be eliminated, thereby decreasing the acid concentration of the uranium-bearing organic stream to the strip column which would facilitate the stripping of the uranium into the aqueous phase. An exploratory laboratory study in batch-countercurrent equipment indicated that satisfactory separation of uranium from plutonium could be obtained with the use of either water or uranyl nitrate solution. However, it appeared that the best results could be obtained using a plutonium strip solution containing about 0.87 *M* uranium (Table 3.10). In addition to the better plutonium-uranium separation obtained, this would give a greater density differential between the aqueous and organic phases. It was felt that part of the uranium product solution from the stripping column could be used as the plutonium extractant stream for the I-B column.

Behavior of Uranium Decay Products in the Purex Process. The behavior of the uranium decay products in the Purex process was of interest because they were found in relatively high concentration in the final plutonium product. It now appears that about 15% of the uranium decay products ($UX_1 + UX_2$) entering the Purex process through the I-AF feed leaves with the final plutonium product. In some cases the amount of $UX_1 + UX_2$ has been found to be considerably greater. It was found that the UX_1 activity refluxes in the I-A column and probably builds up in concentration to over 100 times its concentration in the original feed. A decontamination factor of 2 to 4 was indicated in countercurrent batch runs with four scrub stages. Additional scrub stages would increase this factor. Nearly all the UX_1 entering the I-B column is stripped

TABLE 3.10

Water or Uranyl Nitrate Solution for Partitioning

Laboratory batch countercurrent study

RUN	BF			BX		BF/BX/BS VOLUME RATIO	NO. OF STAGES		PRODUCTS			
									BU		BP	
	URANIUM (*M*)	HNO_3 CONCEN-TRATION (*M*)	PLUTONIUM PER MILLION PARTS OF URANIUM	URANIUM (*M*)	HNO_3 CONCEN-TRATION (*M*)		PARTI-TIONING	SCRUB	URANIUM (mg/ml)	PLUTONIUM PER MILLION PARTS OF URANIUM	PLUTONIUM (mg/ml)	mg OF URANIUM PER mg OF PLUTONIUM
M-82	0.44	0.21	960	0	0	10/6/10	5	6	52.5	48	0.215	0.002
M-83	0.43	0.28	1260	0	0	10/6/10	7	4	54	1.6	0.21	0.58
M-84	0.44	0.23	1160	0	0	10/7.5/15	7	4	41.2	1.9	0.136	0.73
M-81	0.42	0.18	1.45	0.82	-0.02	10/6/10	8	7	115	0.04	0.00031	0.77
M-88	0.43	0.26	950	0.87	-0.03	10/6/10	7	6	116	1.1	0.183	0.012

out with the plutonium, and in the second cycle a decontamination factor of approximately 2 is obtained in the II-A column. Special consideration for the separation of the UX_1 activity from the plutonium may be required.

Study of a 20% TBP First-Cycle Flowsheet. The initial demonstration of the August flowsheet for the Purex process in the pilot plant pulse column indicated much lower flooding rates than had been expected. Therefore a 20% TBP first-cycle flowsheet, which resulted in a greater density difference between the aqueous and organic phases which was expected to result in higher flooding rates, was studied in the laboratory. With the TBP concentration reduced to 20%, it was necessary to reduce the uranium feed concentration to 250 mg/ml in order to maintain 85% uranium saturation of the solvent phase. In addition it was necessary to increase the nitric acid concentration from 2 to 3 *M* to obtain satisfactory extraction of the plutonium. This process was demonstrated in laboratory-batch countercurrent equipment, and the densities of the aqueous and organic phases at the top of the scrub section were found to be 1.12 and 0.91, respectively. This provided a density difference of 0.21 as compared to 0.15 obtained with the 30% TBP flowsheet.

Further work in the pilot plant has demonstrated that the increase in density difference will not be required, and therefore further study of the 20% TBP flowsheet will not be necessary.

Effect of Nitric Acid and TBP Concentration in the Second Plutonium Cycle. The nitric acid concentration was varied from 1.5 to 7 *M* and the tributyl phosphate concentration in the solvent was varied from 5 to 30% in order to determine the effect on the distribution coefficient of plutonium, gross beta activity, and nitric acid. The maximum separation of plutonium from gross beta activity was obtained at 7 *M* nitric acid with no significant effect noted as being due to the variation in TBP concentration. However, in stripping, both low TBP concentration and low nitric acid concentration were desirable for optimum results (Tables 3.11 and 3.12).

Second Plutonium Cycle Packed Column Test. The second plutonium cycle was demonstrated in a packed column using the plutonium product stream (I-BP) from the first solvent-extraction cycle for which 100-g/T uranium was used as the feed. The total plutonium loss for the second plutonium cycle was 0.1%; the gross beta decontamination factor was 13. The individual plutonium losses were 0.01% for the TBP removal step, 0.02% for the extraction loss, and 0.07%

TABLE 3.11

Gross Beta and Plutonium Separation Factors as Functions of Nitric Acid and TBP Concentrations

Aqueous feeds: prepared from column-produced I-BP which was oxidized with 0.1 *M* $NaNO_2$ and digested 20 min at room temperature, and the nitric acid concentration adjusted by addition of 16 *M* HNO_3

Aqueous feed composition: Pu(III), 1.8 x 10^6 α c/min/ml; β, 3.5 x 10^4 c/min/ml; $Fe(NH_2SO_3)_2$, 0.03 *M*; uranium, less than 0.1 mg/ml

HNO_3 IN FEED (*M*)	TBP IN SOLVENT (%)	PLUTONIUM DISTRIBUTION COEFFICIENT, O/A	GROSS BETA DISTRIBUTION COEFFICIENT, O/A	SEPARATION* FACTOR
1.5	5	0.04	0.005	8.0
	10	0.15	0.02	7.5
	15	0.29	0.04	7.2
	20	0.35	0.07	5.0
	25	0.45	0.10	4.5
	30	0.51	0.12	4.3
3	5	0.5	0.03	17
	10	1.8	0.09	20
	15	3.0	0.15	20
	20	3.0	0.21	20
	25	6.0	0.27	22
	30	7.3	0.33	22
5	5	1.9	0.05	38
	10	5.7	0.14	41
	15	9.4	0.22	43
	20	13.2	0.30	44
	25	17.0	0.37	46
	30	20.7	0.42	49
7	5	3.2	0.07	49
	10	10.0	0.19	53
	15	17.0	0.31	55
	20	24.0	0.44	55
	25	30.9	0.57	54
	30	37.7	0.69	55

*Separation factors calculated as plutonium distribution coefficient ÷ gross beta distribution coefficient.

TABLE 3.12

Gross Beta and Plutonium Stripping Distribution Coefficients as Functions of Nitric Acid and TBP Concentrations

Organic phases from batch extractions (Table 3.11) stripped with equal volumes of water

HNO_3 IN FEED (*M*)	TBP IN SOLVENT (%)	HNO_3 IN SOLVENT (*M*)	PLUTONIUM DISTRIBUTION COEFFICIENT, O/A	GROSS BETA DISTRIBUTION COEFFICIENT, O/A
1.5	5	0.06	0.02	<0.01
	10	0.11	0.02	0.30
	15	0.16	0.04	0.19
	20	0.21	0.08	0.35
	25	0.25	0.11	0.45
	30	0.28	0.25	0.48
3	5	0.11	0.01	< 0.003
	10	0.21	0.03	0.01
	15	0.33	0.05	0.06
	20	0.41	0.19	0.15
	25	0.50	0.45	0.18
	30	0.57	0.76	0.24
5	5	0.15	0.006	0.02
	10	0.31	0.03	0.03
	15	0.47	0.17	0.04
	20	0.61	0.50	0.09
	25	0.74	0.92	0.18
	30	0.74	1.52	0.32
7	5	0.17		
	10	0.34	0.11	0.02
	15	0.53	0.35	0.07
	20	0.70	0.65	0.12
	25	0.85	1.16	0.19
	30	1.01	2.19	0.28

for the stripping loss. The individual decontamination factors were: for ruthenium, 70; for zirconium, 18; for the rare earths, 106; and for $UX_1 + UX_2$, 1.5. When correction was made for the $UX_1 + UX_2$, the gross beta decontamination factor for fission products was 35. The final plutonium product contained the following contaminants per gram of plutonium: 1×10^8 beta counts, 6×10^4 gamma millivolts, 152 mg of iron, 24 mg of nickel, and 16 mg of chromium. About 85% of the activity associated with the plutonium was due to the presence of $UX_1 + UX_2$.

The August flowsheet conditions were used for this run. The I-BP solution accumulated during the hot first-cycle run was scrubbed with Amsco 123-15, the volume was reduced to 5 *M* nitric acid, and the solution was oxidized with 0.1 *M* sodium nitrite. The feed was then extracted countercurrently with 10% TBP solvent in a 1½-in.-diameter column with a 24-ft extraction section and a 16-ft scrub section. The ratios of feed to scrub to solvent were 3:2:10. Stripping was carried out in a 2-in.-diameter column with a packed height of 40 ft, using a volume of water equal to that of the solvent.

Electrolytic Scavenging of Plutonium from Uranium Solution. Plutonium may be removed from a uranium solution by the partial precipitation of the uranium in the cathode cell of an acid-base diaphragm cell. This process was studied to determine if sufficient separation could be obtained in such a cell of the plutonium from the uranium in the uranium product stream of the first-cycle Purex process, thus perhaps eliminating the need for a second uranium cycle. In this study a solution containing 50 g of uranyl nitrate hexahydrate per liter was contained in the cathode cell while solutions of 10% sodium nitrate and 0.1 *M* nitric acid were in the anode cell. When 0.6% of the uranium was precipitated 97% of the plutonium was removed. The results of this study indicate that by the precipitation of 1% of the uranium, a decontamination factor of the order of 100 for plutonium could be obtained. No further work on this procedure is planned for the present.

Plutonium Isolation — Peroxide Precipitation Study. In the proposed Savannah River flowsheet plutonium from the Purex process will be precipitated as plutonium peroxide before hydrofluorination and reduction of the metal. While the use of plutonium peroxide in this way is now a standard procedure, the feed solution from the Purex process differs somewhat in composition, and some alterations in the procedure may be desirable.

Solubility of the plutonium peroxide precipitate is a function of the temperature, the peroxide concentration, and the iron concentration. The presence of more than 0.005 *M* iron in the feed solution sharply increases the plutonium losses in the supernatant. The effect of iron on plutonium peroxide solubility is being studied. The rate of decomposition of hydrogen peroxide at 25°C was determined for solutions containing 10% hydrogen peroxide, 0.01 *M* ferric ion, and 0.5, 1.0, and 2.0 *M* nitric acid. At these acid concentrations, 4.0, 1.5, and 0.6%, respectively, of the total initial hydrogen peroxide was decomposed per hour. With no nitric acid present, the decomposition rate was so rapid it could not be determined. The decomposition rate of hydrogen peroxide at the 2 *M* nitric acid concentration used for the precipitation of plutonium appears to be too slow to affect the plutonium peroxide solubility. Therefore the decrease in the plutonium peroxide yield with increasing iron concentration does not appear to be a result of catalytic decomposition of the hydrogen peroxide.

This work will be continued along with the determination of separation factors for uranium, chromium, nickel, fission products, and phosphate.

Solubility of Tributyl Phosphate. The solubility of tributyl phosphate from a 30% tributyl phosphate—70% Amsco solvent mixture when in contact with an aqueous solution whose acidity varied from water to 4 *M* nitric acid and where uranium concentration varied from water to 75 mg/ml was determined at room temperature. The solubility of tributyl phosphate in contact with water was 0.013 g per 100 ml; it decreased with the addition of nitric acid and uranyl nitrate (Table 3.13). These data were determined by batch-equilibration studies using P^{32}-labeled tributyl phosphate furnished by the ORNL Chemistry Division, and they are believed to be accurate within a factor of 2.

Tributyl Phosphate Hydrolysis. The extent of the hydrolysis of tributyl phosphate in various concentrations of nitric acid from 1 to 8.6 *M* was determined at the solution boiling point with a few measurements at room temperature and at 60 to 70°C. With only the amount of tributyl phosphate present required to saturate the aqueous phase, the hydrolysis appeared to be a first-order reaction with respect to the TBP concentration. At the boiling point 10% of the TBP was hydrolyzed in 0.35, 0.55, and 1.9 hr at 8.6, 5.4, and 1.04 *M* nitric acid, respectively. At 60°C, with 5.4 *M* nitric acid only 0.5% of the TBP was hydrolyzed in 6 hr.

TABLE 3.13

Solubility of TBP (from 30% Solution in Kerosene) in Various Aqueous Solutions

SOLUTION	TBP SOLUBILITY (g/100 ml)
Water	0.013
0.4 *M* HNO_3 in water	0.012
1.6 *M* HNO_3 in water	0.01
4.0 *M* HNO_3 in water	0.006
Uranyl nitrate, uranium concentration, 25 mg/ml	0.01
Uranyl nitrate, uranium concentration, 50 mg/ml	0.0075
Uranyl nitrate, uranium concentration, 75 mg/ml	0.0037

With a 30% tributyl phosphate—Amsco solvent present in contact with 6 *M* nitric acid, 0.4% of the total tributyl phosphate present was hydrolyzed in 3 hr. This rate is significantly greater than would be predicted from the rate of hydrolysis in the aqueous phase alone. Apparently a considerable portion of the hydrolysis occurred in the organic phase. In a similar experiment carried out at room temperature, with the 30% TBP—Amsco solvent in contact with 7 *M* nitric acid, approximately 0.05% of the total tributyl phosphate present was hydrolyzed in 24 hr. Since tributyl phosphate is hydrolyzed in steps to phosphoric acid, the amount hydrolyzed is not a true representation of the plutonium losses which might be expected since only the intermediates in the hydrolysis effect the plutonium extraction.

In a test which simulated the evaporation of the first-cycle plutonium product stream (I-BP), it was found that approximately 1.8% of the tributyl phosphate was hydrolyzed. The test was carried out using a 1 *M* nitric acid solution (with and without 1 g of uranyl nitrate hexahydrate per liter in the feed solution) saturated with labeled TBP which was evaporated to a 15% heel in a period of 1.7 hr. It was found that 97.7% of the tributyl phosphate in the feed had distilled unchanged and that 80% of the TBP remaining in the evaporator was hydrolyzed. This experiment was repeated carrying out the distillation at 75 mm Hg; only 0.24% of the tributyl phosphate was hydrolyzed. Under these conditions 99.1% of the tributyl phosphate distilled off, and 34% of that remaining in the evaporator was found to have hydrolyzed.

On the basis of these data it appears feasible to concentrate the I-BP stream fivefold without previous scrubbing if (1) no organic phase is present, (2) the holdup time is less than 10 to 15 min in the evaporator, or (3) if the concentration is carried out at reduced pressure. Since TBP is hydrolyzed in steps, eventually yielding relatively harmless phosphoric acid, it is quite possible that the amount of DBP or MBP present may be much smaller than the amount of tributyl phosphate hydrolyzed. For this reason the data on the hydrolysis of TBP should be considered as indicating the maximum amount of dibutyl phosphate which may be encountered. The actual amount may be much less.

