SECRET
SECURITY INFORMATION

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360642 6

ORNL-1448
Progress

AEC RESEARCH AND DEVELOPMENT REPORT

CHEMICAL TECHNOLOGY DIVISION

QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING NOVEMBER 20, 1952

Classification Cancelled
Or Changed To
By Authority Of
By Date 9.13.71
Date 11.10.71

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

CLASSIFICATION CANCELLED
DATE July 12, 1979 (DOE REVIEW ORDER)
DECLASSIFICATION OFFICE
OAK RIDGE NATIONAL LABORATORY
AUTHORITY DELEGATED BY ERDA

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
UCC
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

RESTRICTED DATA
This document contains Restricted Data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

SECRET
SECURITY INFORMATION

[redacted]

ORNL-1448

This document consists of 26 pages.
Copy 4 of 139 copies. Series A.

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

QUARTERLY PROGRESS REPORT

for Period Ending November 20, 1952

F. L. Steahly – Division Director
F. R. Bruce – Chemical Development Chief
W. K. Eister – Unit Operations Chief
H. K. Jackson – Pilot Plant Chief
F. L. Culler – Process Design Chief

DATE ISSUED

JAN 27 1953

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

[redacted]

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360642 6

[redacted]

ORNL-1448
Progress

INTERNAL DISTRIBUTION

1. G. T. Felbeck
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-13. Central Files
14. C. E. Center
15. C. E. Larson
16. W. B. Humes (K-25)
17. L. B. Emlet (Y-12)
18. A. M. Weinberg
19. E. H. Taylor
20. E. J. Murphy
21. E. D. Shipley
22. F. C. VonderLage
23-24. F. L. Steahly
25. R. C. Briant
26. J. A. Swartout
27. S. C. Lind
28. A. H. Snell
29. A. Hollaender
30. M. T. Kelley
31. G. H. Clewett
32. K. Z. Morgan
33. J. S. Felton
34. A. S. Householder
35. C. S. Harrill
36. C. E. Winters
37. D. W. Cardwell
38. E. M. King
39. W. K. Eister
40. F. R. Bruce
41. F. L. Culler
42. J. O. Dovis
43. H. K. Jackson
44. R. S. Livingston
45. C. P. Keim
46. C. D. Susano
47. F. W. Hurd (K-25)
48. S. Cromer (K-25)
49. R. E. Engberg
50. R. N. Lyon
51. C. B. Graham
52. R. B. Briggs
53. D. D. Cowen
54. P. M. Reyling
55. G. C. Williams
56. E. P. Wigner (consultant)

EXTERNAL DISTRIBUTION

57-63. Argonne National Laboratory
64. Armed Forces Special Weapons Project (Sandia)
65. Armed Forces Special Weapons Project (Washington)
66-72. Atomic Energy Commission, Washington
73-75. Brookhaven National Laboratory
76. Carbide and Carbon Chemicals Company (C-31 Plant)
77-78. Carbide and Carbon Chemicals Company (K-25 Plant)
79-80. Carbide and Carbon Chemicals Company (Y-12 Plant)
81. Chicago Patent Group
82-87. duPont Company

[redacted]

[redacted]

88-93. General Electric Company, Richland
(1 copy to G. F. Hill and 1 copy to F. W. Albaugh)
94. Hanford Operations Office
95-99. Idaho Operations Office (1 copy to Phillips Petroleum Co.)
100. Iowa State College
101-104. Knolls Atomic Power Laboratory
105-107. Los Alamos
108-110. Mound Laboratory
111. Naval Research Laboratory
112-115. New York Operations Office
116. Patent Branch, Washington
117. Savannah River Operations Office (Augusta)
118. Savannah River Operations Office (Wilmington)
119-122. University of California Radiation Laboratory
123-124. Vitro Corporation of America
125-129. Technical Information Service, Oak Ridge

[redacted]

[redacted]

Reports previously issued in this series are as follows:

ORNL-268	Period Ending May 31, 1949
ORNL-467	Period Ending August 31, 1949
ORNL-530	Period Ending November 30, 1949
ORNL-663	Period Ending February 28, 1950
ORNL-763	Period Ending May 31, 1950
ORNL-846	Period Ending August 31, 1950
ORNL-936	Period Ending November 20, 1950
ORNL-1000	Period Ending February 20, 1951
ORNL-1061	Period Ending May 20, 1951
ORNL-1141	Period Ending August 20, 1951
ORNL-1311	Period Ending February 10, 1952
ORNL-1328	Period Ending May 20, 1952
ORNL-1385	Period Ending August 20, 1952

[redacted]

[redacted]

CONTENTS

	Page
ABSTRACT	1
INTRODUCTION	1
SUMMARY	1
1. PUREX PROCESS	2
Purex Process Demonstration	2
Recovery of Plutonium from Metallurgical Wastes	2
2. SCRUP PROGRAM	2
3. WASTE METAL RECOVERY	3
4. HOMOGENEOUS REACTOR FUEL REPROCESSING	3
5. THOREX PROCESS	4
Process Chemical and Engineering Studies	4
Pulse-Column Studies	4
Plant Design	7
6. INTERIM-23 PROCESS	7
7. IDAHO CHEMICAL PROCESSING PLANT	7
8. WASTE TREATMENT STUDIES	8
9. ISOLATION PROCESSES FOR PLUTONIUM AND URANIUM	9
Savannah River Plant Operating Limits	9
10. HOMOGENEOUS REACTOR SLURRIES	9
Optimum Calcination Temperature for Preparation of $UO_3 \cdot H_2O$	9
Corrosion of Type 347 Stainless Steel with $UO_3 \cdot H_2O$ Slurries	10
Relation Between Particle Size and Sedimentation Rate	10
Preparation of $UO_3 \cdot H_2O$ from Ammonium Uranyl Carbonate	10
Uranium Oxide Chemistry	10
Uranyl Carbonate Chemistry	10
Uranium Trioxide Monohydrate Slurry Irradiation Experiments	11
11. VOLATILITY	11
Chlorine Trifluoride Process Evaluation	11
Plutonium Recovery from Chlorine Trifluoride Process Residue	11

[redacted]

[redacted]

12. ELECTROCHEMISTRY 12

13. ION EXCHANGE 13

Higgins Contactor 13
Uranium Recovery from Ore Leach Liquors 13
Preparation of Uranium Hexafluoride 13
Preparation of Nitrate-Free Ammonium Uranyl Carbonate 14
Evaluation of New Ion-Exchange Materials 14

14. CHEMICAL ENGINEERING RESEARCH 15

Solvent Extraction 15
Special Equipment 15
Equipment Decontamination 15
Cost Studies 16
Metal Dissolution 17
Feed Preparation and Service Functions 17

[redacted]

CHEMICAL TECHNOLOGY DIVISION

F. L. STEAHLY, DIRECTOR
VIRGINIA WELLS, SECRETARY

W. D. LANHAM, SPECIAL ASSIGNMENT
MARTHA GERRARO, REPORTS EDITOR
BETTYE BURNS, TYPIST

C. W. SCHERSTEN, ASSISTANT TO DIRECTOR
MARGERY HELMS, SECRETARY
J. W. CLARK, PROCUREMENT
H. B. GRAHAM, TECHNICIAN
AUGUSTA DOBBIN, JANITRESS
AOLA JOHNSON, JANITRESS

CHEMICAL DEVELOPMENT SECTION[1]

F. R. BRUCE,[2] SECTION CHIEF
O. C. DEAN, SPECIAL ASSIGNMENT
JOAN RUSSEL, SECRETARY
BETTYE PHIFER, TYPIST
J. E. FARMER, TECHNICIAN
C. F. KECK, TECHNICIAN
C. J. SHIPMAN, TECHNICIAN

PUREX

J. R. FLANARY, PROBLEM LEADER
R. L. FOLGER[3]
L. E. LINE[3]
V. J. REILLY[3]
V. A. RYAN[3]

TECHNICIANS
L. A. BYRD
E. R. JOHNS

HOMOGENEOUS REACTOR CHEMICAL PROCESSING

D. E. FERGUSON, PROBLEM LEADER
G. I. CATHERS
C. V. ELLISON
R. G. MANSFIELD
R. A. McNEES
W. E. TOMLIN

TECHNICIANS
W. B. HOWERTON
R. C. SHIPWASH
O. K. TALLENT

HOMOGENEOUS REACTOR FUEL SLURRY STUDIES

F. R. BRUCE,[2] PROBLEM LEADER
J. O. BLOMEKE
J. P. McBRIDE
L. E. MORSE

THOREX

A. T. GRESKY, PROBLEM LEADER
M. R. BENNETT
S. S. BRANDT[3]
K. L. MATTERN[4]
W. T. McDUFFEE, JR.
J. E. SAVOLAINEN
R. P. WISCHOW

TECHNICIANS
R. C. LOVELACE
J. F. TALLEY
C. T. THOMPSON

VOLATILITY

R. E. LEUZE, PROBLEM LEADER
C. E. SCHILLING

SPECIAL PROBLEMS

R. E. BLANCO, PROBLEM LEADER
M. O. BARRINGER
G. A. EATON
J. V. FRIEL
A. H. KIBBEY
N. A. KROHN
L. D. LYNCH

TECHNICIANS
D. M. HELTON
J. F. LAND

ELECTROCHEMISTRY

J. A. McLAREN, PROBLEM LEADER
J. H. GOODE
H. L. PEELER

ISOLATION

D. C. OVERHOLT, PROBLEM LEADER
D. G. KARRAKER[3]
D. A. ORTH[3]
R. H. RAINEY
F. W. TOBER[3]

TECHNICIANS
J. M. DELOZIER
C. W. GREENE
D. R. HENDRIX

ION EXCHANGE STUDIES

I. R. HIGGINS, PROBLEM LEADER
J. T. ROBERTS

TECHNICIAN
W. E. SHOCKLEY

PROCESS DESIGN SECTION

F. L. CULLER, SECTION CHIEF
F. C. McCULLOUGH, SPECIAL PROBLEMS
LUCILLE KUYKENDALL, SECRETARY
MAY PEPPER, SECRETARY

IDAHO CHEMICAL PLANT

H. E. GOELLER, PROBLEM LEADER
F. N. BROWDER (IDAHO)
E. J. FREDERICK[5] (IDAHO)
R. J. KLOTZBACH (IDAHO)
E. L. NICHOLSON (IDAHO)
A. M. ROM (IDAHO)
J. B. RUCH (IDAHO)