Plutonium(III)-DBP System. Since in the first cycle the plutonium is reduced to the III state before stripping, the effect of DBP on Pu(III) has received some consideration. The procedure used here consisted in reducing the plutonium to the III state in dilute nitric acid, then contacting the plutonium solution with either kerosene or TBP-kerosene containing small amounts of DBP. Reducing with ferrous ion was impractical owing to the formation of an emulsion with DBP containing some of the organic phase, presumably as a result of formation of a precipitate of iron dibutyl phosphate which acts as protective colloid to the organic droplets. The reducing agent used successfully was sulfur dioxide. A TBP wash was employed to check for complete reduction; then the aqueous solution was washed successively with 1% DBP in kerosene and with butyl acid phosphate (largely monobutyl phosphate) in kerosene. The distribution coefficient (O/A) was 0.016 with TBP solution, indicating freedom from Pu(IV) or Pu(VI). The first 1% DBP wash gave a distribution coefficient of 0.35; the second, 1.0. The distribution coefficient for the butyl acid phosphate was 0.24. The experiment was repeated, and again the distribution coefficient for 1% DBP in kerosene increased after the first contacting. A test made with 0.1% DBP in kerosene gave the same results, that is, 0.39 and 0.92 for the distribution coefficient on the first and second wash. When the DBP was dissolved in kerosene containing 27% TBP, however, the distribution coefficient did not rise. Its value with 0.1% DBP was 0.27 and 0.15 on the first and second contacting. The behavior of DBP in the presence of dissolved iron may be more of a problem in the I-B column than its effect on Pu(III).

Plutonium(IV)-DBP System. Since one of the principal objectives of this work is the determination of the effect of hydrolysis of TBP on plutonium

losses, the effect of pure dibutyl phosphate (DBP) on plutonium losses has been investigated. The first product of hydrolysis of TBP is DBP, which forms a very strong soluble complex with Pu(IV). The formation of this complex will result in loss of Pu(IV) in stripping operations, such as in the II-B column.

The experiments were performed by extracting Pu(IV) into purified TBP solution and then adding small known amounts of DBP. This solution simulated a II-AP solution containing known amounts of DBP. The simulated II-AP was successively stripped with six equal volumes of water to remove essentially all Pu(IV) uncomplexed by DBP. The activity remaining in the solvent after the fourth and sixth strip was determined as well as the activity in the sixth aqueous strip solution. These results are given in Table 3.14 together with the calculated plutonium losses. The percentage losses may not be so high with the higher plutonium concentrations contemplated for the Savannah River plant.

It may be concluded from this work that a DBP concentration of 5 to 10 × 10^{-4}% may cause plutonium losses.

TABLE 3.14

Effect of DBP Concentration on Plutonium(IV) Losses

Feed: 30% TBP—70% Amsco, 6.5 × 10^5 Pu α c/min/ml

Extractant: Water

DBP CONCENTRATION (%)	PLUTONIUM CONCENTRATION (c/min/ml)			DISTRIBUTION COEFFICIENT, O/A	PLUTONIUM LOSS (%)
	4th STRIP, ORGANIC	6th STRIP			
		ORGANIC	AQUEOUS		
None added	1.19 x 10^3	850	120	7	0.13
0.0001	1.13 x 10^3	565	50	11	0.09
0.001	6.6 x 10^4	5.03 x 10^4	744	6.8	7.7
0.01*	2.2 x 10^5	2.2 x 10^5	1.44 x 10^3	150	60

*Organic phase originally 3.6 x 10^5 Pu α c/min/ml.

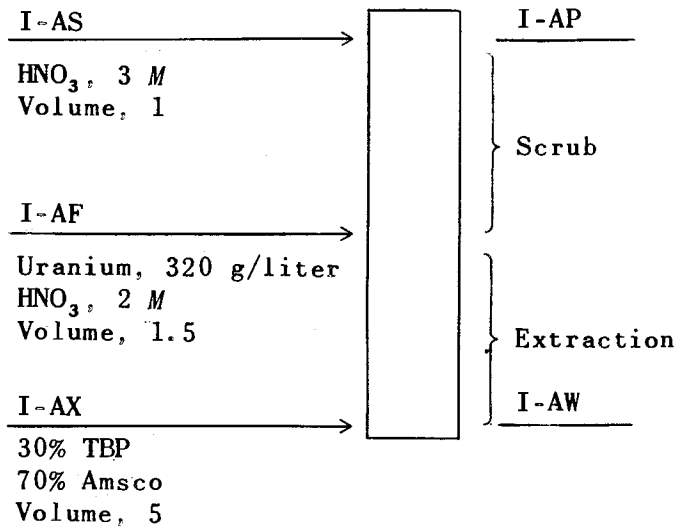
Pulse-Column Studies. Purex solvent-extraction studies in a pulse column using various heights of 2-in.-i.d. true-bore glass pipe indicated that in a uniform diameter compound "A" column sufficient amplitude and frequency must be obtained in order to drive the organic phase through the extraction plates, but they should not be of a magnitude which will give severe emulsification (and subsequent flooding) in the scrub section. In a column consisting of a 2-in.-i.d. by 4-ft scrub section, scrub section throughputs up to 1050 gal/sq ft/hr were obtained at amplitude and frequency ranges of 0.40 to 1.0 in. and 40 to 80 cycles/min, respectively, whereas in a 12-ft scrub section only 700 gal/sq ft/hr throughputs could be obtained and these only within narrower amplitude and frequency ranges (0.40 to 0.90 in. and 40 to 50 cycles/min). The 1050 gal/sq ft/hr scrub section throughput was satisfactorily maintained during one 6-hr run using (1) the 4-ft scrub section, (2) a pulse amplitude of 1.0 in., and (3) a pulse frequency of 58 cycles/min, in which the uranium loss in the 4-ft extraction section was about 0.6%.

Purex I-A column flooding studies were first made in a 2-in.-i.d. by 4-ft extraction and a 3-in.-i.d. by 4-ft scrub column at the pilot plant frequency (58 cycles/min). Under conditions of increasing throughputs and amplitudes (0.90 to 1.25 in. in extraction and 0.39 to 0.54 in. in scrub) the following results were noted: (1) a scrub section throughput of 1050 gal/sq ft/hr (double the pilot plant rate) was obtained at the high amplitudes (1.25 in. in extraction) before flooding was observed; (2) an emulsion in the scrub section was observed at the pilot plant throughputs and amplitudes (0.90 to 1.25 in.); (3) heating the entering streams did not reduce the emulsion; and (4) the emulsion did not in these tests cause the column to flood.

Since the amplitude in the 3-in.-i.d. scrub section could not be increased above 0.54 in. with the use of the present pump piston (1.125 in. diameter), the scrub section was revised to 2-in.-i.d. pipe (same as the extraction section), enabling the use of amplitudes up to 1.33 in. in both sections. Up to 1050 gal/sq ft/hr throughputs were obtained at an amplitude of 1.0 in. without flooding. This was demonstrated in a run lasting over 6 hr and yielding uranium loss values of about 0.6%. Reducing the amplitude to 0.5 in. caused flooding in the scrub section at throughputs as low as 750 gal/sq ft/hr. Tests in which the scrub section was lengthened from 2 in. i.d. by 4 ft to 2 in. i.d. by 12 ft decreased the throughput in the scrub section from 1050 to 700 gal/sq ft/hr and narrowed the operable amplitude range (0.40 to 1.0 vs. 0.40 to 0.90 in.) before flooding (Table 3.15). Preliminary

TABLE 3.15

Flooding and Extraction Studies in a Purex "A" Pulse Column



Plates: stainless steel, 1/8-in. holes, 23% free area

Plate spacing: 2 in.

Plate thickness: 18 gage

COLUMN DIMENSIONS				THROUGHPUT IN SCRUB SECTION		OPERABLE RANGE			URANIUM LOSS (wt %)
EXTRACTION		SCRUB				AMPLITUDE (in.)			
DIAMETER (in.)	HEIGHT (ft)	DIAMETER (in.)	HEIGHT (ft)	kg OF URANIUM PER DAY	VOLUME (gal/sq ft/hr)	EXTRACTION	SCRUB	FREQUENCY (cycles/min)	
2	4	3	4	69 - 207	235 - 700	0.9 - 1.25	0.39 - 0.54	58	
				300	1050	0.9 - 1.00	0.39 - 0.43	58	
2	4	2	4	72 - 140	550 - 1050	1.0		58	0.6
2	4	2	12	62	500	0.40		40 - 100	
						0.70		40 - 80	
						1.00		20 - 40	
				92	700	0.40		40 - 58	
						0.70		20 - 80	
						1.00		20 - 58	
				140	1050	0.40		Inoperable	
						0.70		30 - 40	
						1.00		Inoperable	

studies using 3/16-in. holes in the scrub plates of the 12-ft section indicated that the flooding rates may be increased 50% over those obtained with 1/8-in. plate holes and that a wider amplitude range can be used. Purex B column studies in a short compound column consisting of 2-in.-i.d. by 4-ft scrub and extraction sections indicated satisfactory operation over 2.5 hr at 1580 gal/sq ft/hr when using a pulse amplitude of 0.8 in. and a frequency of 58 cycles/min. The uranium loss over the 4-ft B scrub section was about 3% (Table 3.16).

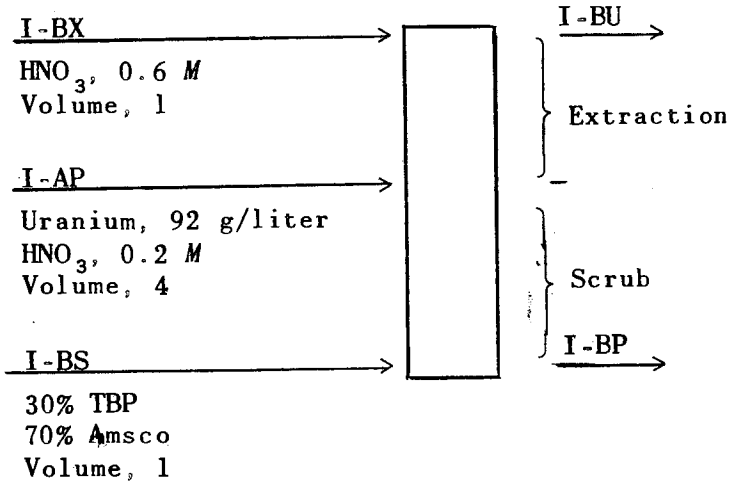
The I-C column operation was studied in an 8-ft by 2-in.-i.d. column, using pulse conditions of 0.56 in. amplitude and 73 cycles/min, to determine the effect of varying the continuous phase, temperature, and plate material on the total column throughput and on the uranium loss. Optimum operation was obtained with stainless steel plates, a continuous organic phase, and a temperature of 50°C. Under these conditions the minimum uranium loss and the maximum flooding rate were obtained. Under all conditions the use of Teflon plates caused lower flooding rates but comparable uranium losses. Operating with the aqueous phase continuous gave higher uranium losses than with a continuous organic phase. Flooding rates were about the same for either phase continuous. Increasing the temperature decreased the uranium loss and raised the flooding rate (Table 3.17).

The results of these pulse-column studies have been found applicable to the pilot plant operation. Pulse column development studies are being continued to broaden the known ranges of operability for this contactor and to test other process applications.

Hot Pilot Plant Runs. During the past quarter the Pilot Plant initiated the demonstration of the Purex process using radioactive solutions with an overall uranium loss of 1.65% and an overall plutonium loss of 1.82%. The best decontamination factor for uranium has been 3.4×10^6 beta and 8.3×10^4 gamma, while for plutonium these factors have been 1.3×10^6 beta and 5.9×10^5 gamma. With 40-g/T feed material, a uranium product containing 10 parts per billion of plutonium and a fission product beta activity 2% that of natural uranium and a gamma activity roughly equivalent to that of natural uranium was obtained. The plutonium product contained approximately 14% uranium based on the weight of plutonium. However, at the full production level of 400 g/T, the uranium content of the plutonium product was the equivalent of only 1.4%.

TABLE 3.16

Flooding and Extraction Studies in a Purex "B" Pulse Column



Plates: stainless steel, 1/8-in. holes, 23% free area

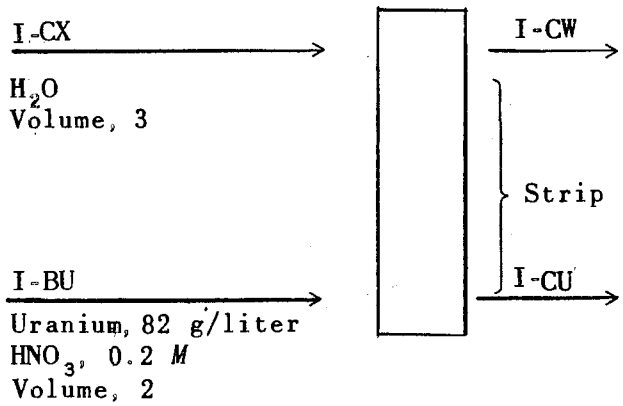
Plate spacing: 2 in.

Plate thickness: 18 gage

COLUMN DIMENSIONS				THROUGHPUT IN EXTRACTION SECTION		OPERABLE RANGE			URANIUM LOSS
EXTRACTION		SCRUB				AMPLITUDE (in.)		FREQUENCY	
DIAMETER (in.)	HEIGHT (ft)	DIAMETER (in.)	HEIGHT (ft)	kg OF URANIUM PER DAY	VOLUME (gal/sq ft/hr)	SCRUB	EXTRACTION	(cycles/min)	(wt %)
2.5	2	2	4	53.0	330	0.50	0.35	20 - 40	
						0.92	0.65	10 - 20	
						1.20	0.85	8 - 20	
				106.0	680	0.50	0.35	20 - 100	
						0.92	0.65	20 - 58	
						1.20	0.85	20 - 40	
				160	1020	0.50	0.35	25 - 110	
						0.92	0.65	20 - 58	
						1.20	0.85	20 - 40	
				150	740	0.92	0.65	58	0.078
						0.70	0.50	58	0.066
						0.50	0.35	58	0.082
						0.50	0.35	75	0.076
2.0	4	2	4	140	1580	0.80 - 1.00		58	
				125	1400	0.80		58	3.0

TABLE 3.17

Variables Affecting Stripping and Flooding Characteristics in a Purex "C" Pulse Column



Column: height, 8 ft; diameter, 2 in.

Plates: 1/8-in. holes, 23% free area

Plate spacing: 2 in.

Plate thickness: Teflon, 0.087 in.; stainless steel, 18 gage

Amplitude: 0.56 in.

Frequency: 73 cycles/min

PLATE MATERIAL	CONTINUOUS PHASE	TEMPERATURE (°C)	URANIUM IN ORGANIC WASTE (mg/ml)	FLOODING RATE (gal/sq ft/ hr)
Stainless steel	Aqueous	20	24.5	1300
	Organic	20	3.0	1100
	Organic	50	0.1	1750
Teflon	Aqueous	20	20.3	900
	Organic	20	8.2	900
	Organic	50	0.09	1480

The plutonium product met the beta and gamma fission products specifications. At full process level of activity, an additional decontamination factor of 2 to 5 will be required (Table 3.18).

This study was carried out in pulse columns for the first cycle and second uranium cycle; however, the second plutonium cycle was carried out in packed columns. Complete details on this work are reported in ORNL-1045. The uranium and plutonium losses were significantly higher than predicted in laboratory work; however, the decontamination factors obtained were equivalent to those previously reported by the Laboratory.

The high uranium losses occurred in the first- and second-cycle strip column and were due primarily to insufficient length of column for the complete extraction of uranium, but partially to the high acid concentration in the organic stream entering the strip column. Reduction of the acidity in the I-B column was effective in decreasing the uranium losses; however, additional length of column will be required. High plutonium losses occurred in the first cycle owing to insufficient length of the I-A extraction section and the I-B plutonium strip section. A significant decrease in the plutonium loss from the I-B column was effected in run HP-5 by decreasing the total throughput in the B column and increasing the amplitude of the pulse. The increase in amplitude probably had the most significant effect on the plutonium loss. In the I-C column the major plutonium loss was in the strip column. Here, by the addition of 0.1 *M* nitric acid instead of water as the strip solution, it was possible to reduce the strip loss from about 1.3 to 0.4%. To further decrease the plutonium strip loss it will probably be necessary to lengthen this column.

In the subsequent program plutonium and uranium losses were significantly reduced, and decontamination factors have been obtained which yield a satisfactory product stream. This work will be reported in detail in the next quarterly report.

Comparison of Packed- and Pulse-Column Performances — Pilot Plant. The operation of the Purex flowsheet was evaluated in the Pilot Plant in both packed and pulse columns. In this evaluation program cold uranium solution feeds were used. The operation and control of the pulse column proved to be as simple as those of the packed column, and standard system pumps gave satisfactory performance for pulsing columns varying from 2 to 4 in. in diameter.

TABLE 3.18

Purex Flowsheet No. 1 — Hot Column Runs

COLUMN SECTION		DIAMETER (in.)	CONTACT HEIGHT (ft)	PULSE AMPLITUDE (in.)	PULSE FREQUENCY (cycles/min)
I-A	Extraction	2	7.5	0.92	58
I-A	Scrub	3	12.5	0.41	58
I-B	Partitioning	2.5	11.5	0.53	58
I-B	Scrub	2	6	0.77	58
I-Bs	TBP Strip	2	15	Packed with ¼- by ¼-in. Raschig rings	
I-C	Strip	4	12	0.56	73
I-D	Extraction	2	8.5	1.00	58
I-D	Scrub	3	8	0.44	58
I-E	Strip	4	15	0.56	73
II-A	Extraction	1.5	30	Packed with ¼- by 3/8-in. Raschig rings	
II-A	Scrub	1.5	10	Packed with ¼- by 3/8-in. Raschig rings	
II-B	Strip	2	40	Packed with ¼- by 3/8-in. Raschig rings	
II-Bs	TBP Strip	1.5	27	Packed with ¼- by 3/8-in. Raschig rings	

RUN	FEED ACTIVITY		FIRST CYCLE						THROUGH TWO CYCLES							
			LOSS (%)		β DECONTAMINATION FACTOR		γ DECONTAMINATION FACTOR		LOSS (%)		β DECONTAMINATION FACTOR		γ DECONTAMINATION FACTOR		Pu IN U (ppb)	U IN Pu (%)**
	Pu (g/T)	β (c/min/ml)	U	Pu	U	Pu	U	Pu	U	Pu	U	Pu	U	Pu		
HP-1	3	7.2×10^6	0.10	5.14	1.9×10^4	8.1×10^3	5.0×10^2	8.5×10^2	2.10	6.12	$>10^4$	4.4×10^5			20	0.2
HP-2	10	1.4×10^7	0.18	2.71	1.6×10^4	9.5×10^3	1.8×10^3	6.8×10^2		3.30		4.2×10^5		1.5×10^4		250
HP-3	60	1.8×10^8	0.67	2.56	6.5×10^3	8.3×10^2	9.9×10^2	1.6×10^2	6.96	5.98	2.1×10^5	2.6×10^5	3.7×10^3	5.4×10^4	30	220
HP-4	50	2.6×10^8	0.52	2.19	1.5×10^4	1.2×10^3	1.7×10^3	2.7×10^2	1.41	3.07	3.2×10^5	5.3×10^5	4.2×10^4	5.5×10^4	13	75
HP-5***	40	2.6×10^8	0.56	1.00	2.3×10^4	1.1×10^4	4.0×10^3	3.8×10^3	1.65	1.19	3.4×10^5	1.3×10^6	8.3×10^4	5.9×10^5	7	1.4

*First-cycle runs 1 through 4 made with 125 kg of uranium per day, No. 5 made with 75 kg per day; second uranium cycle runs 1 and 3 made with 100 kg of uranium per day, Nos. 4 and 5 made with 75 kg per day.

**Corrected to 400- g/T basis.

***In Run HP-5 the diameter of the I-A scrub column was reduced from 3 to 2 in. and the amplitudes were changed to: 0.92 in. for the I-A scrub column, 0.75 in. for the I-B partitioning column, and 1.08 in. for the I-B scrub columns; the II-A column feed point changed to 16 ft extraction, 24 ft scrub.

The efficiency of the packed column vs. that of the pulse column was determined on the basis of the height of a theoretical solvent-extraction unit (HTU). It was found that the HTU's for uranium for the I-A extraction, I-B scrub, and I-C strip sections were 0.87, 0.98, and 1.7 ft, respectively, for the pulse column, and 1.9, 1.6, and 6.8 ft, respectively, for the packed column (Table 3.19). Therefore the efficiency of the pulse column was between 1.6 and 4 times greater than the packed column, depending on the process conditions. In addition, it was found that the flooding capacity of the pulse column was approximately 6 times that of the packed column. The scrub section of the I-A column was found to be the limiting flow capacity for both the pulse and packed columns. For the packed column the total throughput at flooding was 100 gal/sq ft/hr, and for the pulse column it was 600 gal/sq ft/hr.

Based on the Pilot Plant work and supporting studies in the Unit Operations Section, it appears that the pulse column will be a satisfactory tool for full-scale plant use.

Acid Recovery from I-AW Waste — Pilot Plant. The possibility of recovering about 80% of the nitric acid from the first-cycle extraction wastes (I-AW) with a final acid concentration of 56% and a gross beta decontamination factor of 4×10^5 has been demonstrated. This run was made with feed from a 40-g/T run (HP-5), and the final recovered acid product contained 10^{-2} microcurie of activity per milliliter. During the evaporation, an overall volume reduction of 20.8 was obtained in the evaporator. The vapor from the evaporator was sent to the center of a rectification column, from the bottom of which the acid was taken and from the top, the water. The water distillate was decontaminated by a factor of 10^6 and contained 1.9% of the total acid. The concentrate discharged from the evaporator after the run contained 8.8 *M* nitric acid in addition to essentially all the fission activity from the original waste feed. The feed rate to the evaporator was 3.75 gal/hr, with the run lasting for 61 hr.

Decontamination of Used Solvents. The tributyl phosphate—Amsco solvent, after use in the Purex process, contains the hydrolysis products of tributyl phosphate, a reaction product of HNO_2 and the Amsco diluent, and some fission product activity. Sodium carbonate or sodium hydroxide solution had been found to be effective in removing the tributyl phosphate hydrolysis product as well as the reaction product of the Amsco diluent. Satisfactory decontamination of the tributyl phosphate solvent has been demonstrated in the Pilot

TABLE 3.19

Comparison of Packed- and Pulse-Column Performance

Flowsheet: Purex No. 1 (August, 1950)

Packed columns: 1/4- by 3/8-in. split Raschig rings

Pulse columns: 1/8-in.-diameter holes, 2-in. plate spacing, 23% free area per plate

		PACKED COLUMN	PULSE COLUMN
Uranium HTU (ft)	I-A extraction*	1.9	0.87
	I-B scrub*	1.6	0.98
	I-C strip**	6.8	1.7
Flooding rate (gal/sq ft/hr)	I-A scrub	100	600

*Based on aqueous phase.

**Based on organic phase.

Plant using a 1-hr wash with one-fifth volume of 0.1 *N* sodium carbonate solution. This solvent from the Clinton level pilot plant run contained about 10^4 β c/min/ml (80% Ru β) prior to treatment. It has been specified that the recovered solvent should contain less than 10^{-8} curies/ml, and this level was obtained with the solvent from the Clinton activity level run. Additional decontamination will be required for the Hanford level run.

Laboratory tests carried out with the same Pilot Plant solvent indicated that sodium hydroxide was more effective than sodium carbonate for decontamination and that the decontamination was increased by a factor of almost 10 in both cases when the temperature was increased from 28 to 90°C. Changing the reagent concentration from 0.1 to 1% had no significant effect on the decontamination. It appeared from these results that the extraction of the activity was not reversible, and therefore only a single batch contacting was necessary. The uranium present in the solvent was also extracted, although when sodium carbonate was used as the decontamination agent it remained in solution. However, when sodium hydroxide was used, a uranium precipitate resulted. Equilibrium time in the laboratory studies was found to be approximately 15 min.

The phase separation time in the laboratory was found to be approximately equal to the time of agitation, with the time required for sodium hydroxide a little longer than for sodium carbonate. In the Pilot Plant, no difficulty has been experienced in phase separation.

Study of this problem will be continued using solvent from the full Hanford activity level pilot plant runs, and samples of solvent have been requested from Knolls to determine the decontamination required when a head-end treatment is incorporated in the Purex process.

Neutralization of Purex I-AW Concentrate with Coating-Removal Solution. The caustic coating-removal solution could possibly be used to neutralize the acid I-AW concentrate before the storage of these Purex process wastes. Assuming that a 20-fold volume reduction of the I-AW is obtained by evaporation, then for each pound-mole of nitric acid in the I-AW concentrate there would be 0.53 lb-mole of sodium hydroxide and 0.64 lb-mole of sodium aluminate from the coating-removal solution (I-AW concentrate, 8 *M* HNO_3; coating-removal solution, 1.5 *M* NaOH, 1.9 *M* $NaAlO_3$). It is desired to neutralize these solutions by the addition of I-AW to the jacket-removal waste to a final *p*H in the range of 8 to 10.

During the acid addition an aluminum hydroxide precipitate started to form at a *p*H of 11, and complete precipitation of the aluminum occurred under these conditions. The volume of the settled aluminum hydroxide precipitate was approximately 14 cc per gram of aluminum. When activity from Clinton slugs was added to the acid, it was found that the final precipitate contained about 90% of the activity in the neutralized solution. The volume of the settled precipitate was approximately 50% of the volume of the I-AW concentrate. The unhindered settling rate of the aluminum hydroxide precipitate was determined to be about 0.2 in. per minute.

The neutralization of the I-AW concentrate with coating-removal solution was satisfactorily demonstrated; however, prior to the use of this procedure, the ease of separation of the aluminum from the fission products should be investigated since the fission products in the I-AW concentrate represent a potential source of radioisotopes.

4. RaLa PROCESS

MTR-RaLa Process Flowsheet. A tentative MTR-RaLa flowsheet for the extraction of radioactive barium from MTR fuel assemblies has been issued. The major steps in the process are:

1. Dissolution of the aluminum in $NaOH-NaNO_3$.
2. Neutralization of the sodium aluminate solution and acid dissolution of the uranium with sulfuric acid.
3. Separation of the insoluble barium sulfate by filtration.
4. Dissolution of the barium sulfate in Versene followed by an ion-exchange purification step.
5. Volume reduction and final purification by precipitation of barium nitrate from 85% nitric acid.
6. Evaporation of the final product to dryness for shipping.

This flowsheet is significantly different than the flowsheet presented in the last quarterly report (ORNL-1000, p. 34) in that Versene is to be used in place of nitric acid for dissolving the barium sulfate precipitate. Also, a fuming nitric acid precipitation step is incorporated in the process to effect the final separation of the barium from sodium. These two changes in the process flowsheet were effective in reducing the overall processing time from 48 to 26 hr and in eliminating the hydrochloric acid that was previously required for separating sodium from barium. The materials construction problem was greatly reduced by the elimination of hydrochloric acid. The Versene ion-exchange procedure was also more effective in separating barium from cerium and strontium. The design of the ORNL RaLa Pilot Plant was initiated on the basis of this flowsheet (Figs. 4.1 and 4.2).

Coprecipitation of Cerium and Barium Sulfate. It was found that 50 to 70% of the cerium activity was coprecipitated with the barium sulfate when the latter was precipitated from the aluminum—uranium sulfate dissolver solution. Three procedures were investigated to prevent the coprecipitation of cerium. The amount of cerium carried was reduced to 12% by lowering the aluminum molarity from 0.8 to 0.4. This was not considered significant in comparison to the large increase in volume and the longer filtration time that resulted.

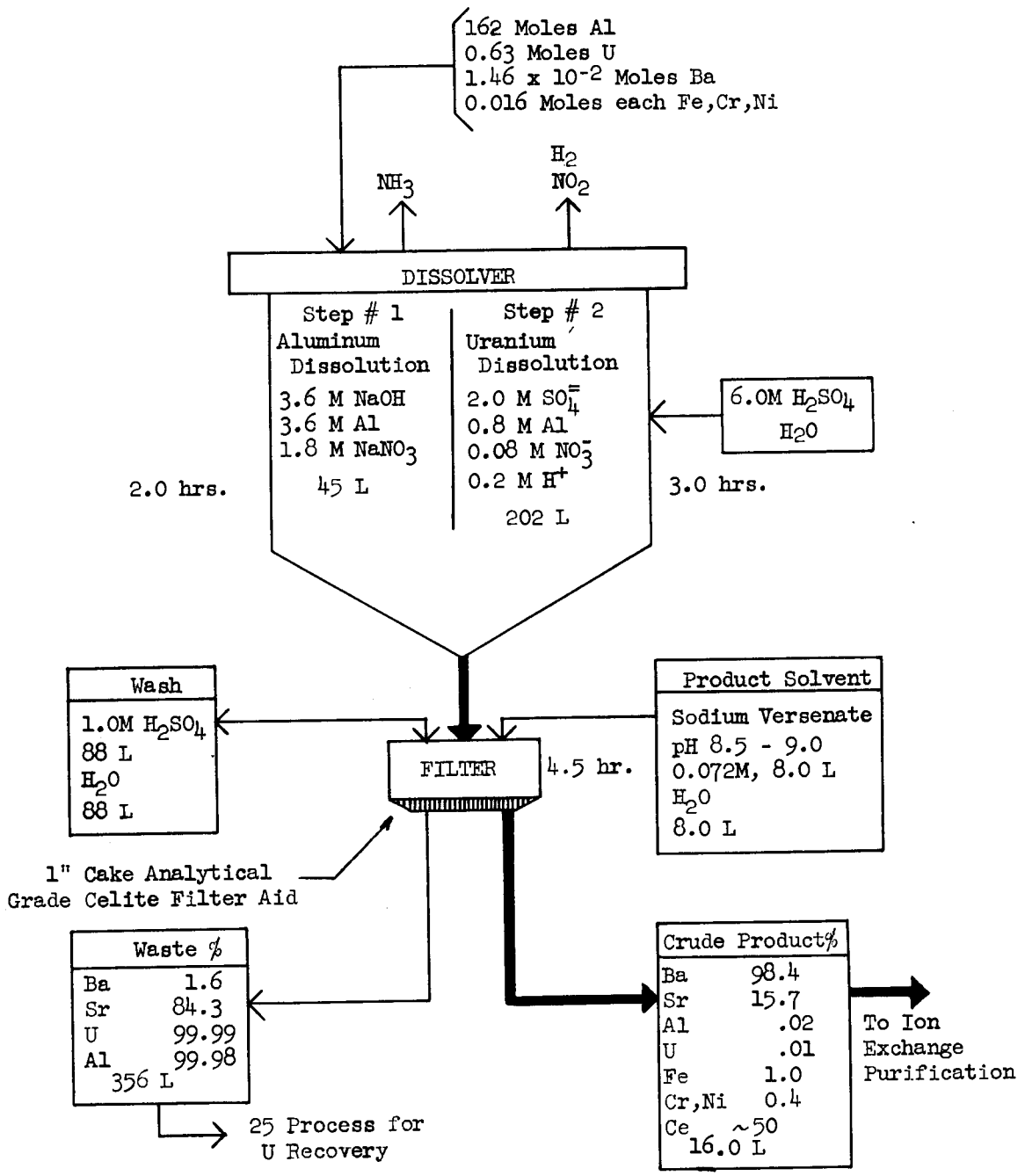
[redacted]