THOREX, METAL RECOVERY

W. E. UNGER, PROBLEM LEADER
G. B. BERRY[6]
B. F. BOTTENFIELD[6]
A. R. IRVINE[6]
K. G. STEYER[6]
W. R. WINSORO
F. E. HARRINGTON, METAL RECOVERY ADDITION

STENOGRAPHER
MARY HUME

SPECIAL PROBLEMS

R. P. MILFORD, PROBLEM LEADER
W. L. CARTER,[6] ASSISTANT PROBLEM LEADER
D. J. ORIOLO,[7] ASSISTANT PROBLEM LEADER
A. C. MARTINSEN[7]
A. G. PRIEBE[7]
A. E. AIKENS[7]
C. G. BAKER[8]
J. W. BOYAR[7]
I. C. CUTLER[7]
M. L. DRABKIN[7]
J. R. FISHER[7]
A. FRANK[7]
C. D. HYLTON
B. LIEBERMAN[9]
W. J. LILLEY[7]
C. S. LISSER[7]
H. H. MESSENHEIMER[6]
B. B. MOONEY[7]
C. A. MOSSMAN[9]
J. A. PERZAN[7]
B. J. ROE[7]
W. F. SCHAFFER
D. WARREN[7]
H. O. WEEREN[6]
W. R. WHITSON[6]

DRAFTSMEN
H. DERMAN[7]
C. CRAKER[7]
R. HOCH[7]
A. KLEVENHAGEN[7]
N. D. LONSDALE[7]
A. PIZZI[7]
P. F. ROSE[7]
W. M. SHEWBROOKS[7]
D. H. SPRENKLE[7]
H. S. WILLIAMS[7]

STENOGRAPHIC STAFF
MARTHA DUFF
ANN HOUSLEY
ESTHER SHELTON[10]

ECONOMIC STUDIES

W. G. STOCKDALE, PROBLEM LEADER
G. W. T. KEARSLEY[6]
P. L. ROBERTSON[6]

PUREX ECONOMIC STUDY
H. L. HULL,[3] PROBLEM LEADER
H. R. ZEITLIN[6]

UNIT OPERATIONS SECTION

W. K. EISTER, SECTION CHIEF
RUTH PENNINGTON, SECRETARY
MARION HOPPE, SECRETARY

SOLVENT EXTRACTION

A. C. JEALOUS,[11] PROBLEM LEADER
J. L. ALSTON[3]
J. R. DEARWATER[12]
P. A. HAAS
R. W. HORTON
E. LIEBERMAN
H. F. MUHLHAUSER[12]
H. E. OSMENT[3]
W. M. WOODS

TECHNICIANS
V. L. FOWLER
G. JONES
J. C. ROSE
H. F. SOARD

SPECIAL EQUIPMENT

T. A. AREHART,[13] PROBLEM LEADER
E. C. ELENER[3]
J. R. PARROTT
G. A. WEST
E. D. YORK

TECHNICIANS
T. D. NAPIER
R. O. PAYNE

RADIATION ENGINEERING

C. D. WATSON,[14] PROBLEM LEADER
M. L. FELDMAN[4]
I. J. GROSS[7]
R. J. McNAMEE
J. A. MOORE[7]
R. D. ROSS[7]
J. C. SUDDATH

TECHNICIANS
G. R. GUINN
F. L. ROGERS

FEED PREPARATION

E. O. NURMI,[15] PROBLEM LEADER
E. D. ARNOLD
L. EVANS[3]
D. L. FOSTER
D. R. LINDOW[3]
C. L. WILLIAMSON[3]

TECHNICIANS
R. D. ARTHUR
G. B. DINSMORE
D. B. MASTERS

CATALYTIC CONSTRUCTION COMPANY REPRESENTATIVES

D. J. ORIOLO, CATALYTIC PROJECT DIRECTOR
A. C. MARTINSON, ASSISTANT PROJECT DIRECTOR
C. C. SCHATTE, ADMINISTRATIVE ASSISTANT
DOLORES J. WASCHER, SECRETARY

DU PONT COMPANY REPRESENTATIVES

R. I. MARTENS, LIAISON OFFICE MANAGER
A. E. WIBLE, ASSISTANT TO THE LIAISON OFFICE MANAGER

A. L. DENNY, ADMINISTRATIVE ASSISTANT
ELLEN TOBER, SECRETARY
ALICE DUFF, CLERK-TYPIST (ORNL)

PILOT PLANT SECTION

H. K. JACKSON, SECTION CHIEF
W. J. GRETER,[9] INSTRUMENTATION
G. S. SADOWSKI, SPECIAL ASSIGNMENT
AGNES HAIR, SECRETARY
MARY LYNN CAMERON, TYPIST
R. B. WATERS, DRAFTSMAN
E. WRIGHT, CLERK

PUREX

D. O. DARBY, PROBLEM LEADER

ENGINEERING
R. B. LINDAUER[2]
S. MANN[16]

ACID RECOVERY
J. W. LANDRY

DATA
J. M. CHANDLER
K. H. McCORKLE
A. J. PECQUET

OPERATIONS
R. H. WINGET
W. D. BURCH, SHIFT SUPERVISOR
D. W. CETNAR,[3] SHIFT SUPERVISOR
R. G. KEELY,[2] SHIFT SUPERVISOR
T. T. THOMPSON,[3] SHIFT SUPERVISOR
G. R. TULLY,[4] SHIFT SUPERVISOR
R. H. VAUGHAN, SHIFT SUPERVISOR

OPERATORS
W. T. BOSTIC
J. H. BROCK
E. W. BROWN
W. J. BRYAN
H. S. CALDWELL
G. D. DAVIS
J. H. GROOVER
R. L. HICKEY
J. E. HIGGINS
W. JENNINGS
C. H. JONES
S. A. McCOSH
R. E. PURKEY
W. A. SHANNON
D. H. SUMMERS
J. R. VEST
C. E. WADDELL
J. H. WALKER

SPECIAL PROBLEMS

R. B. LINDAUER,[2] PROBLEM LEADER

SCRUP

W. H. LEWIS, PROBLEM LEADER
R. E. BROOKSBANK
W. O. DANIEL,[3] SHIFT SUPERVISOR
J. L. MATHERNE
C. E. PICKETT,[3] SHIFT SUPERVISOR
J. W. SCHAUER,[3] SHIFT SUPERVISOR
D. J. SKOVHOLT,[3] SHIFT SUPERVISOR

OPERATORS
C. W. BOATMAN
W. E. LEDBETTER
J. F. LOCKMILLER
R. J. SHANNON
D. E. SPANGLER
S. E. SPENCER
G. R. THOMPSON
H. C. THOMPSON
C. H. TIPTON

DECONTAMINATION

R. B. KEELY,[2] PROBLEM LEADER

THOREX

E. M. SHANK, PROBLEM LEADER
M. A. TURNER
J. W. ULLMANN

RAGS

W. B. WATKINS,[3] PROBLEM LEADER

[1] C. P. JOHNSTON, ON LOAN TO MATERIALS CHEMISTRY DIVISION
[2] DUAL CAPACITY
[3] DU PONT PERSONNEL
[4] CALIFORNIA RESEARCH AND DEVELOPMENT COMPANY PERSONNEL
[5] ON LOAN FROM ANALYTICAL CHEMISTRY DIVISION
[6] ON LOAN FROM ENGINEERING DEPARTMENT
[7] CATALYTIC CONSTRUCTION COMPANY PERSONNEL
[8] ON LOAN FROM MATERIALS CONTROL GROUP
[9] ON LOAN FROM INSTRUMENT DEPARTMENT
[10] ON LOAN FROM PERSONNEL DEPARTMENT
[11] RESPONSIBLE IN THIS SECTION FOR PUREX AND THOREX
[12] NATIONAL LEAD COMPANY OF OHIO PERSONNEL
[13] RESPONSIBLE IN THIS SECTION FOR RaLa, METAL RECOVERY, AND SPECIAL PROBLEMS
[14] RESPONSIBLE IN THIS SECTION FOR WASTE DISPOSAL AND SLURRY STUDIES
[15] RESPONSIBLE IN THIS SECTION FOR "25" PROCESS AND HR FUEL REPROCESSING
[16] ATLANTIC REFINING COMPANY PERSONNEL

[redacted]

PUBLICATIONS

ORNL reports issued during this quarter are as follows:

R. E. Blanco, *Laboratory Development of the MTR-RaLa Process for the Production of Barium*^{140}, ORNL-1148 (Aug. 19, 1952).

I. R. Higgins, *A Countercurrent Solid-Liquid Contactor for Continuous Ion Exchange*, ORNL-1310 (Sept. 4, 1952).

Chemical Technology Division Progress Report for Period August 1, 1951 to February 10, 1952, ORNL-1311.

Chemical Technology Division Quarterly Progress Report for Period Ending May 20, 1952, ORNL-1328.

J. R. Flanary, S. V. Castner, R. L. Folger, L. E. Line, Jr., V. J. Reilly, V. A. Ryan, and E. B. Sheldon, *Progress Report: Purex Process Laboratory Development, February Through April, 1952*, ORNL-1343.