FIGURE 4.1

Drawing No. 11241
FLS-658

FLOWSHEET: MTR - RaLa PROCESS --PART I
(Over all process time 26 hours)
Full Scale: I MTR Assembly

CAUSTIC - SULFATE PROCESS



CHEM·TECH·DIV··LAB·SEC··JEF·5-14-51-6

[redacted]

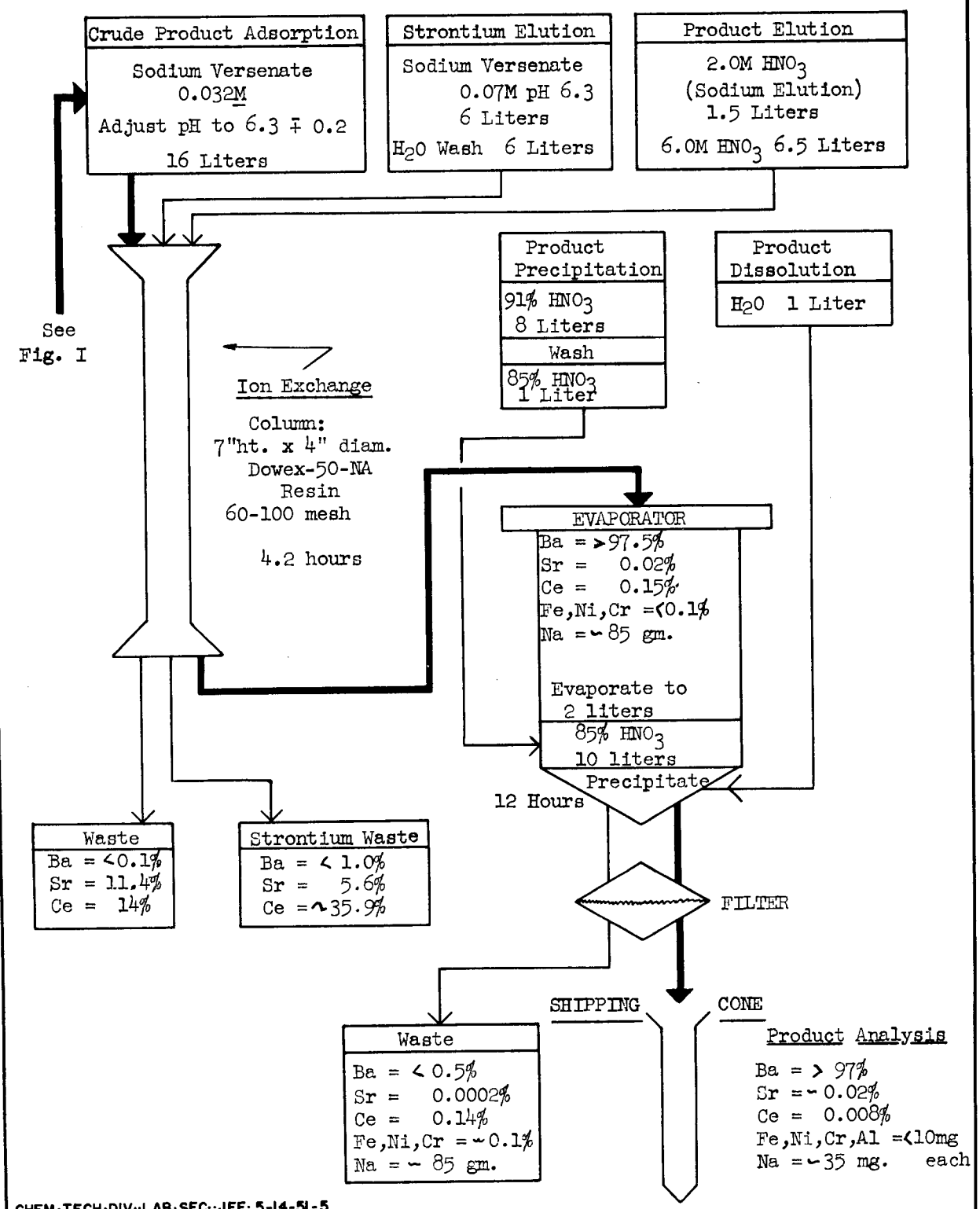
[redacted]

FIGURE 4.2

FLOWSHEET: MTR - RaLa PROCESS - PART II

Drawing #11242 FLS-658

PURIFICATION OF BARIUM BY THE VERSENE ION EXCHANGE PROCESS



CHEM·TECH·DIV··LAB·SEC··JEF· 5-14-51-5

[redacted]

An attempt was made to reduce the cerium and prevent its hydrolysis during precipitation by the addition of hydrogen peroxide with the sulfuric acid. This procedure lowered the cerium carried to 18%, which was considered to be insufficient. The barium sulfate cake was washed with sodium Versenate at a *p*H of 4 to 5 in an attempt to dissolve the cerium and leave the barium on the filter. Cerium is known to be more strongly complexed than barium under these conditions, but the results show that equal percentages of barium and cerium were dissolved, indicating that the two cations were coprecipitated.

Barium Sulfate Solubility in Nitric Acid. The solubility of barium sulfate was determined as a function of nitric acid concentration using radiobarium as a tracer. Barium sulfate solubility varied as a straight-line function from 0.03 g/liter in 0.1 *M* nitric acid to 0.33 g/liter in 4 *M* nitric acid (Fig. 4.3). In 6 *M* nitric acid, the solubility was greater than that indicated by a straight-line function.

Comparison of the Ion-Exchange Procedures for Barium Purification. The nitric acid ion-exchange process for barium purification was investigated in an attempt to eliminate *p*H determinations of hot feeds as required for the Versene process. However, it was found that the nitric acid procedure was not sufficiently effective in separating cerium from barium and that as many as three barium nitrate precipitations would be required to obtain the required product purity. The nitric acid procedure was then modified to allow the elution of the cerium and strontium by Versene, but this was not found to be a significant improvement. It was concluded that the determination of the *p*H required for the Versene procedure would be necessary to ensure minimum processing time and to obtain a product of satisfactory purity (Table 4.1).

Distribution Coefficient of Barium and Process Impurities in the Dowex-50—Nitric Acid System. The distribution coefficients, K_d, for barium, strontium, cerium, uranium, mercury, and aluminum were determined for the Dowex-50—HNO_3 system in an effort to determine the optimum conditions for the purification of barium by selective elution with HNO_3. The K_d's, defined as the mass per gram of oven-dried resin divided by the mass per milliliter of solution are shown in Fig. 4.4 as a function of the nitric acid concentration. It is seen that the best separations could be made at 0.1 *M* HNO_3, but, since the K_d's are so high at this concentration, the time needed for elution would be prohibitively

TABLE 4.1

Comparison of the Nitric Acid, Nitric Acid—Versene, and Versene MTR Ion-Exchange Processes

Basis: 1 assembly = 2 g of barium

PROCESS	COLUMN SIZE (in.)	ION EXCHANGE: COLUMN PRODUCT: VOLUME (liters)	ION EXCHANGE: COLUMN PRODUCT: (% of total) Ba	ION EXCHANGE: COLUMN PRODUCT: (% of total) Sr	ION EXCHANGE: COLUMN PRODUCT: (% of total) Ce	ION EXCHANGE: COLUMN PRODUCT: g of Na	ION EXCHANGE: TOTAL PROCESS TIME (hr)	ESTIMATED EVAPORATION TIME* (hr)	PRECIPITATION (85% HNO_3): NO. OF PRECIPITATIONS	PRECIPITATION (85% HNO_3): TOTAL TIME (hr)	SHIPPING CONE EVAPORATION (hr)	FINAL PRODUCT: (% of total) Ba	FINAL PRODUCT: (% of total) Sr	FINAL PRODUCT: (% of total) Ce	FINAL PRODUCT: g of Na	TOTAL TIME (hr)
Nitric acid	6 X 10	100	97	0.2	50	0	26 ± 2	10	3	3	10	95.5	0.19	0.006		49
Nitric acid—Versene	6 X 14	32	97	0.02	5	3.7	~17	3	2	2	10	96	0.02	0.01	<1	~32
Versene (requires pH adjustment of feed)	4 X 7	8	97	0.02	0.15	~85	4.2	1	1	1	10	96.5	0.02	0.008	<1	16.2

*Assuming that evaporation is not performed continuously as the solution leaves the column.

FIGURE 4.3

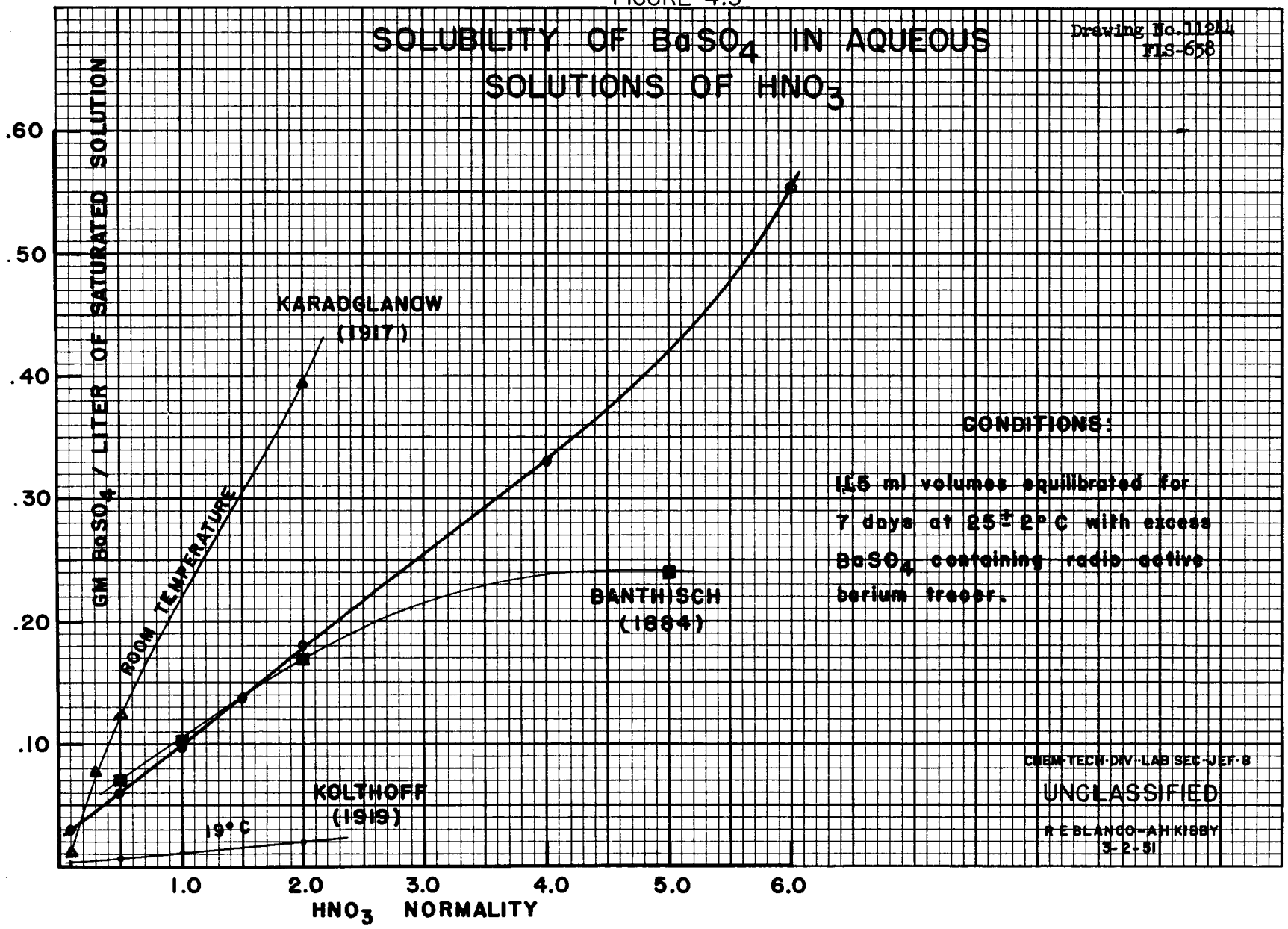
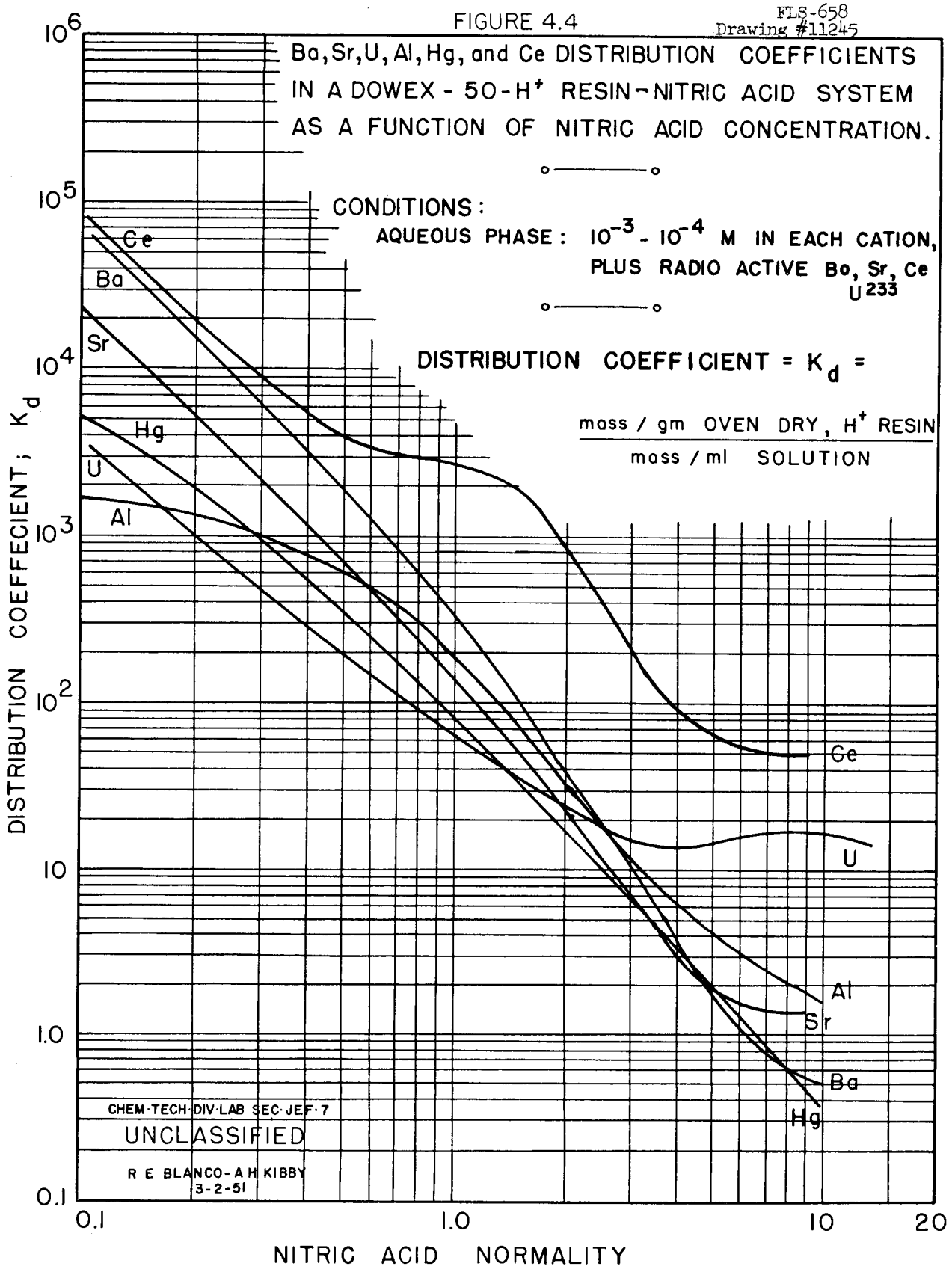

SOLUBILITY OF $BaSO_4$ IN AQUEOUS SOLUTIONS OF HNO_3
Drawing No. 11244
FLS-658
GM $BaSO_4$ / LITER OF SATURATED SOLUTION
.60
.50
.40
.30
.20
.10
KARAOGLANOW (1917)
ROOM TEMPERATURE
BANTHISCH (1884)
KOLTHOFF (1919)
19° C
CONDITIONS:
1.5 ml volumes equilibrated for 7 days at 25 ± 2° C with excess $BaSO_4$ containing radio active barium tracer.
CHEM-TECH-DIV-LAB SEC-JEF-8
UNCLASSIFIED
R E BLANCO-A H KIBBY
3-2-51
1.0
2.0
3.0
4.0
5.0
6.0
HNO_3 NORMALITY

FIGURE 4.4

FLS-658
Drawing #11245



long. The best separation conditions, a compromise between operating time and efficiency of separations, were determined by actual column runs as 1.5 *M* HNO_3.

Normally log-log plots of K_d vs. concentration of complexing agent are straight lines. The curves obtained are attributed to the formation of nitrate complexes at the higher concentrations and hydrolysis of some of the cations at the lower nitrate concentrations. An attempt will be made to calculate the $(BaNO_3)^+$ and $(SrNO_3)^+$ dissociation constants.

Comparison of Dowex-50 and XE-100 Cation-Exchange Resins. A new resin, XE-100, was evaluated for use in the RaLa process. The capacity of this new resin was equivalent to that of Dowex-50, namely 5.28 millequivalents per gram of oven-dried resin, but its cross-linkage was only 4% as compared to 12% for Dowex-50. Theoretically this should make possible a faster flow rate since the diffusion rate should be faster. However, column tests showed that the separation of barium and strontium was much poorer with XE-100 than with Dowex-50 at similar flow rates. In addition, low cross-linkage of the XE-100 resin allowed it to swell about 25% as it changed from the sodium to hydrogen form as compared to about 5% for Dowex-50.

Characteristics of the technical grade and the c.p. grade Dowex-50 were also compared. It was found that the barium-strontium separation efficiencies of these resins were not significantly different but that about 20% more of 1 *M* hydrochloric acid was required to elute sodium from the c.p. resin than from the technical grade.

Study of the Precipitation of Barium Nitrate from Fuming Nitric Acid. Precipitation of barium nitrate from fuming nitric acid was found to be effective for separating barium from sodium, cerium, iron, chromium, and nickel. As a result, this procedure is to be used in the MTR RaLa process and will replace the hydrochloric acid elution of sodium from the ion-exchange resin. This procedure was not effective for separating barium from strontium and lead. Barium loss in the 85% nitric acid precipitation was about 0.5% when the initial barium concentration was 0.2 g/liter. Strontium was quantitatively precipitated with the barium, and about 5% of the cerium remained with the barium. About 50% of the lead, when present in equal concentrations with barium, was carried. This study showed that the solubility of sodium in

80% nitric acid under these conditions was 14 to 16 g/liter vs. a theoretical 30 g/liter at 85% nitric acid (Table 4.2).

ORNL RaLa Process Modification Program. The ORNL RaLa Process Modification Program covers the development of a process, the modification of existing equipment, and the design and installation of new equipment in order to improve the yield and purity of the radioactive barium separated in this process from irradiated Hanford slugs. This process involves the following steps: metal dissolution, sulfate precipitation, carbonate metathesis, ion exchange, nitric acid precipitation, and final product evaporation. The modification program included the addition of filters for clarifying the metal solution, separation of the barium sulfate precipitate and the metathesis precipitate, installation of ion-exchange equipment, installation of a tantalum-lined vessel for the final barium nitrate precipitate, and installation of product charging facilities to accommodate the product carrier adopted by the customer. This program has now been completed and two runs have been made in the modified equipment. The first run, made through the plant at 1 to 5% of the expected process level of activity, indicated very satisfactory operation. In the second run, made at full-plant design activity level, there was similarly satisfactory operation through to the final ion-exchange elution step of the product. Owing to a valve failure, the product was run into the waste and it was necessary to reprocess this solution through the stand-by ion-exchange solution. During this operation approximately 75% of the product was lost. However, the equipment in the second ion-exchange cubicle operated satisfactorily. This program has been completed with the exception of minor modifications of the ion-exchange equipment to increase operability.

The major process question to be demonstrated in this plant is the effect of irradiation on the holdup of barium on the resin. These runs have indicated that the high-level radiation did not seriously affect the barium product yield or purity; however, the equipment failure prevented clear evaluation of the irradiation effects, and it will be necessary to wait until the next run in order to establish more firmly this situation. This run is now scheduled for sometime in August, 1951.

MTR RaLa Process Program. The MTR RaLa Process Program has as its objective the separation and decontamination of Ba^{140} from irradiated fuel assemblies. The work on the process chemistry is nearing completion in the

TABLE 4.2

Final Purification of Ba^{140} by Fuming Nitric Acid Precipitation

Simulated column products from ion-exchange step (full scale)

Runs 1 and 3

2.0 g of barium
0.02 g of strontium
153.5 g of sodium
no cerium carrier

Run 2

2.0 g of barium
0.02 g of strontium
0.1 g of cerium
no sodium

2.5 g of lead
0.8 g of nickel
0.8 g of chromium
1.5 g of iron

Precipitation conditions:

Run 1: 8.3 liters of 80% HNO_3; washed with 1 liter of 85% HNO_3
Run 2: 6.8 liters of 78% HNO_3; washed with 1 liter of 85% HNO_3
Run 3: 12.0 liters of 85% HNO_3; washed with 1 liter of 85% HNO_3

Product dissolution:

1.6 liters of H_2O

RUN NO.	PRODUCT ANALYSIS*												
	Ba	Sr	Ce	Fe		Ni		Cr		Pb		Na	
	(%)	(%)	(%)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)	(g)
1	~99.5	~98	~17									15.5	23.79
2	99.9	99.3	~4	<0.2	<3.0	<0.2	<1.6	<0.2	<1.6	~50	~1250		
3	99.6	95.2	5.8			<0.2	<1.6	<0.2	<1.6			0.02	0.033

*The % indicates percent of total.

laboratory, and work was started during the past quarter on the design of the pilot plant equipment and unit operations studies to support the design efforts. The schedule for this work is as follows: laboratory study, January to September, 1951; pilot plant design, May to December, 1951; pilot plant operation, March to September, 1950; plant design, January to June, 1952; plant start-up date, May, 1953.

The tentative chemical material balance flowsheet has been issued and a conceptional equipment flowsheet has been prepared. Flowsheets are also being prepared for evaluation of the heat balance, the activity level, and the off-gas system. It is planned to install this pilot plant in Cells 6 and 7 of Building 3019. The cell layout drawings are about 50% complete, and equipment design has been initiated on the dissolver, the fuming nitric acid precipitator, and the ion-exchange equipment. Work is now in progress in the Unit Operations Section to evaluate the ion-exchange column.

The Pilot Plant is being designed to operate on full-chemical scale and approximately 10% full-activity level. The equipment to be installed in the Pilot Plant will be, in all cases where it is possible, a full-scale prototype of the equipment to be installed in the Idaho plant, where the plant operation is scheduled to be carried out.

5. IDAHO CHEMICAL PLANT DESIGN

Effect of Initial Nitric Acid Concentration on Dissolution Rate of Aluminum — Laboratory Study. The optimum initial nitric acid concentration for rapid dissolution of 2S aluminum was found to be 7.5 to 8.0 *M*. In this laboratory study the molar ratio of the aluminum to mercury catalyst was held constant and oxygen was absent from the system. The initial acid concentration was varied from 2.3 to 11.4 *M* with a minimum solution time being obtained between 7.5 and 8.5 *M*. The effect of the initial acid concentration on the composition of the off-gas was also determined. The off-gas contained 30 to 40% NO, 30 to 40% N_2O, 20 to 25% N_2, 2 to 5% NO_2, and 0.5% H_2.

Dissolution of Uranium-Aluminum Alloy — Unit Operations Study. A procedure for nitric acid dissolution of 7.5% uranium—92.5% aluminum alloy slugs, 1.36 in. in diameter and 8 in. long, was desired in setting up the design of the Idaho Chemical Processing Plant. The ultimate goal was a procedure meeting as nearly as possible the following requirements:

1. Complete dissolution.
2. Dissolving time less than 20 hr.
3. Final dissolving solution 1.6 *M* in aluminum.
4. Final dissolving solution 0.2 *M* acid deficient.
5. Minimum amount of chemical additives.
6. Maximum acid economy.
7. Simple in operation and minimum equipment.

Working with these requirements in mind, the following four procedures were developed:

Procedure 1

Dissolving time, 10 hr
Dissolver temperature, 100 to 103°C
HNO_3, 3.6 moles per mole of alloy diluted to 4.75 *M* added at start,
0.4 mole per mole of alloy diluted to 4.0 *M* added at third hour
$Hg(NO_3)_2$, 5% of alloy weight
Condenser, downdraft
Reflux, 10 to 20% total volume per hour returned to dissolver
Oxygen, admitted to system between dissolver and condenser

Procedure 2

Dissolving time, 10 hr
Dissolver temperature, 100 to 103°C
HNO_3, 4.35 moles per mole of alloy diluted to 4.75 *M* added at start
$Hg(NO_3)_2$, 5% of alloy weight
Condenser, downdraft
Reflux, 10 to 20% of total volume per hour drawn off and collected for use as feed make-up; dissolver volume maintained constant by hot water addition
Oxygen, admitted to system between dissolver and condenser

Procedure 3

Dissolving time, 10 hr
Dissolver temperature, 100 to 103°C
HNO_3, 4.35 moles per mole diluted to 5 *M* and added at start
$Hg(NO_3)_2$, 5% of alloy weight
Condenser, updraft
Reflux, 10 to 20% of total volume per hour returned to dissolver
Oxygen, admitted to system between dissolver and condenser

Procedure 4 (extruded slugs)

Dissolving time, 4 hr
Dissolver temperature, 100 to 103°C
HNO_3, 4.0 moles per mole of alloy diluted to 4.25 *M* and added at start
$Hg(NO_3)_2$, 2% of alloy weight
Condenser, updraft
Reflux, 10 to 20% of total volume per hour returned to dissolver
Oxygen, none

Procedures 1, 2, and 3 were developed for cast slugs. All three procedures require the same dissolving time (10 hr), produce approximately the same completeness of dissolution (93 to 100%), and approximately the same final solution (1.2 *M* in aluminum and 0.8 to 1 *M* acid). All these procedures require the same amount of $Hg(NO_3)_2$ catalyst (5%); they differ only from the standpoints of acid economy and equipment requirements. Procedures 1 and 2 are favored over procedure 3 because of greater savings in acid economy (0.2 to 0.3 moles of H^+ per mole of alloy). Procedures 1 and 3 require the same amount of equipment, but procedure 2 requires an extra tank for storage of condensate. For these reasons procedure 1 is recommended for cast slugs.

Procedure 4 was developed for extruded slugs. It more nearly meets the criteria for a satisfactory procedure than any of the cast slug procedures.

The final solution concentrations are in the proper range (0.2 *M* acid deficient, 1.2 to 1.4 *M* in aluminum). The dissolvings are complete in 4 hr, and the procedure is operationally simple.

In developing the four afore-mentioned procedures, the following variables were investigated:

1. Dissolving characteristics of cast slugs as compared with those of extruded slugs.
2. Optimum initial acid normality.
3. Optimum acid-to-alloy mole ratio.
4. Chemicals needed other than nitric acid, and their concentrations.
5. Effects of downdraft condenser as compared with those of updraft.

In studies on the dissolving characteristics of slug types it was found that extruded slugs dissolved in 4 hr whereas cast slugs required 10 hr under optimum conditions. The extruded slug dissolution rate was very uniform throughout, but the cast slug surface developed deep pits and in all cases the center core of the slug was attacked first. This difference in dissolving characteristics is felt to be due to the crystalline structure of the slug.

It was found that the optimum initial HNO_3 concentration, 4 to 5 *M* acid, gave the most rapid dissolution. An optimum mole ratio of 4.0 moles of HNO_3 per mole of alloy was found for procedures 1 and 4. The optimum ratio for procedures 2 and 3 was 4.35 moles per mole.

Mercuric nitrate is necessary as a catalyst in the nitric acid dissolution of uranium-aluminum alloy slugs. It was found that 5% of the alloy weight as mercuric nitrate is the optimum amount for complete dissolution. Other chemicals suggested for breaking passive films produced little or no beneficial effects.

From the standpoint of acid economy, studies were made on characteristics of acid recovery of downdraft and updraft condensers. The downdraft condenser recovered 0.2 to 0.3 more moles of nitric acid per mole of alloy than did the same condenser connected as an updraft condenser. This increase in recovered acid is due to the fact that in a downdraft condenser there is countercurrent

cooling and cocurrent absorption, resulting in more efficient cooling, and the entire condenser surface is wetted wall, giving higher absorption surface and more time for oxidation of NO to NO_2 while still in contact with an absorbing surface. The updraft condenser uses cocurrent cooling and countercurrent absorption, condensing all the water vapor in the lower portion of the condenser.