D. C. Overholt, F. W. Tober, and D. A. Orth, *An Ion-Exchange Process for Plutonium Isolation and Purification*, ORNL-1357 (Sept. 16, 1952).

D. C. Overholt, *An Ion-Exchange Process for* U^{233} *Isolation and Purification*, ORNL-1364 (Sept. 22, 1952).

R. E. Blanco, A. H. Kibbey, and J. H. Pannell, *Radiation Stability Studies*, ORNL-1379 (Sept. 22, 1952).

Chemical Technology Division Quarterly Progress Report for Period Ending August 20, 1952, ORNL-1385.

[redacted]

CHEMICAL TECHNOLOGY DIVISION QUARTERLY PROGRESS REPORT

ABSTRACT

Work done on the following problems is reported: Purex, Scrup, Thorex, and Interim-23 processes; homogeneous reactor fuel preparation and product recovery; Idaho chemical plant development; waste metal recovery; waste treatment; isolation, volatility, electrochemical, ion-exchange, solvent-extraction, metal-dissolution, cost, and equipment decontamination studies.

INTRODUCTION

The major programs during the last quarter in the Chemical Technology Division were Purex process development, Thorex process development, and development of processes for homogeneous reactor fuel preparation and product recovery.

In the Chemical Development Section, Purex process work was concerned chiefly with variables in the ion-exchange coupling step. Chemical studies in the Thorex process were continued. Emphasis in the homogeneous reactor fuel reprocessing program was shifted to continuous removal processes, and studies in the fuel preparation program continued to be made on the preparation of slurries and their properties. Preliminary work on evaluation of the chlorine trifluoride process for preparation of UF_6 was begun, and studies on the recovery of plutonium from the residue were continued. Work on electrochemical preparation of heavy hydrogen was continued. Various applications of the ion-exchange method were considered, and further work was done on determination of the permissible operating limits for the Savannah River ion-exchange process.

In the Unit Operations Section, work was concentrated on the Thorex process.

In the Pilot Plant Section, the Purex solvent-extraction runs were continued, and the Scrup and Interim-23 programs were completed. The RAGS process for off-gas decontamination was successfully operated.

In the Design Section, Purex material flowsheets were completed. Preliminary plant design for the Thorex process was continued. Design and construction of the Idaho plant have been completed.

SUMMARY

Purex Process. Additional pilot-plant runs were made satisfactorily, and the uranium and plutonium products were shown to meet specifications. The preparation of material flowsheets, the first phase of a Purex plant design, was completed.

Homogeneous Reactor Fuel Reprocessing. A method of removing plutonium from the reactor continuously by the settling of insoluble PuO_2 was found to be attractive.

Thorex Process. Modifications were made in the chemical flowsheet, and the sizes of the columns required for pilot-plant equipment were determined by pulse-column studies. Preliminary plant design is scheduled for completion by the end of 1952, and plant startup is scheduled for April 1953.

Homogeneous Reactor Slurries. Several starting materials for the preparation of $UO_3 \cdot H_2O$ were found to be attractive.

Volatility. About 99% of the plutonium in the chlorine trifluoride residue was shown to be extractable with tributyl phosphate under the proper conditions.

Electrochemistry. Conditions for increasing the separation of the hydrogen isotopes in an electrolysis cell were found.

Chemical Engineering Research. A solution was found that was capable of removing scale from the homogeneous reactor piping system without causing excessive corrosion of the pipes. A large-scale packed-column trickle type of dissolver was installed.

1. PUREX PROCESS

The purpose of the Purex project is to develop and demonstrate a continuous solvent-extraction process that will be more efficient and economical than other processes used for the separation and decontamination of plutonium and uranium from irradiated uranium metal. The scope of the project includes chemical and equipment development and the design, construction, and operation of a pilot plant.

The Purex No. 1 flowsheet is to be used at the Savannah River plant, with an ion-exchange process to couple the solvent extraction with the peroxide precipitation.

PUREX PROCESS DEMONSTRATION

Twenty-nine Purex solvent-extraction pilot-plant demonstration runs have now been completed. Product specifications were met, with gross beta and gamma decontamination factors of the order of 10^6 for uranium and of 10^7 for plutonium. Satisfactory recovery was obtained for both uranium and plutonium, 99.7 and 99.3%, respectively, including feed preparation losses. Nitrogen dioxide gas was found to be suitable for continuous plutonium valence adjustment in the feed solution of the second plutonium cycle.

The final solvent-extraction uranium product obtained from slugs irradiated to 550 Mwd/ton at Hanford and cooled for 120 days met specifications and was satisfactory for feed material at K-25. Uranium from a 63-day-cooled feed material met specifications after standing for an additional 30 days. Five additional runs will be made on 60-day-cooled Hanford slugs in response to a Hanford request for information pertinent to their Purex installation.

The plutonium from the six runs, HCP-10 through 15, was processed through the ion-exchange coupling step under cyclic conditions.[1] The final plutonium product had a plutonium concentration of 45 g/liter. The resin columns were successfully decontaminated with oxalic acid after run HCP-15 was completed.

Large discrepancies occurred in the uranium and plutonium balances made through the ion-exchange system. These discrepancies indicate that under the conditions of the runs the analytical methods now in use are not suitable.

A detailed progress report on the ion-exchange separation has been prepared.[2]

RECOVERY OF PLUTONIUM FROM METALLURGICAL WASTES

The metallurgical waste recovery process has been developed and demonstrated on a pilot-plant scale. A completion report[3] is being issued.

---

[1] D. C. Overholt, D. A. Orth, F. W. Tober, R. H. Rainey, and D. G. Karraker, *Isolation Studies, Quarterly Report, August Through October, 1952*, ORNL-1449 (to be published).

[2] D. C. Overholt, F. W. Tober, and D. A. Orth, *Progress Report: Ion Exchange Isolation Processes for Plutonium and U^{233}*, ORNL-1397 (Dec. 4, 1952).

[3] R. L. Folger, E. B. Sheldon, and S. V. Castner, *Recovery of Plutonium from Metallurgical Wastes*, ORNL-1442 (to be published).

2. SCRUP PROGRAM

The second phase of the Scrup program, which had as its objective the recovery of plutonium from the bulk of the Chalk River irradiated uranium, has been completed. A total of 3140 g of plutonium was recovered with a product concentration of 39 to 42 g of plutonium per liter and a product acidity of 5 to 6 *N*. This product meets Button Line requirements for peroxide precipitation. In the first phase of the program – the recovery of plutonium with various radiation histories – the product was recovered by batches, without mixing, and the concentration was only 8 to 30 g/liter. The total transfer to waste for the program was 1.22 g of plutonium, or approximately 0.05%.

The uranium recovered in the Scrup process was not concentrated or purified; it is being stored for future processing.

3. WASTE METAL RECOVERY

The purpose of the Metal Recovery project is to develop a chemical process for the recovery of uranium from both the bismuth phosphate process waste at Hanford and the metal waste at ORNL and to recover the uranium from the ORNL waste. The process wastes are the most easily available supply of uranium. The program includes chemical and equipment studies and the design, construction, and operation of the ORNL metal recovery plant.

Upon completion of the Scrup program on September 15, decontamination of building facilities was started to permit necessary changes and additions required for processing of tank-farm metal wastes for uranium and plutonium recovery. Decontamination was completed and process conversion was begun by November 1. It is anticipated that feed preparation for the Metal Recovery program will be started early in December.

A request for the installation of facilities for a second uranium cycle is being prepared.

4. HOMOGENEOUS REACTOR FUEL REPROCESSING

The purpose of the Homogeneous Reactor Fuel Reprocessing program is to develop a chemical process for recovery of the products from a homogeneous plutonium producer. The work will include chemical and equipment development, pilot-plant development, and design, construction, and operation of a plant to process the fuel from the intermediate-scale reactor. Studies have, in general, been confined to a heavy-water solution of a uranyl sulfate type of fuel, but some of the results apply also to a uranium oxide slurry fuel. Details of the studies are given in HRP quarterly reports.[1]

The feasibility of the Purex type[2,3] of process as applied to a uranyl sulfate solution plutonium producer has been established.[4] Emphasis on chemical processing development has now shifted to continuous removal of the plutonium from the reactor. Development of the continuous-removal process that has been discussed previously[1] could effect a saving of about $10 per gram of plutonium and at the same time result in production of plutonium with a very low Pu^{240} content.

The most attractive method being considered is the settling of insoluble PuO_2. The rate of hydrolysis and precipitation of Pu(IV) from 1 *M* uranyl sulfate is such that an equilibrium concentration not exceeding 0.01 mg of plutonium per milliliter in solution can be expected under reactor conditions. The total plutonium content (soluble and insoluble) of the reactor fuel solution can be maintained at about 0.02 mg/ml by an efficient physical separation of the insoluble PuO_2. Data obtained to date indicate that the hydrogen formed during the decomposition of the fuel solution will be sufficient to ensure the maintenance of the plutonium in the insoluble tetravalent state.

Preliminary laboratory-scale studies have been made on decontamination of plutonium from a homogeneous reactor by thenoyl trifluoroacetone (TTA) chelation. Results indicate that it may be possible to dissolve the PuO_2 from the reactor in TTA-benzene and thus obtain cheap and easy separation and decontamination of plutonium from fission products in the same step.

Earlier work[3] indicated that radiation damage to the 30% TBP solvent used in the Purex extraction of homogeneous reactor fuel would not significantly affect the decontamination of uranium and plutonium. However, further work has shown that irradiated solvent forms insoluble material during retreatment and that detectable unsaturation occurs in the solvent upon irradiation, which may lead to the formation of organic iodides with radioactive iodine. Such compounds would complicate the solvent cleanup process.