EBR Slug Dissolving. A full-scale model of the Enriched Breeder Reactor (EBR) dissolver was built, and tests were initiated to determine its operating characteristics. The EBR slugs are approximately 0.36 in. in diameter and 1.8 in. long. The slugs contain about 58 g of uranium and are jacketed with about 3.7 g of aluminum. The small size of the EBR slug made it possible to design a 4-in.-diameter dissolver which could never become critical. The objective of this study was to determine the operating procedures required to yield a final solution containing 1.28 *M* uranium, 0.27 *M* aluminum, and 0.2 *M* acid-deficient solution and to determine the composition, rate, and total volume of gas evolved during the dissolution.

In the initial test it was found that it would not be possible to follow the operation of the dissolver by temperature or specific gravity because of the small size of the dissolver. Therefore the major variables to be studied were (1) the acid-to-metal ratio, and (2) the length of dissolving time. It is planned to dissolve the aluminum jacket along with the uranium metal and the procedure to be used will be as follows:

1. Eighteen slugs will be charged to the dissolver and the jackets removed with a 40% nitric acid solution containing 1% mercury (as mercuric nitrate) on the basis of the weight of the aluminum. The mole ratio of acid to aluminum will be 3.1.

2. Nine EBR slugs will be charged to the dissolver, and nitric acid with the mercuric nitrate catalyst required for the aluminum will be added. Each dissolving will be carried out so as to dissolve the jacket and nine uranium slugs, and in such a manner as to produce the desired final solution.

3. Nine jacketed EBR slugs are again charged to the dissolver and the operation is repeated.

The initial tests have indicated that approximately 3.5 moles of nitric acid is required to dissolve 1 mole of metal (Table 5.1). A dissolving time

TABLE 5.1

EBR Slug Dissolving

Dissolver: full-scale, subcritical, 4 in. i.d., 15½ in. high
Condenser: downdraft type, 1.3 sq ft in surface area
Dissolver steam chest pressure: 25 psig
Initial nitric acid concentration: 40% in jacket dissolution, 55% in regular dissolution
Reflux flow: 30 cc/min

RUN NO.	URANIUM (g)			ALUMINUM (g)			NITRIC ACID ADDED (moles)	DISSOLVING TIME (hr)	PERCENTAGE DISSOLVED		FINAL SOLUTION COMPOSITION (*M*)			NITRIC ACID / METAL DISSOLVED (mole/mole)[b]	GAS EVOLVED / METAL DISSOLVED (liters/mole)[b]
	REMAINING FROM PREVIOUS RUN	CHARGED	TOTAL AT BEGINNING OF RUN	REMAINING FROM PREVIOUS RUN	CHARGED	TOTAL AT BEGINNING OF RUN			URANIUM	ALUMINUM	$UO_2(NO_3)_2$	$Al(NO_3)_3$	HNO_3[a]		
6	0	513	513	0	33.5	33.5	4.0	2-2/6	14.0	88.1	0.28	0.93	+0.75	3.30	30.6[c,d]
7	435	518	953	4.0	33.3	37.3	-	2-1/6	6.2	43.5	0.24	0.59	-	-	38.1[d,e]
8	894	518	1412	21.1	32.0	53.1	10.9	1-2/6	21.1	41.6	0.48	0.53	+1.85	3.64	34.5
9	1166	519	1675	22.1	31.7	53.8	12.5	4-5/6	29.6	100	1.12	1.08	+0.30	3.50	40.9
10	1109	516	1705	0	33.4	33.4	11.7	6	26.0	100	1.02	0.68	-0.20	3.76	37.0[f]
11	1261	518	1779	0	33.0	33.0	15.1	6	36.8	100	1.55	0.69	-0.38	3.54	36.8[f]
12	1124	518	1642	0	33.8	33.8	12.2	5-2/6	30.1	100	1.06	0.64	+0.50	3.68	36.6
13	1148	518	1666	0	34.3	34.3	13.0	5-3/6	34.7	100	1.29	0.67	+0.50	3.51	34.9
14	1088	517	1605	0	33.6	33.6	12.2	6	32.7	100	1.30	0.74	+0.88	3.50	43.3
15	1080	519	1599	0	32.9	32.9	12.3	7	35.8	100	1.39	0.73	+0.95	3.34	41.2
16	1026	521	1547	0	32.9	32.9	11.8	6-3/6	35.2	100	1.34	0.72	+0.74	3.38	41.0
17	1003 598	0	1003	0	0	0	6.1	6	-	100	1.00	-	+3.00	3.59	53.7[g]

(*a*) (+) or (-) indicates excess H^+, or H^+ deficiency (OH^- excess).

(*b*) Metal dissolved = uranium + aluminum dissolved.

(*c*) Dissolver empty at beginning of run.

(*d*) Jacket dissolution run.

(*e*) Acid lost during run.

(*f*) Design change in reflux line made after this run.

(*g*) When examined after this run dissolver was found to be empty.

of 5 to 7 hr has not been sufficient to obtain the acid-deficient solution, and apparently the dissolving time will have to be increased.

Approximately 40 liters of gas was evolved per mole of metal dissolved. The maximum gas evolution rate (about 1.6 liters/min) occurred between 20 and 40 min after the run began.

The composition of the total gas evolved varied from 50 to 95% NO, 0 to 30% NO_2, 0 to 11% CO_2, 0 to 3% O_2, 0 to 9% N_2O, 0 to 1.6% CO, 0 to 5% H_2, and 2.5 to 28.6% N_2.

The work on this problem is to be continued.

Reduction of Nitrous Oxide. Nitrous oxide, N_2O, is not removed along with the NO and NO_2 by oxidation and water scrubbing. Nitrous oxide is more readily adsorbed than krypton or xenon, and it therefore interferes with their removal from the gas stream, and must be removed prior to the adsorption step. This is a particularly important operation for the Idaho Chemical Processing Plant because uranium-aluminum alloy dissolution produces larger quantities of nitrous oxide than dissolution of uranium metal.

Two procedures are now under consideration for the reduction of nitrous oxide. The first involves the reduction of the N_2O in a copper bed. When nitrous oxide is passed through a hot copper bed it is reduced, with the nitrogen gas passing through the bed and the oxygen reacting with the copper to form cuprous oxide. It was found that at 600°C the reduction rate was 7 times less than the same reaction carried out at 800°C. It was also found that at 800°C about 80% of the copper was converted to cuprous oxide before N_2O breakthrough, and that the N_2O was partially decomposed into nitrogen and oxygen gas and both gases passed through the bed.

The feasibility of decomposing the nitrous oxide on activated alumina was investigated with the idea that it might be possible to carry out this reaction at a lower temperature. However, the experiment was not successful. In a laboratory test carried out at 400°C at a rate of 45 cc/min 6 g of activated alumina reduced the N_2O content from 71.5 to 7% for a period of about 20 min. Greater reduction of the nitrous oxide concentration would be required, and it has been concluded that this procedure would not eliminate the use of a copper bed.

The second procedure involved the reduction of nitrous oxide in a hydrogen atmosphere with a palladium catalyst to initiate the reaction. Preliminary tests of a commercial unit known as the Pure Gas Oxidizer, model 30, have indicated that it is effective for the removal of N_2O and oxygen and that, if the concentration of N_2O is held below 10% of the total gas stream, no explosion will occur. The reaction is exothermic, and no heat has to be applied to the unit in order to initiate the reaction. The temperature at which the reaction takes place is a function of the reaction rate, and runs have been carried out successfully at 200 to 350°C. The study of this technique is to be continued to determine its effectiveness for other nitrogen oxides, the explosive limits of operation, and the effects of flow rate and bed depth on the efficiency of operation.

Design Study. Design for the Idaho Chemical Processing Plant for which the Oak Ridge National Laboratory is responsible was approximately 90% complete as of June 1, 1951. Major effort is now being expended on the preparation of accountability, analytical, criticality, operating, testing, and start-up manuals which will be required upon completion of construction of the plant at the Idaho Reactor Testing Station.

The overall design is approximately 80% complete, and construction by the Bechtel Corporation is approximately 30% complete. The scheduled completion date for the processing and laboratory buildings is January 1, 1952.

The following design work is now in progress at Oak Ridge National Laboratory:

1. Samplers for process solutions in the main process and waste process buildings.
2. First-cycle feed sampler for mass isotopic analysis of uranium; unit will decontaminate 200 ml of hot feed for the determination of the U^{235} to U^{238} ratio.
3. Mechanical and optical system for viewing fuel slugs and assemblies under water.
4. Bulk samplers for first-cycle raffinate.
5. Cooling system for final waste storage tank for first-cycle raffinate.
6. Clean-up system for removal of nitric and nitrous oxides, iodine, carbon dioxide, xenon, and krypton.

7. EBR charger-carrier and slug chute.

8. Product carriers for shipment of decontaminated uranium.

9. Arrangement and equipment for production storage vault.

10. Arrangement and equipment for chemical stock room.

11. Investigation of possibilities for installation of electrolytic decontamination facilities in chemical processing equipment.

A field engineering group, composed of Oak Ridge National Laboratory and Foster Wheeler personnel, is now being established at the chemical plant site. Approximately twenty Oak Ridge National Laboratory employees, representing all the skills required to follow construction, to test and accept equipment, and to assist in plant start-up, will be assigned to Idaho for periods of time varying from six months to one year.

6. VOLATILITY STUDY

Chlorination Reaction Rates. A study on chlorination was initiated during this period to determine the adaptability of chlorination procedures to ore and reactor product separation problems. One specific objective of this study is to develop a metal dissolution procedure that will be applicable to the new fuel materials, such as stainless steel and zirconium, which are not readily soluble in nitric acid. In addition, because chlorine is relatively cheap (2.7 to 3 cents per pound) chlorination methods may be useful in the recovery of uranium from ore. Some of the problems involved in this study are: (1) high chlorination temperatures are required with the attendant problem of materials of construction, (2) suitable methods for handling materials which sublime and condense to solids on walls are needed, (3) handling of solids after condensation is necessary, and (4) determination of the decontamination obtained by fractional distillation procedures.

In initial studies chlorination temperatures were determined for aluminum (500°C), 4% uranium-aluminum alloy (550 to 600°C), uranium metal (750 to 800°C), and Uravan ore (750 to 800°C). In all cases the reaction rate was rapid, and except with the Uravan ore only very small residues of unchlorinated materials were left in the reactor. The reactor for the test was made of high silica glass (Vitreosil) heated by an electric furnace.

This program is to be continued, studying the chlorination reaction of other reactor materials and ores and the separation of the chlorinated product.

Fluoride Study — Flowmeter Development. The fluoride program includes studies of the absorption and volatility characteristics of the source and fissionable materials as well as those of fission products. Owing to the chemically reactive nature of the fluoride compounds, much of the time has been spent in solving laboratory equipment problems, and during the past quarter the development of a flowmeter for metering the flows of liquid and gaseous UF_6 was the major problem. A thermo type flowmeter originally used at Y-12 had been adapted to this problem. Its design involved a *U*-shaped (1/8-in.) nickel tubing set in a heavy base of nickel stock, with an electric heater wound around the tube at the bend. By measuring the differential temperature produced by the combined effect of the heater and the liquid flow, the rate of flow is determined. The calibration of this meter for the UF_6

gas has been completed successfully, and its calibration with liquid UF_6 is now in progress.

During the coming quarter it is hoped to resume the adsorption and volatility study.

Electrolytic Fluorination of Uranium Metal. It is desirable to establish a procedure for converting uranium metal to UF_6 electrolytically. Previous studies using a KF-2HF electrolyte were not successful, and during the past quarter a liquid hydrogen fluoride electrolyte solution was evaluated. In this case a relatively insoluble UF_4 sludge was produced, and it was necessary to add about 0.1 *M* LiF to the liquid HF bath in order to obtain sufficient conductivity in the solution at the anode to carry out this reaction.

These studies are to be continued to determine the effect of eliminating various impurities now present in these electrolyte solutions.

7. RADIOCHEMICAL WASTE TREATMENT

Cottrell Electrostatic Precipitator. The Cottrell electrostatic precipitator installed on the off-gas system from the iodine production unit at ORNL was previously reported to have a decontamination efficiency of about 80% for this gas. This efficiency was determined by filtering samples of air before and after the precipitators through CWS No. 6 paper. These results have not reflected the precipitator efficiency for particle removal owing to the fact that gaseous iodine is adsorbed on CWS No. 6 paper.

The gas stream before and after the Cottrell precipitator was then evaluated using a cascade impactor. It was found that relatively complete removal (more than 99.9%) of the solid particulate matter was effected.

The CWS No. 6 filters before and after the precipitator are continuing to be used; however, instead of direct counting of these filters, they are being examined radioautographically and radiochemically. By the radioautograph procedure the number of radioactive particles is determined, and the filter is then chemically leached and the radioactivity of the solution is determined. Activities other than iodine may be assumed to be particulate matter and their concentrations determined in this fashion.

The Cottrell electrostatic precipitator serves the RaLa production unit as well as the iodine production unit, and this evaluation technique is to be applied to the Cottrell precipitator during the next RaLa run scheduled for the coming quarter.

8. ELECTROCHEMICAL STUDIES

Electrolux Process Development Study. "Electrolux" is the name that has been selected for the separation process involving electrolytic techniques for the separation of uranium, plutonium, and fission products from reactor fuel. This process is similar in many respects to that earlier developed at K-25 and reported in K-601. However, the purpose of the original process was to recover the uranium from the Hanford metal waste. Laboratory equipment has now been set up to demonstrate and evaluate the Electrolux process on a 200-g scale.

The following steps are included in the Electrolux Process:

1. Electrolytic dissolution of uranium in sodium bicarbonate solution.
2. Plutonium and rare earth precipitation in an acid-base cell.
3. Electrodeposition of ruthenium.
4. Adsorption of fission products on fuller's earth.
5. Uranium precipitation in an acid-base cell.
6. Uranium reduction in UF_4 precipitation.

A run using a section of an ORNL slug which had been irradiated 399 days and cooled 150 days has been started and is to be continued.

9. HOMOGENEOUS REACTOR CHEMISTRY

Uranium Trioxide—Bentonite Slurry. Neutron irradiation of the uranium trioxide—bentonite slurry was demonstrated to have no significant effect on the stability of this slurry. In this test, 12 samples were irradiated for one week at a neutron flux of 5×10^{11} and at a temperature of 250°C. Control samples were heated for one week at 250°C. Excellent agreement of the settled volume of the duplicate samples was found after these samples had settled for a period of three weeks at room temperature (Table 9.1).

It was indicated by electron-microscope study that a major function of the bentonite in the slurry was to reduce the growth of the uranium trioxide crystal.

Preparation of Uranium Peroxide. The uranium trioxide for these slurry studies has always been prepared by decomposing uranium peroxide, $UO_4 \cdot 2H_2O$. Therefore an investigation was started to study the effect of variations in the preparation of uranium peroxide on the final form of UO_3, with the object of obtaining uniform particle size of the uranium trioxide. Under these conditions, particle growth would be expected to be minimized.

The procedure involved in the preparation of uranium peroxide involved the dropwise addition of peroxide solution to uranyl nitrate solution. By varying the direction of addition, the temperature, the *p*H, and the additive to the solution, it is hoped that the means of obtaining a uniform product will be found. The studies will be continued.

Thorium Oxide—Bentonite Slurry. Thorium oxide slurries containing 1000 g of thorium per liter and about 1 wt % fractionated bentonite have been demonstrated to be stable at 250°C for periods of at least two weeks with no appreciable change in properties. These slurries have also been irradiated at a neutron flux of about 5×10^{11} for periods up to one week at 100°C without evidence of radiation decomposition. These tests were carried out in sealed quartz tubes. Similar tests in a stainless steel autoclave under strong agitation have always resulted in the deposition of the bentonite on the walls of the container and the resulting failure of the slurry. The cause of the deposition is unknown; the bentonite is apparently unaltered chemically and may be readily reslurried with the thorium to give the stable slurries at room temperature.

TABLE 9.1

Preliminary Experiments on Irradiation of Natural Uranium Trioxide—Water Slurries at 250°C

Slurry composition:

Uranium (natural), 40 g as anhydrous UO_3

Bentonite, 1000 ml of a suspension of 13 g of dialyzed bentonite solids, average particle size below 25 mμ

Experimental conditions:

Heating, 250°C for one week

Irradiation, in hole 12 of ORNL reactor (neutron flux approximately 5×10^{11})

Settling time, three weeks at room temperature

Experiments carried out in 4-mm-i.d. sealed quartz tubes in duplicate

OXIDE	RATIO OF SETTLED SOLIDS VOLUME TO TOTAL SLURRY VOLUME	
	HEATED-ONLY SLURRY (control)	HEATED AND IRRADIATED SLURRY
H: anhydrous UO_3 (Harshaw) prepared by decomposing $UO_2(NO_3)_2$; appeared to contain some undecomposed $UO_2(NO_3)_2$	0.63 0.67	0.69 0.69
M: anhydrous UO_3 from decomposed $UO_4 \cdot 2H_2O$ prepared by adding 30% H_2O_2 (excess) to a $UO_2(NO_3)_2$ solution at *p*H 2.5 (this type of oxide was used in all previously reported results)	0.81 0.85	0.83 0.99
E: anhydrous UO_3 from decomposed $UO_4 \cdot 2H_2O$ prepared by adding $UO_2(NO_3)_2$ solution dropwise to excess 3% H_2O_2; both solutions being 0.1 *M* in free HNO_3	0.70 0.80	0.69 0.75

As in the case of the uranium oxide slurry, the amount of bentonite required is a function of the particle size. Twenty-five millimicron bentonite material requires only about 1 wt % to yield a stable slurry. However, with naturally occurring bentonite, with a particle range of 10 to 25 μ, nearly three times as much bentonite was required. Reducing the size of thorium oxide particles also decreases the amount of bentonite required. However, no appreciable damage was observed using thorium particle sizes smaller than 1 μ.

The deleterious effect of iron on bentonite-stabilized thorium slurries was noted, but attempts to remove the iron were unsuccessful. Electrodialysis and ion exchange removed ionic iron, or iron that was readily replaced with hydrogen ion, but this represented a small percentage of the total amount of iron. During the size fractionation of the bentonite it was observed that most of the iron was eliminated with the heavy fractions of bentonite. Iron could also be completely hydrolyzed in an autoclave at 250°C after 48 hr. However, the iron was intimately mixed with the bentonite, and no separation could be accomplished without chemically altering the bentonite.

The viscosities of the thorium oxide—bentonite slurries range from 500 to 4000 centipoises at varying rates of shear.

Thorium Oxide Slurry. Preliminary tests indicated that a thorium oxide slurry with a particle size of 0.1 to 0.5 μ may be sufficiently stable to eliminate the need for a stabilizing agent. Also, the viscosity of this slurry was considerably lower than that for a thorium oxide—bentonite stabilized slurry.

The viscosity and settling were determined at a concentration of 1000 g of thorium per liter as the oxide. Viscosity was measured by means of a model LVS Whitfield viscometer. At 6 rpm the viscosity was 1200 to 1400 centipoises, while at 60 rpm the viscosity was 140 to 150 centipoises. The finely divided thorium oxide was very surface-active, tending to form loosely bound agglomerates. However, after standing for periods as long as one month the material was easily redispersed.

A small project is underway to investigate certain of the naturally occurring silicates as antipacking agents. The crysotile variety looks promising. Such low neutron cross-section materials do not act as dispersing agents but merely prevent packing in the event of slurries allowed to stand for a long period of time without agitation.

Fuel Recovery Process for the HRE. The fuel for the HRE is essentially an aqueous solution of uranyl sulfate. The uranium is primarily U^{235}, and, therefore, no significant amount of plutonium is produced during reactor irradiation. The major objective of the fuel recovery process for the HRE is the separation of uranium from fission products. It is probable that after the uranium has been used as fuel in the HRE it will be returned to production channels and not sent back through the reactor. This will limit the build-up of undesirable uranium isotopes.

The most direct method for the recovery of the uranium from the HRE fuel will be by a Purex type solvent-extraction process. The preparation of the reactor fuel for recovery will involve only the addition of nitric acid. It is probable that existing facilities at ORNL may be used for recovery of this fuel.

An alternate procedure involving filtration, ion exchange, and electrolysis has been studied on a laboratory scale. The outstanding advantages of this process over the solvent-extraction process are (1) it is not necessary to add other chemicals such as nitric acid to the fuel solution itself, and (2) the fuel inventory would be significantly reduced. By this process the fuel could be returned directly to the reactor without requiring further chemical conversion. This procedure could be used for the semicontinuous processing of the fuel from the reactor. The process was demonstrated on a laboratory scale to give decontamination factors of about 90 for rare earths, barium, and iodine, about 70 for samarium and strontium, 55 for ruthenium, 43 for molybdenum, and 18 for cesium, with a uranium loss of approximately 0.2%. The feed solution for this study was a normal uranyl sulfate solution that had been irradiated for two days in the X reactor and cooled for one day. The solution was then spiked to simulate the concentration of fission products expected after one day irradiation in the HRE (Table 9.2).

The tentative ion-exchange flowsheet for the HRE process (Fig. 9.1) was based on the assumption that 5% of the fuel from the reactor will be withdrawn each day and that this will be held up for one day for cooling. After the irradiation the solution was filtered through Celite filter aid, and significant removal of barium, ruthenium, iodine, tellurium, and molybdenum was obtained. The solution was then passed through a hydrogen form of a cation-exchange resin (Dowex-50). The capacity of the resin bed is such that only about 5%

TABLE 9.2

Decontamination of HRE Fuel

Fuel: 3.3 liters of UO_2SO_4 solution containing 40 g of uranium per liter, total of 132 g of uranium (4.7% of total in HRE)

Activity: 1 g of UO_2SO_4; 40 hr in X pile; cooled 1 day

Dead fission products: 1 day's production of rare earths, strontium, cesium, barium, ruthenium, iodine, tellurium, and molybdenum, and 10 days' production of zirconium (assuming 1 g of U^{235} burn-up per day)

Procedure:

1. Filter: ½-in. analytical grade Celite
2. Ion-exchange column: Dowex-50, 1 by 4.4 in. (50 ml); adsorption time, 1 hr
3. Ion-exchange uranium holdup elution: 0.05 *M* $CuSO_4$, 1400 ml; elution time, 6 hr
4. Electrolysis:
   - *A*, 100 ml of effluent from step 2, copper cathode, lead-silver anode, 0.2 amp for 1 hr
   - *B*, 100 ml of effluent from 1400 ml of step 3, copper cathode, platinum anode

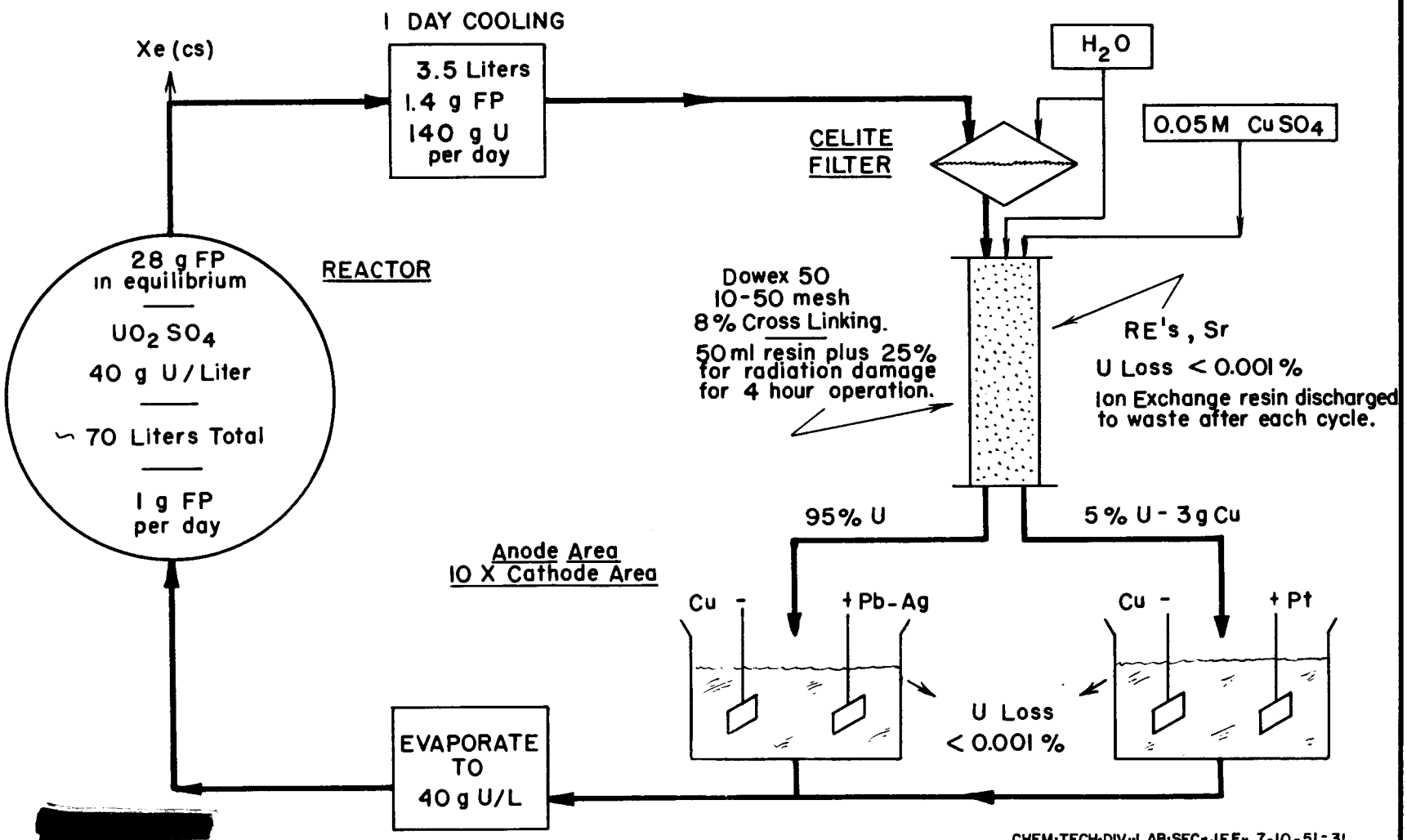
STEP	FISSION PRODUCTS REMOVED (%)								URANIUM HOLDUP (mg)
	RARE EARTHS	Sr	Cs	Ba	Ru	I	Te	Mo	
1				90	24	30	76	14	
2	93	69							4650 (full scale)
3									202 (full scale)
4					21	59	6	29	0.99 (1/30 scale)
Total	93	69	0	90	45	89	82	43	

FIGURE 9.1

[redacted]

DWG No 11694

PROCESS FOR CONTINUOUS FISSION PRODUCT REMOVAL FROM THE HRE



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of the uranium is held on the bed at uranium saturation. Therefore, only those fission products more strongly adsorbed than uranium are held up on the ion-exchange bed, and under these conditions rare earths and strontium are separated from the uranium. The uranium is eluted from the resin bed by a copper sulfate solution. The electrolysis of the uranium fuel solution effluent using a copper cathode and a compound anode of lead and silver effected the partial removal of ruthenium, iodine, and samarium on the anode, while ruthenium and molybdenum were plated out on the cathode. The uranium elutriant was electrolyzed to remove copper from the solution, using a platinum anode and a copper cathode. The product solution from the two electrolyses were then combined and evaporated to the desired feed concentration.

No further work is planned on a fuel-recovery process for the HRE at the present time because it has been requested that the laboratory program emphasize the development of a process for a plutonium converter type homogeneous reactor.

Fuel Recovery for a Plutonium-Producer Homogeneous Reactor. Fuel for the plutonium-producer homogeneous reactor now under consideration is a uranyl sulfate solution. In this reactor, normal uranium is used as the fuel, and the objective of the recovery process is the separation of the plutonium, uranium, and fission products. The choice of the process to be used is largely dependent upon whether the uranium is to be returned directly to the reactor or if it is to be sent back through an isotopic enrichment prior to its return to the reactor. This is dependent upon whether it is cheaper to send it to the isotopic enrichment plant, and then return the product to the reactor, or to take highly enriched U^{235} and spike it to the depleted fuel solution for return to the reactor. This problem is now being evaluated by the Long Range Reactor Group.

If the uranium is to be returned to the isotopic enrichment plant, then the most direct procedure, as in the case of the HRE, is to use a modified Purex type solvent-extraction process. The operability of this process is now well established, and little development work will be required.

The major development work is now concerned with development of an ion-exchange procedure for the extraction of plutonium and fission products from the uranyl sulfate solution. The advantages of this process are, first, that chemical conversion of the fuel would not be required for processing or its

return to the reactor and, second, that the inventory of fuel for the reactor would be minimized. The future laboratory program will consider two processes: (1) a cation-exchange process for the removal of zirconium, rare earths, and strontium, and (2) fuller's earth adsorption for the removal of zirconium and cesium, followed by an anion exchange for the removal of molybdenum, iodine, samarium, and ruthenium. The first process would be used at more frequent intervals than the second in order to limit the conversion of the plutonium to its higher isotope. For both these processes the resin column would be designed to contain about 5% of the uranium at saturation. It is proposed then to elute the column with nitric acid and pass this elutriant through a Purex type solvent-extraction process for the separation of plutonium and uranium from the fission products.

10. SOLVENT EXTRACTION STUDY — CENTRIFUGAL CONTACTOR EVALUATION

The Pup model of the Podbielniak centrifugal contactor is now being evaluated to compare its operability with other solvent-extraction contactors such as the packed column, pulse column, and mixer settlers. The centrifugal contactor has three major advantages over the others:

1. Compactness. A 700-gal/hr unit occupies a space of about 4 by 4 by 3½ ft.
2. Smaller density differential. It is reported that the required density differential between liquid phases may be on the order of 0.02.
3. Small solution holdup. Only about 5 to 10 gal is held up in the rotor of a 700-gal/hr unit.

The major disadvantage of this unit is the high speed of the rotor and the necessity for maintaining mechanical seals on the shaft. The Podbielniak Pup model has a rotor 17 in. in diameter and about 2 in. deep which rotates at a speed of about 5000 rpm. The maximum flow capacity of this unit is about 500 ml/min.