Ten batches, a total of 418 kg, of enriched uranium-bearing material salvaged from homogeneous reactor experiments are being processed to recover the 690 g of uranium (450 g of U^{235}), which will be converted to uranyl sulfate for reuse in the homogeneous reactor. The present schedule calls for completion of the work in November 1952.

---

(1) See, for example, F. R. Bruce, D. E. Ferguson, G. I. Cathers, R. G. Mansfield, and W. E. Tomlin, *HRP Quar. Prog. Rep. Oct. 1, 1952*, ORNL-1424, p. 125.

(2) *Chem. Tech. Quar. Prog. Rep. Aug. 20, 1952*, ORNL-1385, p. 4.

(3) *Chem. Tech. Quar. Prog. Rep. May 20, 1952*, ORNL-1328, p. 4.

(4) F. R. Bruce, D. E. Ferguson, G. I. Cathers, R. G. Mansfield, and W. E. Tomlin, *HRP Quar. Prog. Rep. July 1, 1952*, ORNL-1318, p. 158.

5. THOREX PROCESS

The purpose of the Thorex program is to develop a process for the separation of U^{233}, Pa^{233}, and thorium. The "23" Process, previously developed through the pilot-plant stage, recovered only U^{233}. The scope of the project includes chemical, equipment, and pilot-plant development work, and plant-conception studies.

A progress report[1] on the laboratory phase of Thorex development work since June 1, 1952 has been prepared and will be issued shortly. A Thorex flowsheet (Fig. 5.1) has been issued which incorporates changes that have been made[2] in process solutions to permit easier control.

PROCESS CHEMICAL AND ENGINEERING STUDIES

The calcium hydroxide slurry treatment mentioned previously[3] has been shown to give a 500- to 1000-fold decrease in aqueous waste production and to have a higher efficiency and di- and monobutyl phosphate removal from, and fission-product decontamination of, the solvent over the sodium hydroxide–sodium carbonate procedures. A scale-model contactor, with a design capacity of 18 liters/hr, has been built and has been operated satisfactorily to produce 900 liters of usable solvent for pulse-column operation in the Thorex development program. The contactor body is a 48-in. length of pyrex pipe with an inside diameter of 6 inches. Four turbine-type impellers spaced through the lower two-thirds of the column and longitudinal baffles give turbulent slurry-liquid contact and prevent channeling. A conical annular baffle and axial baffles in the top section of glass pipe eliminate swirl and enable an enlarged conical settling section at the top of the contactor to discharge clarified solvent.

Preliminary indications are that tributyl phosphate (TBP) decomposition, which occurs in the Thorex BT stream partly as a result of contact with light and air, can be prevented by washing the BT solution with Amsco prior to the distillation, by distilling it at a low temperature and pressure, or by a combination of these two methods. TBP occurs in the BT stream at a concentration of about 0.25 g/liter, and prevention of the hydrolysis is a prerequisite for phosphate decontamination of the thorium product or for recycling the evaporated BT solution through the process.

Mantle-grade thorium nitrate tetrahydrate contains silica, which causes emulsions in the solvent-extraction process. The salt has been purified sufficiently for use in pulse-column studies by adding 70% HNO_3 to the crystals and refluxing for 4 hr at the boiling point (above 130°C). The silica is dehydrated and can be filtered off, although the filtration step is not essential.

Nitric acid dissolution of thorium dioxide crystals that had been calcined at temperatures of 600, 1200, and 1650°C was found to be rapid and complete in the presence of fluoride. In the absence of fluoride, the percentage of dissolution was low, and it decreased as the calcination temperature was increased.

Complicated facilities for preparation of the acid-deficient aluminum nitrate scrubbing solution could be eliminated if satisfactory dibasic aluminum nitrate could be obtained commercially. Results of preliminary investigations on the preparation of this compound showed that it could be precipitated, as an anhydrous, amorphous white powder, with acetone or with an isopropyl alcohol–diethyl ether mixture from a solution 4.0 *M* in aluminum and 8.0 *M* in hydroxyl ion.

PULSE-COLUMN STUDIES

The height and cross-sectional dimensions of the pulse columns for the Thorex pilot plant and a range of operable flow rates and pulse conditions are being determined in 2-in.-dia columns. The equipment includes a 24-ft vertical column and a concatenated column made up of six 6-ft sections linked in series and mounted on a rack, with an over-all height of about 10 ft for the assembly. Specifications to be met by the pilot-plant equipment include:

1. a thorium throughput of 100 kg/day at about 60% of flooding,
2. uranium and thorium losses of less than 0.1% in the extraction-scrub column,

(1) A. T. Gresky, W. T. McDuffee, J. E. Savolainen, S. S. Brandt, K. L. Mattern, M. R. Bennett, and R. P. Wischow, *Laboratory Development of the Thorex Process – Progress Report*, ORNL-1431 (to be published).

(2) *Chem. Tech. Quar. Prog. Rep. May 20, 1952*, ORNL-1328, p. 6.

(3) *Chem. Tech. Quar. Prog. Rep. Aug. 20, 1952*, ORNL-1385, p. 5.

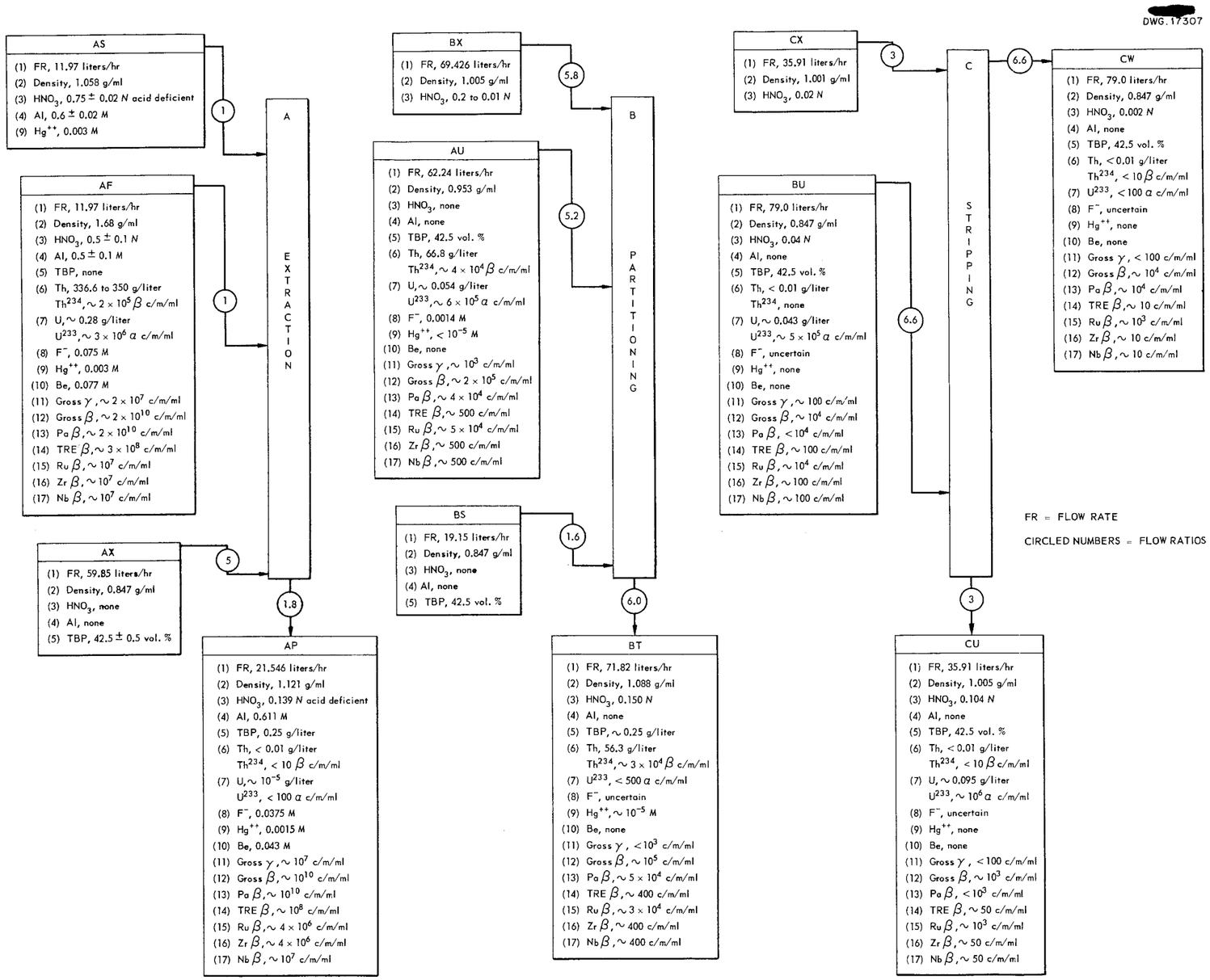

Fig. 5.1. Thorex Flowsheet, October 1952. Basis: 100 kg of thorium per day; slugs irradiated at 10^{13} neutrons/cm^2·sec for 150 days, cooled for 60 days.

3. a uranium loss of less than 0.1% in the preferential strip column,
4. a thorium separation factor of 5×10^4 in the preferential strip column,
5. a uranium loss in the strip column of less than 0.1%.

Pulse studies to date indicate that a 3-in.-dia A column with a 12-ft-high extraction section will be adequate to process 100 kg of thorium per day. It is thought that a 20-ft scrub section will be necessary to obtain the desired fission-product decontamination factor.

Preferential strip-column studies in an experimental concatenated column indicate that a 4-in.-dia B column will be required for a 100-kg/day throughput of thorium. A 12-ft scrubbing section will probably give satisfactorily low uranium losses. Satisfactory thorium separation factors have not been obtained with an 18-ft stripping section; tests in a 24-ft stripping section are planned. The possibility of an increased rate of hydrolysis of TBP in the presence of high concentrations of thorium (column A product stream), which would cause a low thorium separation factor, is being investigated.

Initial tests indicate that for a C column, a 3-in.-dia size will be satisfactory.

PLANT DESIGN

Preliminary plant design is scheduled for completion by the end of the year. Startup of the pilot plant, which will use available Purex plant equipment, was initially scheduled for January 1, 1953 but has been rescheduled for April 1, 1953 to permit additional important Purex investigations. Approximately 500 items of equipment for the pilot plant have been ordered, and deliveries to date are complete on about 15% of the orders placed. Engineering design of the A-column, scrub-makeup area is about 75% complete, and detailed design on the solvent-recovery, makeup and pretreatment area is to begin in November. One continuous charger has been designed for the thorium dissolver feed, and an alternate design is in progress.

6. INTERIM-23 PROCESS

The Interim-23 program, the purpose of which was to produce a specified amount of U^{233} ("23") from irradiated thorium, has been completed. The first request for approximately 1500 g of U^{233} and the second request for an additional 1000 g were both filled; a total of 2.64 kg of U^{233} was produced.

The isolation process used in the program was identical with that described in a previous report[1] except for a change in the elution cycle. The acidity of the 2 *M* ammonium acetate elutriant was increased from 0.2 *M* acetic acid to 1 *M* acetic acid, with a corresponding increase in the plutonium product from a concentration of 75 to 100 g/liter to a concentration of 130 to 140 g/liter.

[1] D. C. Overholt, *An Ion-Exchange Process for U^{233} Isolation and Purification*, ORNL-1364 (Sept. 22, 1952).

7. IDAHO CHEMICAL PROCESSING PLANT

The first and most important phase of the Idaho Chemical Processing Plant program is concerned with planning for satisfactory operation of the plant. ORNL has assisted in the design, field engineering, and plant acceptance tests. The second phase is concerned with solving the problems that inevitably arise in scaling up work from pilot-plant to full-scale operations. ORNL engineers and technicians will remain at Arco until operation of the plant at full activity levels starts; this is now scheduled for January 1953.

Design and construction of the plant have now been completed. Bechtel Corp., the construction company, has released for preliminary operation all parts of the plant; Foster Wheeler Corp., the architect-engineer company, has completed all work in the New York office but is maintaining a field group to complete the testing and to prepare as-built drawings for the project.

The American Cyanamid Co. has completed water runs and aluminum nitrate runs and is now operating the main process building with natural

uranium feed. The analytical laboratory is being operated three full shifts per day. The liquid-waste evaporator has been operated with water. The liquid-waste storage tanks and disposal system have been completed and tested and are ready for use. The xenon-krypton removal system has been pressure tested and is ready for operational tests.

A few items that remain to be completed are (1) samplers and sample carriers, (2) ladders and catwalks in cells, (3) miscellaneous equipment for sample handling, and (4) reports on corrosion of type 347 stainless steel with high-level wastes.

All operating manuals have been prepared in rough draft and are being reviewed in the light of experience gained during the preliminary operation of the plant.

8. WASTE TREATMENT STUDIES

The purpose of the Waste Treatment program is to develop the processes and equipment required to reduce the radioactivity discharged from ORNL processes to a nonhazardous level. The program includes chemical, equipment, pilot plant, and design work on contaminated gaseous, liquid, and solid wastes. Minimizing the contaminated wastes discharged from chemical operations at ORNL has the added benefit of leading directly to efficient means of waste disposal from large-scale radiochemical plants.

A Radioactive Gas Separation (RAGS) process[1] for decontaminating the off-gas from the dissolution of irradiated uranium was installed in the ORNL pilot plant and was successfully operated. It was demonstrated to be capable of recovering all the nitrogen oxides as reusable nitric acid. The nitrogen-oxygen mixture that was discharged from the process contained no detectable quantity of radioactive fission products. An over-all volume reduction factor (volume of dissolver off-gas per volume of krypton-enriched gas for storage) of 500 for the gas to be stored was demonstrated for the process, storage at atmospheric pressure being assumed. Storage at 800 psig would give an over-all reduction factor of 25,000.

The cost of installing a RAGS plant to process the off-gas from a Purex plant processing 5 tons of uranium per day was estimated to be $1,000,000. The annual cost of operating such a facility was estimated to be $400,000.

The RAGS pilot plant was designed to accommodate the off-gas evolved from the dissolution of 100 kg of full-Hanford-level uranium per day. The Purex pilot-plant dissolver off-gas, which constituted the feed gas for the RAGS process, consisted of NO, NO_2, N_2, CO_2, I_2, Xe, Kr, water vapor, and suspended radioactive solids. The gas mixture was processed as follows:

1. Suspended liquids and solids were removed by a cyclonic type of entrainment separator.
2. Water vapor was removed by a downdraft condenser.
3. Radioactive iodine was removed by reaction with silver nitrate in a packed tower at 300 to 400°F.
4. Radioactive particulate matter was removed by a glass-wool filter.
5. Nitrogen oxides (NO and NO_2) were removed by simultaneous oxidation and absorption with nitric acid.
6. Carbon dioxide was removed by a sodium hydroxide scrubber.
7. Water vapor was partially removed by adsorption on alumina.
8. Radioactive krypton and xenon were removed from the residual gas by adsorption on silica gel at −183°C.
9. Nitrogen and oxygen were released to the atmosphere.

[1] W. B. Watkins, *Summary of the ORNL Pilot Plant Development of the Radioactive Gas Separation Process*, ORNL-1410 (Dec. 12, 1952).

9. ISOLATION PROCESSES FOR PLUTONIUM AND URANIUM

The purpose of the Isolation program is to develop processes that will be more economical and will give a purer product than existing processes used to separate plutonium and uranium. The scope of the program includes chemical, equipment, and pilot-plant development and design studies. At present, emphasis is on ion-exchange methods.

The major part of the isolation work during this quarter has been concerned with applications to specific processes (cf. "Scrup Program" and "Interim-23 Process," this report). A few laboratory-scale ion-exchange experiments with more general application have also been made. Radiochemical decontamination of the Purex IIBP stream from zirconium and niobium with silica gel was found to be insufficient to justify the inclusion of a silica-gel adsorption step in the Savannah River plant isolation process. In experiments on the effects of metal ions on gas formation in the ion-exchange column, the cations of iron, nickel, chromium, aluminum, copper, and manganese were found to have no observable effects. The decontamination from chromium attained for plutonium in the ion-exchange process was found to be high, that from manganese and iron was slight, and that from aluminum and nickel was negligible.

SAVANNAH RIVER PLANT OPERATING LIMITS

Further work has been done on determining the permissible limits for the operating variables of the ORNL ion-exchange process as applied at the Savannah River plant. Two series of runs, which consisted of 15 complete cyclic runs, have been completed in the small-scale columns (0.8 in. in diameter by 14 in. in height) previously described.[1] The objective – a product cut with a plutonium concentration of 50 g/liter – was easily attained under the operating conditions specified for the Savannah River plant flowsheet. The results indicated that wide deviations from the flowsheet conditions are permissible. The behavior of the resin was no different at the end of the 15 complete cyclic runs. Details of these experiments will be given in a report now in preparation.[2]

[1] D. C. Overholt, F. W. Tober, and D. A. Orth, *Progress Report: Ion-Exchange Isolation Processes for Plutonium and U^{233}*, ORNL-1397 (Dec. 4, 1952).

[2] D. C. Overholt, D. A. Orth, F. W. Tober, R. H. Rainey, and D. G. Karraker, *Isolation Studies, Quarterly Report, August Through October, 1952*, ORNL-1449 (to be published).

10. HOMOGENEOUS REACTOR SLURRIES

The purpose of the Homogeneous Reactor Slurry program is to develop a method for preparing uranium and thorium systems to be used as fuel media in homogeneous reactors. Details of the work are reported in the Homogeneous Reactor Project quarterly reports.[1] The development of fuel systems other than aqueous solutions is important because the use of aqueous fuels is limited by solubility considerations, corrosion problems, and the cross sections of added anions. The program has thus far been concerned primarily with the development of uranium slurries, with emphasis on uranium trioxide; a limited amount of work has been done on fused fluoride salt systems. Studies will include an investigation of methods of preparing slurries and the determination of their radiation stabilities.

[1] See, for example, F. R. Bruce, J. O. Blomeke, J. M. Fulmer, L. E. Morse, and J. P. McBride, *HRP Quar. Prog. Rep. Oct. 1, 1952*, ORNL-1424, p. 27.

OPTIMUM CALCINATION TEMPERATURE FOR PREPARATION OF $UO_3 \cdot H_2O$

Nitrate-free $UO_3 \cdot H_2O$ for use as a homogeneous reactor fuel slurry is prepared by calcining uranium oxide crystals at a temperature high enough to decompose them and liberate trapped ions, hydrating the residue at 90°C, and autoclaving the hydrate at 250°C for 4 hr or longer. The treatment is repeated until a product of sufficiently high purity is obtained. The maximum calcination temperature, which is also the temperature that gives maximum purification, that could be used without reducing the metal to the tetravalent state was found to vary with the type of oxide used as the starting material. Mallinckrodt UO_3 could be calcined at 400°C, and $UO_3 \cdot H_2O$ rods could be calcined at 375°C without reduction of the uranium, but $UO_4 \cdot 2H_2O$ was partially reduced at 350°C. The final product in each case was in the form of

$UO_3 \cdot H_2O$, but that from $UO_3 \cdot H_2O$ rods had the smallest particle size, 3 μ in diameter, and the lowest soluble uranium concentration, 3 ppm. The rods were the most difficult material to work with, but, on the basis of current information, they appear to be the most attractive starting material. However, since $UO_4 \cdot 2H_2O$ must be obtained in the preliminary steps of preparing the rods, the peroxide is still considered to be of interest.