The Purex I-C column process conditions were used for the preliminary evaluation of the Pup. By changing the continuous phase from aqueous to organic, the uranium loss was decreased from 9.3 to 5.3%. Increasing the flow rate from 200 to 400 ml/min increased the uranium loss from 2.9 to 7.6%, and when the extraction temperature was increased from 20 to 60°C, the uranium loss was decreased from 5.3 to 0.3% (Table 10.1).

TABLE 10.1

Podbielniak Pup Test with Purex I-C Feeds

Aqueous feed: 3 volumes of demineralized water

Organic feed: 2 volumes of 30% TBP, 70 mg of uranium per milliliter, 0.04 *M* HNO_3

TOTAL FLOW RATE (ml/min)	CONTINUOUS PHASE	TEMPERATURE (°C)	URANIUM CONCENTRATION IN ORGANIC RAFFINATE	
			(mg/ml)	(%)
250	Aqueous	20	6.5	9.3
250	Organic	20	3.7	5.3
200	Organic	20	2.9	4.1
260	Organic	20	3.7	5.3
300	Organic	20	5.2	7.4
400	Organic	20	7.6	10.9
250	Organic	20	3.7	5.3
250	Organic	60	0.2	0.3

11. CHALK RIVER MATERIAL — PLUTONIUM RECOVERY FROM THE ISOLATION PROCESS WASTE

Approximately 10% of the plutonium from the Chalk River material was contained in the raffinate from the methyl isobutyl ketone solvent extraction that was used for its isolation. These raffinates were reworked using a tributyl phosphate solvent-extraction procedure followed by ion exchange, and approximately 98% of the plutonium was recovered, reducing the isolation loss to 0.2%. The uranium and plutonium were extracted with 15% tributyl phosphate to separate it from aluminum, iron, and chromium with a plutonium loss of 1 to 3%. Extraction was carried out in a ½-in.-diameter pulse column with a 32-in. extraction section and an 8-in. scrub section. The scrub section, in which a 1 *M* nitric acid solution was used, was very effective in removing iron and chromium. The final concentration of the iron and chromium in the plutonium-uranium strip product was reduced to 1 and 5 parts per million, respectively. The plutonium loss was due to an inadequate number of extraction stages. The plutonium was separated from the uranium by reducing the plutonium to the trivalent state, adsorbing it on a Dowex-50 cation-exchange resin bed, eluting the uranium with 0.25 *M* sulfuric acid, and finally eluting the plutonium with 6 *M* nitric acid. The plutonium loss in the ion-exchange step was approximately 0.1%.

In preliminary studies the distribution coefficient for plutonium(III), plutonium(IV), and uranyl ion were determined in a 0.25 *M* nitric acid solution to be 4.3×10^3, 2.6×10^4, and 1×10^2, respectively (Dowex-50 resin:solution). While plutonium(IV) was more strongly adsorbed than plutonium(III), indicating a better separation from uranyl ion, it was found that plutonium(IV) polymerized and disproportionated, and high plutonium losses resulted during uranium elution. With plutonium in the trivalent state, it was found that the plutonium losses during adsorption and uranium elution were on the order of 3×10^{-4}%. It was found that 40 to 50 column volume changes were required to remove 99% of the uranium with 0.25 *M* sulfuric acid. At the completion of the uranium elution the plutonium band occupied about 110% of its original volume.

About 35 column volumes of 6 *M* nitric acid were required to elute 99% of the plutonium from the resin bed. During plutonium elution a vigorous evolution

of gas was observed owing to rapid oxidation of plutonium(III) to plutonium(IV) by nitric acid. This gas evolution effectively blocked the column for downflow operation. Upflow plutonium elution corrected this situation and also increased the maximum product concentration from 10 g/liter for downflow to 130 g/liter for upflow conditions.

To avoid gas evolution during plutonium elution 3 *M* sulfuric acid was investigated since plutonium sulfate is not oxidized as rapidly as plutonium nitrate. This was successful in eliminating gas evolution, but the maximum plutonium concentration in the product eluate was only 34 g/liter. However, the major drawback was that the product volume reduction could not be carried out by evaporation, and plutonium sulfate precipitation in 11.35 *M* sulfuric acid and 20% ethyl alcohol was required. Under these conditions, at 10°C the solubility of plutonium sulfate was 0.12 g/liter.

Amberlite XE-100, a cation-exchange resin, was considered as an alternate to Dowex-50 for this process. However, the capacity of the XE-100 was considerably lower than that of Dowex-50 (1.6 vs. 2.3 equivalents) and is no longer being considered.

Development work on the ion-exchange procedure for plutonium isolation is continuing for possible application to the product solution from the Purex process.

12. SPECIAL EQUIPMENT STUDY

Concrete Penetration Test. Past experience has demonstrated that concrete is easily penetrated by liquid-borne radioactivity and is subsequently difficult to decontaminate. A study is therefore being initiated to determine qualitatively the extent to which concrete is penetrated by liquid-borne activity and to define the factors controlling such penetration. This program will be carried out with the cooperation of the Research and Development Division of the Portland Cement Association. The Portland Cement Association will furnish standard concrete specimens needed for tests covering variables such as water to cement ratios, specific surface of aggregates to paste ratios, curing time, and surface finishes. These samples, with dimensions of approximately 2½ by 2½ by 1½ in., will be contaminated under standard conditions and then sectioned by sawing with a diamond-tipped saw blade cooled by liquid nitrogen. Distribution of the radioactivity will be determined by radioautograph or other means to be developed.

Radiation Damage Studies. Radiation studies are now being carried out using a Co^{60} gamma source. The specific source being used in the ORNL work has an intensity of about 10^4 r/min of 1.2-Mev gamma radiation. The samples being tested are inspected visually and by standard physical tests such as specific gravity, tensile strength, shear strength, elongation, breaking energy, water adsorption, and Rockwell hardness. The radiation limit for polythene and polystyrene plastics was found to exceed 10^9 r. With Teflon 10^7 r seemed to be the maximum radiation adsorbed without serious damage. Silicone and Hycar rubber gasket material had a radiation limit of about 10^6 r (Table 12.1). This study is being continued on surface coatings and other plastic and rubber materials.

Tubing Connector Test. Tubing connectors for stainless steel tubing are being tested to determine their leak tightness vs. their ease of assembling. Under the present test conditions they are assembled and filled with a 1.5 *M* aluminum nitrate solution, air pressure (80 psi) is applied for 4 min and then turned off for 1 min, and the number of cycles on the setup is recorded.

From preliminary results, it appears that Parker Triple-lok tube fittings are the most satisfactory. It is important to secure proper flares, and a

TABLE 12.1

Physical Properties of Hycar and Silicone Rubber After Irradiation by the ORNL Co^{60} Gamma Source at Various Intensities

MATERIAL TESTED	SHORE HARDNESS					TENSILE STRENGTH (psi)					ELONGATION (%)				
	0 r	10^4 r	10^6 r	10^7 r	10^8 r	0 r	10^4 r	10^6 r	10^7 r	10^8 r	0 r	10^4 r	10^6 r	10^7 r	10^8 r
Hycar 520-9-41-2	71	70	73	72	80	1357	1288	1327	1330	808	190	155	150	135	50
Hycar 1004	72	77	78	81	92	2225	1877	2420	2589	1631	235	230	255	208	35
Silicone 13004	62	65	66	74	95	277	245	260	282	151	58	50	62	25	5
Silicone 13006	84	84	85	87	96	555	540		528	135	36	36		25	25

special field flaring tool was set up which included the standard type of punch and anvil operated by a small hydraulic cylinder. This has been demonstrated to give much more satisfactory flares, and the results of the work are to be discussed with the Parker Company.

The other type fittings to be tested are the Koncentrik, the Swagelok, and the Walseal. The Koncentrik fitting is a flared type fitting similar to the Parker which incorporates Teflon gaskets to compensate for poor flares. The use of a Teflon seal is not particularly attractive because of its cold flow characteristic and because of its low radiation-damage level. It was difficult to obtain a leak-tight system with Swagelok fittings, but when these leaks were stopped by further tightening of the connectors, a total of almost 9000 air surges were applied with no leaks developing. It was found that when using the Swagelok fitting the tube should be drawn back approximately 1/16 to 1/8 in. from the shoulder of the connector before finally setting the ferrule. In this way a leak-tight fitting could be fairly assured. The Walseal coupling is a sweat type coupling which was found to be highly vulnerable to acid corrosive attack when a silver brazing alloy was employed to make the joint.

Test of Coated Ducts. Coated ducts (about 12 in. i.d.) are being investigated to find a satisfactory substitute for stainless steel for radioactive off-gas duct-work systems. Two steel sections painted with Amercoat-44 and Amercoat-55 and two plastic-lined concrete sections using Amerplate T-lock 92Y (vinyl) and polyethylene T-lock appeared unchanged except for a slight ballooning inward of the plastic lining which was noted when it was inspected after three months of service in an off-gas system carrying acidic fumes at a negative pressure of 40 in. of water; at the end of two months additional service no further damage has appeared evident.

Surface Evaluation for the ORNL General Purpose Hood. The surface coatings to be applied to the structure of the ORNL general purpose hood were evaluated on the basis of chemical attack and decontamination. After examination of the baked enamel samples submitted by various hood manufacturers, the coatings submitted by the Laboratory Furniture Company was recommended. The Kewaunee coating was a second choice, but its resistance to methyl isobutyl ketone was very poor. The coatings submitted by Sheldon and Browne-Morse were not recommended for this use.

Decontamination of Stainless Steel by Electrostripping. Previous work has shown that electrostripping was very effective for the removal of radioactivity from stainless steel surfaces and that both electrolytic and electropolishing techniques were effective. It has now been concluded that the electropolishing technique is limited to relatively small surfaces because of the fact that a minimum of 0.1 amp/sq in. is required for effective decontamination, whereas larger surface areas may be decontaminated using electrolytic techniques at current densities as low as 0.01 amp/sq in.

In general, the electrolytic technique employing a 2% sulfuric acid electrolyte may be the preferred procedure. With this solution it was found that the decontamination of 347 stainless steel is not affected by temperature or surface roughness; that the corrosion rate without applied current was negligible; that at 0.01 amp/sq in. metal loss was less than 0.4 mil per 1000 coulombs per square inch; that the current throwing power to a hidden surface was approximately 85%; and that by the use of a stainless steel cathode instead of copper only about 1% of the activity was deposited on the cathode.

13. LIST OF REPORTS PUBLISHED DURING PERIOD FEBRUARY 10 TO MAY 10, 1951

DOCUMENT NO.	TITLE	AUTHOR	DATE
	SCRUP		
CF-51-2-49	Visit to Chalk River, Ontario, Feb. 2, 1951	H. K. Jackson E. C. Stewart	2/12/51
ORNL-880	Summary Report of ORNL Pilot Plant Program for the Recovery of Plutonium from Chalk River and Hanford Fuel Rods	A. T. Gresky N. J. Rigstad	3/21/51
CF-51-3-96	Program and Budget Assumptions for SCRUP	C. W. Schersten	3/29/51
	PUREX		
CF-51-2-93	Revised Pilot Plant Program	H. K. Jackson	2/19/51
CF-51-2-145	Solvent Extraction Chemistry of TBP	T. C. Runion	2/28/51
CF-51-2-124	Rare Gas Adsorption Project	J. O. Davis	2/23/51
ORNL-962	Chemical Technology Pilot Plant Report, November, 1950 to January, 1951	H. K. Jackson	3/8/51
CF-51-3-40	Informal Progress Report for the Pilot Plant Section	H. K. Jackson	3/13/51
CF-51-4-2	The Effect on Decontamination of Acidifying the Solvent in the Purex IA Column	W. B. Lanham	4/2/51
CF-51-5-69	Run 11HP-3 Summary (Includes 11HP-3A)	J. W. Ullmann	5/10/51
CF-51-5-87	Progress Report for Pilot Plant Section	H. K. Jackson	5/10/51
	IDAHO CHEMICAL PROCESSING PLANT		
CF-51-2-153	Meeting on Criticality Conditions in the Idaho Chemical Processing Plant, 2/26/51	R. J. Klotzbach	2/28/51
CF-51-3-88	Chemical Processing Plant Samples	A. M. Rom	3/20/51
CF-51-3-106	Information on the Idaho Chemical Processing Plant	F. L. Culler	3/30/51
CF-51-4-69	Vacuum Regeneration of Adsorbers	S. H. Jury	4/16/51
CF-51-4-107	EBR Material for Chemical Processing Plant	F. L. Culler	4/23/51
CF-51-4-112	Notes on Conference with ANL on STR Chemical Processing	H. A. Ohlgren	4/23/51
CF-51-5-35	Production of Kilocurie Quantities of Fission Products from Idaho Chemical Processing Plant Wastes	F. L. Culler	5/7/51
	RaLa		
CF-51-3-45	Request Supplement, Corrosion Tests — MTR RaLa Equipment	E. M. Shank	3/15/51

DOCUMENT NO.	TITLE	AUTHOR	DATE
CF-51-4-36	Low Level Break-in-Run 706-D Modification Project	W. E. Unger	4/19/51
CF-51-4-85	Radiation Test of Ion Exchange Resin	W. E. Unger	4/19/51
CF-51-5-9	ORNL RaLa Process "Crud" Filter — Water Test	R. W. Hinterleiter	5/1/51
CF-51-5-10	ORNL RaLa Process Filters Type 2	R. W. Hinterleiter	5/1/51
CF-51-4-45	MTR-B Schedule	W. E. Unger	5/8/51
	HOMOGENEOUS REACTOR		
CF-51-3-78	A Survey of Homogeneous Reactor Chemical Processing	F. R. Bruce	3/19/51
CF-51-5-46	Observations on the Stability of Uranyl Sulfate Solutions	T. C. Runion L. E. Morse	5/9/51
	VOLATILITY		
ORNL-980	Dry Fluoride Process Status Report	R. E. Leuze	3/27/51
	SLURREX PROCESS		
CF-51-3-96	Laboratory Equilibrium Data on Uranium Refinery Feeds from Pilot Plant Runs at Mallinckrodt Chemical Works	T. C. Runion	3/24/51
CF-51-4-53	AEC Feed Materials Plant, Cincinnati, Ohio	F. L. Steahly	4/11/51
CF-51-4-155	Uranium Ores Recovery Pulse Column Tests	A. C. Jealous	4/26/51
	23 PROCESS		
CF-51-3-99	Letter to Dr. D. R. Miller	F. L. Steahly	3/29/51
CF-51-4-70	Separation of U^{233} and/or Pa^{233} from Irradiated Thorium	F. L. Steahly	4/13/51
	MISCELLANEOUS		
CF-51-2-102	Recovery of Uranium from Natural Waters of the United States	F. R. Bruce D. E. Ferguson	2/17/51
CF-51-3-80	Unit Operations Status Report	J. O. Davis	3/19/51
CF-51-3-91	Unit Operations Status Report	J. O. Davis	3/26/51
CF-51-4-8	Unit Operations Status Report	J. O. Davis	4/2/51
CF-51-4-49	Unit Operations Status Report	J. O. Davis	4/10/51
ORNL-1000	Chemical Technology Division Quarterly Progress Report for Period Ending February 20, 1951	Edited by W. K. Eister	5/4/51
CF-51-5-36	Proposal for the Development of a Combined Centrifuge Filter Process Vessel	F. L. Culler	5/7/51