Preparation of pure $UO_3 \cdot H_2O$ by thermal decomposition of $(NH_4)_4(CO_3)_2 \cdot UO_2CO_3$ (cf. "Preparation of $UO_3 \cdot H_2O$ from Ammonium Uranyl Carbonate," this report) or of UO_2CO_3 is being considered.

CORROSION OF TYPE 347 STAINLESS STEEL WITH $UO_3 \cdot H_2O$ SLURRIES

The corrosion tests on type 347 stainless steel[2] were continued with studies on the effect of fission products. It was concluded that traces of fission products in the slurries would cause little, if any, more corrosion than pure $UO_3 \cdot H_2O$ alone. For the tests, samples of type 347 stainless steel were exposed in rocking bomb autoclaves to $UO_3 \cdot H_2O$ slurries containing nonradioactive ions in the same concentrations that would be expected for fission products after 30 hr of irradiation. Penetration rates of 0.2 to 1.1 mils per year were observed; these rates are of the same order of magnitude as those observed[2] in the absence of ions of the fission-product type.

RELATION BETWEEN PARTICLE SIZE AND SEDIMENTATION RATE

Work on the relation between particle size and sedimentation rate[2] was continued with the development of an equation relating surface area and particle diameter. An equation[3] relating particle size and sedimentation rate was shown to be applicable to slurries containing 100 g of uranium per liter but not to those of higher uranium concentrations. Another equation[4] was tested with slurries having a uranium concentration of 200 to 500 g/liter and was found to give particle-size values in good agreement with those obtained from surface area measurements by nitrogen adsorption.

[2] *Chem. Tech. Quar. Prog. Rep. Aug. 20, 1952*, ORNL-1385, p. 7.

[3] E. B. Allison and P. Murray, *Sedimentation from Concentrated Suspensions in Relation to Particle Size*, AERE M/R 829 (Nov. 26, 1951).

[4] L. P. Hatch and S. Isakoff, *Fluid Dynamics of Porous Systems*, BNL-1106.

PREPARATION OF $UO_3 \cdot H_2O$ FROM AMMONIUM URANYL CARBONATE

Tetra-ammonium uranyl tricarbonate, "AUC," $(NH_4)_4(CO_3)_2 \cdot UO_2CO_3$, was made for use as an intermediate in the preparation of $UO_3 \cdot H_2O$. Preliminary indications are that oxide of the desired purity may be obtained more easily from this compound than from other starting materials that have been considered. The method was suggested by the fact that many metallic oxides prepared by thermal decomposition of their carbonates have a low bulk density, which indicates a large surface area, and therefore may be easily freed from residual impurities.

Two methods of preparing AUC have been used. In one method, ammonium diuranate is precipitated from uranyl nitrate solution and then metathesized to AUC in a concentrated solution of ammonium carbonate. In the other method, the uranyl ion is sorbed from a uranyl nitrate solution on a column of Dowex-50 cation-exchange resin, and the uranium is eluted with ammonium carbonate solution (cf. "Ion Exchange," this report). Neither method has yet been fully evaluated.

URANIUM OXIDE CHEMISTRY

A sample of Harshaw UO_3, which had been prepared by thermal decomposition of uranyl nitrate by a procedure similar to that of Mallinckrodt, but which had been subjected to a further reduction in size, was used in the preparation of $UO_3 \cdot H_2O$. Preliminary indications are that the smaller particle size is of no advantage in the calcination-hydration procedure.

URANYL CARBONATE CHEMISTRY

High-purity $UO_3 \cdot H_2O$ platelets were converted to relatively pure UO_2CO_3 in a rocking autoclave at 250°C with CO_2 at a pressure of 600 to 1000 psi and a reaction time of 15 hours. The product, which may be of interest as a slurry fuel, as an intermediate in the production of pure UO_3, or as a reagent in the chemical processing of slurry systems, was in a very finely divided form and showed excellent slurry-producing properties in both high and low concentrations. The addition of 0.005 *M* Na_2CO_3 to the oxide before the reaction with CO_2 resulted in the formation of a milk-white product that was very fluid and considerably more stable than the UO_3 or UO_2CO_3 slurries previously studied.

URANIUM TRIOXIDE MONOHYDRATE SLURRY IRRADIATION EXPERIMENTS

Irradiation in the ORNL graphite reactor of a natural-uranium $UO_3 \cdot H_2O$ platelet slurry containing 250 g of uranium per liter at a relatively low power density (0.05 watt/ml) did not impair the slurry-forming properties of the platelets. The irradiated slurry was readily recovered from the bomb in which the experiment was performed, and there was no evidence of caking. The high purity of the oxide used (0.01% NO_3^-) and the close control of the in-reactor temperature may have been important factors in the study.

11. VOLATILITY

The purpose of the Volatility program is to study the application of volatility techniques to the solution of AEC separation problems. The study will include consideration of volatile compounds of uranium, plutonium, and fission products and consideration of structural materials of interest in the reactor program. Both chemical and equipment development studies will be made.

Several methods for removing stainless steel cladding from reactor fuels have been investigated during this quarter. Attempts to form volatile carbonyls by treating types 316 and 347 stainless steel with carbon monoxide at 50 to 150°C and 1 atm were unsuccessful. Chlorine gas at 500 to 850°C reacted with type 347 stainless steel at a penetration rate of 0.10 in./hr. During the reaction, all the chlorides were sublimed from the reaction area; most of the sublimate was water soluble. This project, together with attempts to prepare antimony pentafluoride and developmental work on the small distillation system for decontamination of UF_6 mentioned last quarter,[1] has been temporarily discontinued so that efforts may be concentrated on the chlorine trifluoride process.

CHLORINE TRIFLUORIDE PROCESS EVALUATION

During this quarter, representatives from the Process Design, Unit Operations, and Chemical Development Sections of the Chemical Technology Division worked with R. A. Gustison of K-25 in preparing a preliminary proposal for continued study of the chlorine trifluoride process for preparation of UF_6. It was proposed that an analysis be made to determine whether the economics justify development of a finished process for handling irradiated natural uranium. Chemical flowsheets suitable for detailed design and cost estimates will be prepared, and chemical information required for economic studies will be developed. Attempts will be made to improve the existing process.

PLUTONIUM RECOVERY FROM CHLORINE TRIFLUORIDE PROCESS RESIDUE

When dejacketed uranium slugs are dissolved by chlorine trifluoride and the UF_6 and excess ClF_3 are evaporated off, the plutonium and fission products remain in the dissolver. About 99% of the plutonium in this residue has been shown to be extractable with 30% tributyl phosphate (TBP). However, the solvent-extraction process is feasible only if sufficient nitric acid (0.3 *M* or more) has been present during dissolution to inhibit the polymerization of Pu(IV), if the plutonium is reduced to Pu(III) with ferrous ion and oxidized to Pu(IV) with nitrite prior to the extraction, and if the aluminum-to-fluoride mole ratio is 3 or more.

The distribution of Pu(IV) and the principal fission products between aqueous aluminum nitrate–nitric acid solutions and 30% TBP in Amsco-123-15 was studied as a function of acidity and nitrate ion concentration. The data indicated that the Pu(IV) extraction coefficient increases rapidly as the total nitrate concentration is raised. The relative extraction of the individual fission products by TBP appears to be dependent upon both acidity and salting strength. At low nitrate and hydrogen ion concentrations (about 0.7 *M*), zirconium and niobium extraction is very slight, but it increases uniformly as the nitric acid strength is raised. Ruthenium extraction is appreciable, but it drops steadily as the nitric acid concentration is increased to 6 *M*. Over the range of acidity investigated, the concentration of rare earths in the aqueous phase is much greater than that in the organic phase. At a concentration of

[1] *Chem. Tech. Quar. Prog. Rep. Aug. 20, 1952*, ORNL-1385, p. 9.

6 *M* nitrate ion, aluminum nitrate, which, on a molar basis, is more than three times as effective as nitric acid as a salting-out agent, greatly increases the extraction of zirconium, ruthenium, and rare earths. From these results it was assumed that the best separation of plutonium from gross fission products would be realized by high-acid extraction coupled with low-acid scrubbing.

In an initial flowsheet evaluation run, a plutonium decontamination from gross beta activity of 1.5×10^4 and from gross gamma of 4×10^3 was demonstrated.

12. ELECTROCHEMISTRY

The purpose of the Electrochemistry program is to study the electrochemical properties of source and fissionable materials and fission products and the application of electrochemical techniques in reducing the costs of separation processes. Studies may include electroplating of fissionable materials for reactor fuels, dissolution reactions, electrolytic preparation of uranium hexafluoride for K-25 feed, separation processes, particularly the continuous separation of fission products from homogeneous reactor fuel, waste concentration processes, and equipment decontamination.

The separation of the hydrogen isotopes by the electrolysis of water, according to the reaction $2H_2O \rightleftharpoons 2H_2 + O_2$, requires a large amount of energy because the cell operates far above the decomposition potential, and the energy of decomposition is not recovered. It has been found possible, however, to use this energy of decomposition to achieve additional separation by reversing the direction of the cell operation. Hydrogen gas may be supplied to an electrode of the primary battery type, at which the hydrogen isotopes are separated by the difference in the rate of formation of light and heavy water. The electrical energy produced by battery action in the formation of water balances the energy required to decompose water. For the purpose of separating isotopes, the decomposition and formation of water may be combined in a single cell provided with a suitable flow of electrolyte. If the cathode used in the forward reaction is of a material such as palladium, which stores the hydrogen that is released, then, when the cell polarity is reversed, the oxygen that is released at this electrode combines with the hydrogen stored there, and the stored energy of decomposition is used to bring about the reverse reaction. Since additional separation of the isotopes is obtained in the reverse reaction, the over-all separation factor is larger for the same expenditure of energy than in the usual method.

As one step in the over-all cell reaction studies, a hydrogen anode was used in conjunction with a palladium cathode of low overvoltage. At cell potentials of less than 0.5 volt, separation factors of 6 to 8 were found during the cathodic hydrogen-deposition stage. The hydrogen-charged cathode was then switched to become a hydrogen anode, and an additional separation factor of 3 to 7 was obtained during the anodic reaction.

In order to determine the best cell conditions for operation, experiments are in progress on the electrode structure and related cell factors, including the time cycle for reversal, local-action currents, and current density.

An effect of current density upon the relative reaction rates of the hydrogen isotopes was measured in a study of chromium plating from a heavy-water bath. The current efficiency for the reduction of chromium oxide to metallic chromium was found to be several times higher in a heavy-water bath than in an ordinary-water bath over the range of current densities commonly used for chromium plating. The current efficiencies are compared in Table 12.1.

As a matter of general interest in the art of chromium plating, it was noted that the heavy-water plating bath not only increased the current efficiency but also increased the throwing power. Heavy, bright deposits were obtained at current densities that gave milky deposits or no deposits at all from the commercial ordinary-water electrolyte.

The chromium-plating experiment may be considered as an electrolytic separation of two elements, hydrogen and chromium. It may be noted that the separation factor is large at certain current densities. In a similar way, the current density may be considered a significant item for increasing the separation factor of the hydrogen isotopes from the equilibrium value of 3 to the value of 8.

TABLE 12.1. COMPARISON OF CURRENT EFFICIENCIES OF CHROMIUM DEPOSITION FROM H_2O AND D_2O CHROMIUM-PLATING BATHS

Bath composition: CrO_3, 250 g/liter
H_2SO_4, 2.5 g/liter

CATHODE CURRENT DENSITY (amp/in.^{2})	CURRENT EFFICIENCY (%)			
	At 40°C		At 50°C	
	In H_2O	In D_2O	In H_2O	In D_2O
0.25	0.0	21.4		16.8
0.5	11.6	33.6	0.0	26.1
1.0	15.1	35.3	11.2	30.4
2.0	19.1	37.0	14.7	33.2
3.0	21.0	39.1	14.2	33.4

13. ION EXCHANGE

The purpose of the Ion Exchange program is to investigate the application of ion exchange to AEC separation problems. The investigations will include evaluation and development of continuous ion exchange as a separation technique and the use of ion exchange for uranium, plutonium, and fission-product separations and for waste processing. The scope of the program will be primarily chemical and equipment development.

HIGGINS CONTACTOR

A laboratory model, with columns ¾ in. in diameter and 6 ft in length, of the Higgins continuous countercurrent ion-exchange contactor[1] has been in operation since March. At least nine runs in which the contactor was operated continuously for a week at a time have been made, and during the rest of the time it was operated almost every day. Repairs have been few, and most of the original accessories are still functioning. Length scale-up of the laboratory model is possible, as shown by the satisfactory operation of a 25-ft-long column. A 4-in.-dia column is being assembled for use in tests to determine whether diameter scale-up is possible. Various accessories, such as valves, timers, and pumps, are being tested to determine which are the most satisfactory models.

[1] I. R. Higgins, *A Countercurrent Solid-Liquid Contactor for Continuous Ion Exchange*, ORNL-1310 (Sept. 4, 1952).

URANIUM RECOVERY FROM ORE LEACH LIQUORS

Experiments have shown[2] that uranium which has been sorbed by an anion-exchange resin from synthetic sulfate and carbonate ore leach liquor can be obtained in a relatively concentrated form and free of excess salts by treating the resin with hydrochloric acid and eluting with water.

PREPARATION OF URANIUM HEXAFLUORIDE

An alternate method of producing UF_6 has been suggested: ion-exchange conversion of the uranyl nitrate from solvent-extraction processes to uranyl fluoride, UO_2F_2, and wet reduction of the uranyl fluoride to uranium tetrafluoride, UF_4. Preliminary investigations indicated that the daily uranium production, 750 lb, of the ORNL metal waste recovery plant could be converted, with negligible losses, from a solution of uranyl nitrate with a uranium concentration of 50 g/liter, to one of uranyl fluoride with a uranium concentration of 100 g/liter in a Higgins type of continuous contactor 9 in. in diameter and 8 ft high. The nitrate would be recovered in 0.4 *N* HNO_3 directly from the sorption column. The uranyl fluoride product would contain just enough hydrogen fluoride to

[2] J. T. Roberts and I. R. Higgins, *Elution of Uranium Sorbed on Anion Exchange Resins from Low-Grade Ore Liquors*, ORNL-1418 (Dec. 6, 1952).

precipitate the uranium as UF_4 on reduction. Preliminary experiments with hydrogen at 200°C and 500 psi gave partial reduction of neutral UO_2F_2 in a stainless steel bomb. A monel bomb has been obtained so that the reaction can be performed in the presence of hydrogen fluoride. Other possible methods of preparation include electrolytic reduction[3,4] and reduction with zinc metal or stannous ion.

PREPARATION OF NITRATE-FREE AMMONIUM URANYL CARBONATE

Uranium trioxide with a low soluble uranium content, which is desirable in homogeneous reactor fuel slurries, can be prepared by ignition of nitrate-free ammonium uranyl carbonate. The preparation of suitable ammonium uranyl carbonate was attempted by sorbing the uranium on Dowex-50, washing the resin free of nitrate ion with water, and by eluting the fluidized bed upflow with 0.5 *M* ammonium carbonate or bicarbonate. This gave an eluate with a uranium concentration of 50 g/liter (cf. "Homogeneous Reactor Slurries," this report). The fluidization permitted continuous removal of the carbon dioxide formed and prevented plugging of the bed with the precipitate that forms but redissolves under the conditions of the process. It is thought that it will be possible to perform this reaction in a modified Higgins contactor.

EVALUATION OF NEW ION-EXCHANGE MATERIALS

A phosphonic cation-exchange resin, C-61, supplied by the Chemical Process Co., has 50% greater capacity than Dowex-50; however, it sorbs hydrogen ion very strongly, and its application in low-pH solutions is restricted. It shows no unusual pickup of fission products from uranyl sulfate solutions. The affinity of alkali metals for C-61 is reversed as compared with Dowex-50. With Dowex-50, the order of affinity is cesium > potassium > sodium > lithium. With the phosphonic resins, the affinity is lithium > sodium > cesium. It may be possible to carry out oxidation-reduction reactions with the phosphonic resins, since they exist in the reduced, phosphonous, state as well as in the oxidized, phosphonic, state.

A phosphoric exchange resin also supplied by the Chemical Process Co. is indicated by the manufacturer to have a high affinity for uranium and certain other ions without interference from bulk cations. With this resin, a distribution coefficient of 170 was obtained for uranium in 1 *M* NH_4Cl, which is better than can be obtained with a sulfonated cation exchanger. This company also supplied a sample of liquid cation exchanger, which is a sulfonated styrene with no cross-linking. Its sorption properties are similar to those of Dowex-50, but its capacity is only about one-fifth that of Dowex-50. Its consistency is about that of rubber latex, and recommendations are that it be used hot.

An inorganic exchanger made by the Minnesota Mining and Manufacturing Co. has possible application in high-temperature high-radiation homogeneous reactor fuel processing. Tests showed that it adsorbs zirconium, niobium, and chromium in tracer amounts very effectively from both 1 *M* UO_2SO_4 and 2 *N* HNO_3. It showed no appreciable affinity for uranium, plutonium, neptunium, or other fission products. Equilibration rates were very slow compared with those of organic cation exchangers.

Phenolic-type homogeneous anion- and cation-exchange membranes have been obtained from Ionics, Inc. Pressed-powder anion- and cation-exchange membranes have been received from Rohm and Haas Co. The selective transfer of neptunium from uranyl sulfate solution was unsuccessful with both anion- and cation-exchange membranes. With the anion-exchange membrane, nitrate was removed from uranyl nitrate, and uranium oxides were precipitated. With the anion-exchange membrane Amberplex-A-1, more than 95% of the nitrate was removed from a 1 *M* alkali-metal salt, with only 0.3% leakage of the cation across the membrane.

---

[3] A. L. Allen, R. W. Anderson, R. M. McGill, and E. W. Powell, *Electrochemical Preparation of Uraniumtetrafluoride Part I. Low Temperature Cell*, K-680 (Nov. 10, 1950).

[4] R. W. Anderson, A. L. Allen, and E. W. Powell, *Electrochemical Preparation of Uraniumtetrafluoride Part II. High Temperature Cell*, K-681 (Dec. 22, 1950).

14. CHEMICAL ENGINEERING RESEARCH

The Chemical Engineering Research program is a long-range program with the objective of reducing radiochemical processing costs. The high cost of radiochemical process plants, approximately ten times that of other chemical plants, emphasizes the need for applied research studies of the chemical engineering aspects of radiochemical processes. The program involves radiochemical unit process and unit operation evaluation studies supported by experimental research effort. Fields of study may include solvent extraction, metal dissolution, liquid-solid separations, ion exchange, evaporation, precipitation, equipment evaluation, materials evaluation, surface decontamination, radiation stability, and plant economic studies.

SOLVENT EXTRACTION

The objective of the Solvent-Extraction program is to evaluate different types of contactors; these include packed, pulsed, and Scheibel columns, mixer-settlers, and the Podbielniak centrifugal contactor. At present, emphasis is being placed on the application of pulse columns to various processes and the development of pulse generators.

Development of the concatenated pulse column[1] for use in locations with low headroom is continuing in a new assembly mounted on a portable rack to emphasize the movability or ease of replaceability of such a contactor. Process tests are being conducted with the Thorex preferential strip operation flowsheet. The major interest is in the optimum geometry of a concatenated pulse column for preferential stripping in the Thorex pilot plant. Extensive studies are being made on the check valves for the concatenated column.

Details of the studies on concatenated columns for the Thorex process pilot plant are given in section 5, "Thorex Process."

Several kinds of check valves, including flapper and ball types, were tested; a disk type of check valve was developed, which appears to be the best choice because it permits the use of all-stainless-steel construction. The ball check valve requires the use of Teflon or ceramic balls, both of which were satisfactory under test conditions but which may not have a long operating life. Stainless steel balls were too heavy and reduced the column capacity by about 25%. The flapper check valve may wear severely at the flapper pin.

The Vickers hydraulic-drive pulser system was operated continuously for 90 days against a 20-ft water head without incident. It was operated at 60 cycles/min and at an amplitude of 1 in. without variation during the 90-day period. After the completion of this test, the Graphitar pulse piston, which had maintained a low leakage rate throughout the test, was examined and found to be in good condition.

The four mechanical-drive, simple reciprocating piston pulsers designed and built for operation of the Metal Recovery columns have been tested and are being installed. Three of the units tested against a 20-ft water head are in excellent condition, as indicated by the low leakage rate of 5 ml/min that they now show. The 6-in.-dia pistons in these units are stainless steel bodies provided with Graphitar rider and seal rings. The rings in the fourth unit do not meet dimensional specifications and have a leakage rate of 100 ml/min. New rings have been ordered.

SPECIAL EQUIPMENT

The immediate objective of the Special-Equipment program is to provide samplers for the Thorex process solutions, which will minimize radiation hazards for operating personnel.

A combination of the Hynec[2] and Argonne[3] samplers was fabricated and tested for Thorex use (Fig. 14.1) and was found to be capable of recirculating 115 ml/min of a thorium nitrate solution with a specific gravity (room temperature) of 1.76 through a head of approximately 30 feet. The diaphragm, which will wipe off the final drops, is expected to prevent spillage or dripping, and the possibility of plugging the hypodermic tubing is minimized by the fact that no liquid passes through it during the recirculation.

EQUIPMENT DECONTAMINATION

The purpose of the Equipment Decontamination program is to carry out fundamental and applied studies aimed at developing improved methods for decontaminating chemical process equipment.

(1) *Chem. Tech. Quar. Prog. Rep. May 20, 1952*, ORNL-1328, p. 11.

(2) *Chem. Tech. Prog. Rep. Aug. 1, 1951 to Feb. 10, 1952*, ORNL-1311, p. 68.

(3) ANL drawing No. CE-2009.

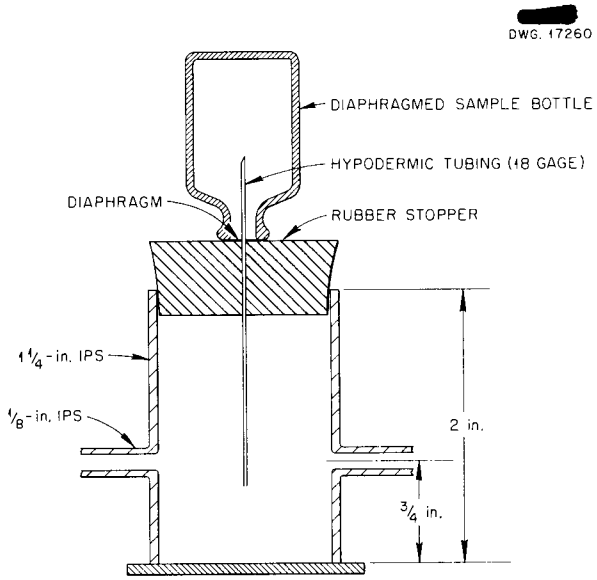

Fig. 14.1. Proposed Thorex-Process Solution Sampler.

Application of these methods to the decontamination of homogeneous reactor components is being studied. Both electrolytic and chemical procedures are being investigated.

Several reagents were found to remove adsorbed fission products from stainless steel with a decontamination factor of greater than 10: 1 *M* oxalic acid at 85°C, an aqueous solution of Versene and sodium hydroxide at 65°C, and an aqueous solution of sodium tartrate and sodium hydroxide at 65°C. Three sources that will be used to contaminate samples for decontamination studies have been received, and it is now possible to obtain three levels of contamination. The accuracy of the method for determining decontamination factors has been increased.

At 85°C, 0.5 *M* oxalic acid, which is the strength normally used in the pilot plant for decontamination, corroded stainless steel at a rate of 0.0063 mil/hr; there was no microscopic evidence of pitting in a 24-hr test.

It has been decided to shift the emphasis in the reagent decontamination studies from recovery of "3-20" reagent[4] to the discovery of more suitable reagents. However, a few, somewhat unsatisfactory, experiments have been made on removing fluoride and fission products from the "3-20" reagent. It was found that about 50% of the available fluoride of the used reagent could be precipitated with $La(NO_3)_3$, with a decontamination factor of 13.2. Precipitation of activities with MnO_2 gave a decontamination factor of 2.2. Complexing of radioactive components with thenoyl trifluoroacetone (TTA), either 1 or 3 *M* solution in benzene, gave a decontamination factor of 1.2. Results of a cost analysis of an acid-recovery process[4] using 50% tributyl phosphate in Amsco showed a pay-off time of 1.75 years. Use of the dilute acid product as a diluent for Thorex dissolver acid would decrease the pay-off time to one year.

To date, work[4] on removing radioactive fission-product contaminants from the homogeneous reactor piping system has proceeded on the assumption that removal of scale from the interior of the piping is necessary for decontamination. Several solutions that have appeared promising for scale removal have also caused excessive corrosion of the piping system. The corrosion caused by one of the most promising decontaminating reagents, Scale-Loosening Solution No. 2 (1 vol. of 37% HCl, 1 vol. of 95% H_2SO_4, 8 vol. of H_2O), was shown to be inhibited by Alkyl Pyridines HB. This inhibitor was superior to 12 others tested, including Rodine 41.[4] The optimum temperature for use of this solution with Alkyl Pyridines HB was determined to be 85°C.

Plans have been completed to prepare fission-product-contaminated stainless steel specimens under simulated homogeneous reactor conditions. These specimens will be used in attempts to desorb fission products from the homogeneous reactor scale to effect decontamination, and the experiments should demonstrate whether scale removal is necessary to produce decontamination.

COST STUDIES

An economic-study program has been undertaken to obtain cost data on design engineering, construction, and operation of radiochemical plants in order that present philosophies and design practices may be reviewed for the ultimate purpose of reducing costs. There are three phases of this program: (1) accumulation of data; (2) determination of the effects on plant costs of various factors such as accountability, criticality, radiation, and waste disposal; and (3) preliminary economic studies for future plants.

[4] *Chem. Tech. Quar. Prog. Rep. Aug. 20, 1952*, ORNL-1385, p. 13.

The analysis of construction costs for the Service Building at the Idaho Chemical Processing Plant has been completed except for inclusion of certain unallocated costs and descriptive matter requested by the AEC. The cost of each of the several systems of the building, expressed as approximate percentages of the total construction cost, is as follows:

	Per Cent of Total
Bare building	30
Miscellaneous building items	12
Steam generator system	27
Compressed air systems (3)	11
Water service systems (3)	20

Other cost analyses are still in progress.

Material flowsheets, which are being prepared as the first phase of a Purex plant design, are complete. Work on equipment flowsheets and plant layouts is being continued.

METAL DISSOLUTION

The objective of the Metal Dissolution work is the conversion from a batch to a continuous dissolution process in the preparation of solid reactor fuels for feeding to recovery plants. In small-scale studies, continuous dissolving has been shown to be feasible for uranium, thorium, and uranium-aluminum alloys.

The large-scale packed-column trickle type of continuous dissolver[4] has been installed, and ten successful dissolvings of uranium-aluminum alloy slugs have been made. The dissolution proceeded satisfactorily with a solvent containing 0.005 *M* $Hg(NO_3)_2$ and either 4.0 or 6.0 *N* in HNO_3. Product concentrations were very uniform throughout any one run, usually varying from the average by not more than 2 g of aluminum per liter and by about 0.1 *N* acid deficiency. Changes in solvent flow rates, which were varied from 100 to 600 ml/min, did not affect the product perceptibly at low flow rates, but a decrease in concentration was indicated as the flow rate was increased above a certain value, which depended on the nitric acid concentration.

Particulate matter that appeared to be small chips of slug was found in the product solution. These particles dissolved easily when the solution was heated to 90 to 100°C for 15 to 20 min, and a small digestion pot is being installed in the product line to dissolve them in future runs.

The dissolving section of the continuous dissolver is a 10-ft length of tubing with an outside diameter of 6 inches. Necessary instrumentation to obtain essentially automatic control is provided. Upon completion of certain modifications that are now being made in the equipment, additional uranium-aluminum alloy dissolutions will be made. Work will then be started on dissolving thorium slugs and on determining process variables for a large-scale Thorex dissolver.

FEED PREPARATION AND SERVICE FUNCTIONS

Approximately 180 liters of dibasic aluminum nitrate produced by dissolving 2S aluminum tubing in 2 *M* $Al(NO_3)_3$ solution was turned over to the Solvent Extraction group to be used as column scrub solution after being passed through an Alsop filter. Alsop pads 60, 69, or 99 proved effective in clarifying this solution; No. 99 gave the best results but had the slowest flow rate.

Various types of stainless steel were exposed to the corrosive action of the thorium dissolving solution, vapor, and condensate for a total of 42.5 hr in seven controlled-acid-addition batch thorium dissolutions. These samples were turned over to the Radiation Engineering group for evaluation.

Two 40-kg batches of thorium nitrate tetrahydrate were digested in the presence of nitric acid to test this method of removing soluble silica in the preparation of a satisfactory feed for Thorex solvent-extraction studies (cf. "Thorex Process," this report). The method proved satisfactory with minor alterations.